

Thermal decomposition of yttrium and lanthanide complexes with mephenamic acid

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Abstract

The thermal decomposition in air of mephenamates of yttrium and lanthanides from lanthanum(III) to lutetium(III) has been studied. During heating, the hydrated complexes $\text{Ln}(\text{C}_{15}\text{H}_{14}\text{O}_2\text{N})_3 \cdot n\text{H}_2\text{O}$ ($n = 3-14$) lose water of crystallization in one (Y, La–Sm, Gd–Lu) or two steps (Eu), then anhydrous (Sm, Gd, Dy, Tm, Lu) or lower hydrated (Y, La–Nd, Eu, Tb, Ho, Er, Yb) complexes decompose directly to oxides or with intermediate formation of very unstable oxycarbonates (La, Nd).

INTRODUCTION

n-(2,3-Xylolilo)-anthranilic acid (known as mephenamic acid or mephacid) is a crystalline solid sparingly soluble in water. It is known as a remedy against pain, fever and inflammation [1]. A survey of the literature shows that recently some patents [2,3] have been published on the preparation of medicines based on mephenamic acid.

Rare earth element complexes with mephenamic acid $\text{C}_{15}\text{H}_{14}\text{O}_2\text{N}$, were previously unknown. In an earlier work, we presented the preparation of yttrium and lanthanide (from lanthanum(III) to lutetium(III)) mephenamates with the molar ratio of metal to organic ligand of 2:3 and different degrees of hydration [4], their IR and X-ray spectra and solubilities in water.

The aim of our work was to examine the thermal decomposition of yttrium and lanthanide mephenamate hydrates during heating in air atmosphere.

EXPERIMENTAL

The thermal stabilities of yttrium and lanthanide (from lanthanum(III) to lutetium(III), without promethium) mephenamates with the general formula $\text{Ln}(\text{C}_{15}\text{H}_{14}\text{O}_2\text{N})_3 \cdot n\text{H}_2\text{O}$ (Table 1) were studied in air atmo-

TABLE 1
Data on dehydration and decomposition of yttrium and lanthanide complexes with mephacid

Complex ^a	Temperature range of dehydration (K)	Mass loss (%)		Loss of H ₂ O (moles)	Temperature range of decomposition (K)	Mass loss (%)		Temperature of oxide formation (K)
		Calc.	Found			Calc.	Found	
YI ₃ ·7H ₂ O	313-453	11.50	11.20	6	523-1043	86.30	85.52	1043
LaI ₃ ·4H ₂ O	323-533	1.90	1.85	1	540-1090	82.14	82.20	1090
CeI ₃ ·12H ₂ O	323-513	6.69	7.00	4	530-1153	82.86	82.79	1153
PrI ₃ ·4H ₂ O	343-575	1.90	1.85	1	584-953	81.42	81.76	953
NdI ₃ ·8H ₂ O	458-563	7.14	7.20	4	583-1043	82.05	81.89	1043
SmI ₃ ·3H ₂ O	323-473	5.85	6.00	3	523-1073	80.00	79.78	1073
EuI ₃ ·14H ₂ O	313-423	1.60	1.62	1				
	443-563	14.64	14.44	9	568-973	81.05	80.95	973
GdI ₃ ·3H ₂ O	313-463	5.80	6.00	3	523-1073	79.36	78.96	1073
TbI ₃ ·12H ₂ O	313-443	11.50	11.50	7	553-1053	80.50	80.57	1053
DyI ₃ ·3H ₂ O	313-443	6.10	6.40	3	533-1013	78.86	78.63	1013
HoI ₃ ·14H ₂ O	313-493	11.08	11.00	7	543-1063	81.30	81.12	1063
ErI ₃ ·8H ₂ O	323-483	6.90	7.20	4	573-1103	80.08	80.17	1103
TmI ₃ ·7H ₂ O	313-483	12.40	13.00	7	513-1063	78.29	78.16	1063
YbI ₃ ·7H ₂ O	313-433	7.06	7.00	4	503-1003	79.35	79.56	1003
LuI ₃ ·4H ₂ O	313-443	7.50	8.00	4	503-993	77.76	77.60	993

^a L = C₁₅H₁₄O₂N⁻.

sphere. The TG, DTG and DTA curves were recorded. The measurements were made with a Q-1500 derivatograph at a heating rate of 10 K min^{-1} . The samples of 100 mg were heated at 1273 K in platinum crucibles with the following sensitivities: TG, 100 mg; DTG, $500 \mu\text{V}$; DTA, $500 \mu\text{V}$. The paper speed was 2.5 mm min^{-1} . Al_2O_3 was used as a standard. The products of decomposition were confirmed by recording IR and X-ray spectra.

RESULTS AND DISCUSSION

On the basis of analysis of the thermal curves recorded for prepared complexes, the temperatures and solid products of decomposition were established. The results obtained are presented in Table 1 and Figs. 1–7. The complexes of yttrium and lanthanides heated in air atmosphere decompose in various ways.

The hydrated mephenamate of europium(III) is stable up 313 K, next loses some water molecules in two steps and then decomposes directly to Eu_2O_3 (Fig. 1, Table 1).

The hydrated mephenamates of samarium(III), gadolinium(III), dysprosium(III), thulium(III) and lutetium(III) (Figs. 2 and 3, Table 1) are dehydrated in one step and then the anhydrous compounds decompose directly to oxides on further heating.

The hydrated complexes of yttrium(III), cerium(III), praseodymium(III) terbium(III), holmium(III), erbium(III) and ytterbium(III) decompose in two steps. In the first step they lose some water molecules and then lower hydrated complexes are decomposed directly to oxides. The hydrated

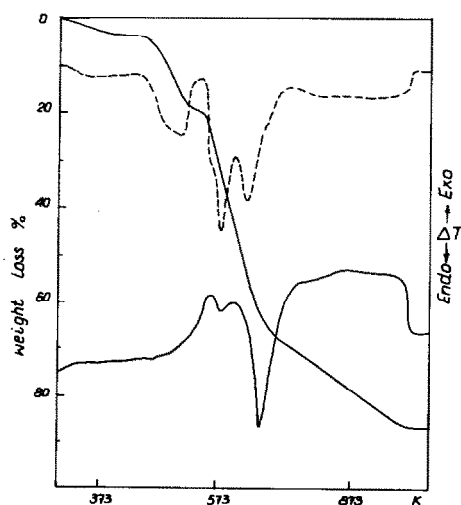


Fig. 1. TG, DTG and DTA curves of $\text{Eu}(\text{C}_{15}\text{H}_{14}\text{O}_2\text{N})_3 \cdot 14\text{H}_2\text{O}$.

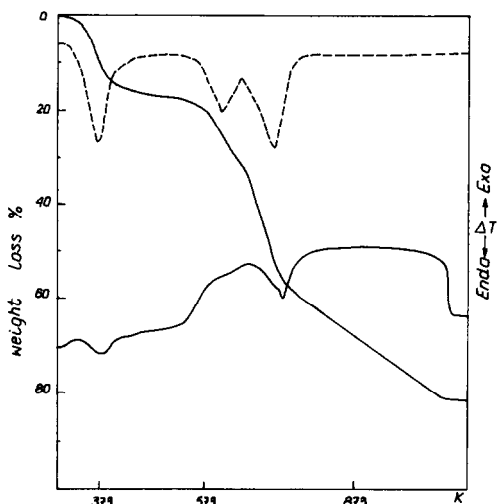
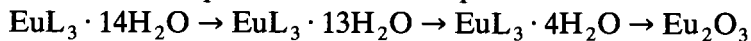


Fig. 2. TG, DTG and DTA curves of $\text{Tm}(\text{C}_{15}\text{H}_{14}\text{O}_2\text{N})_3 \cdot 7\text{H}_2\text{O}$.

mephenamates of lanthanum(III) and neodymium(III) lose some water molecules on heating and then decompose to oxides with intermediate formation of unstable oxycarbonates.

The results indicate that the thermal decomposition of hydrated rare earth element mephenamates can be presented in the following manner:



$\text{LnL}_3 \cdot x\text{H}_2\text{O} \rightarrow \text{LnL}_3 \rightarrow \text{Ln}_2\text{O}_3$ where Ln stands for Sm, Gd, Dy, Tm or Lu.

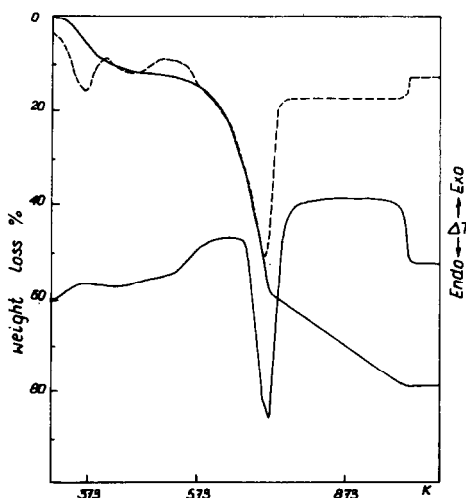


Fig. 3. TG, DTG and DTA curves of $\text{Lu}(\text{C}_{15}\text{H}_{14}\text{O}_2\text{N})_3 \cdot 4\text{H}_2\text{O}$.

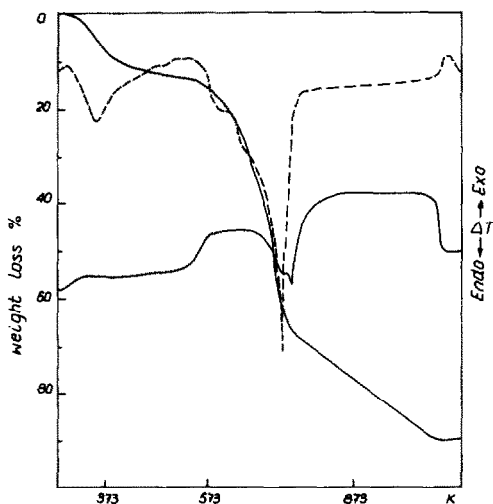


Fig. 4. TG, DTG and DTA curves of $Y(C_{15}H_{14}O_2N)_3 \cdot 7H_2O$.

$LnL_3 \cdot xH_2O \rightarrow LnL_3 \cdot yH_2O \rightarrow Ln_2O_3, CeO_2, Pr_6O_{11}, Tb_4O_7$ where $x > y$ and Ln stands for Y, Ho, Er or Yb.

$LnL_3 \cdot xH_2O \rightarrow LnL_3 \cdot yH_2O \rightarrow Ln_2O_2CO_3 \rightarrow Ln_2O_3$ where $x > y$ and Ln is La or Nd.

The dehydration process is connected with an endothermic effect but the decomposition and the combustion of organic ligand with strong exothermic effects. On the DTA curves the exothermic effects observed as plateaux without a maximum indicate that for the complexes of yttrium, lanthanum–neodymium, terbium, holmium, erbium and terbium these

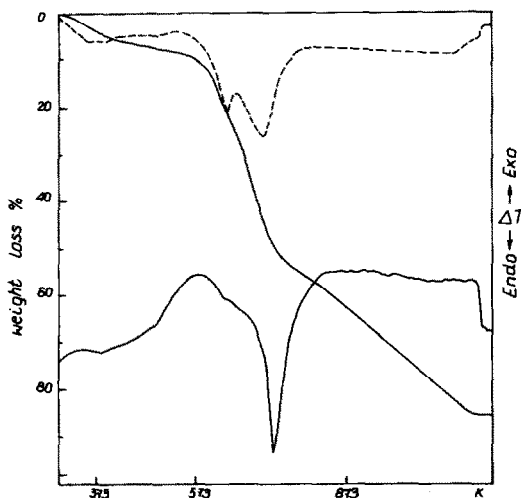


Fig. 5. TG, DTG and DTA curves of $Ce(C_{15}H_{14}O_2N)_3 \cdot 12H_2O$.

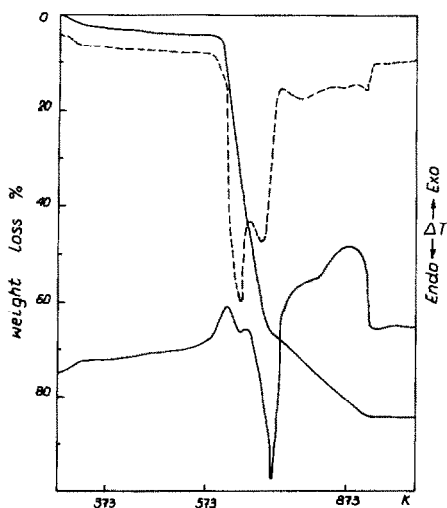


Fig. 6. TG, DTG and DTA curves of $\text{Pr}(\text{C}_{15}\text{H}_{14}\text{O}_2\text{N})_3 \cdot 4\text{H}_2\text{O}$.

processes occur simultaneously but the exothermic processes dominate. The very strong endothermic effect at 440–460 K is connected with decomposition of intermediate very unstable products which have not been identified. The process of combustion of the remaining organic ligand and deflagration of residue of carbon are observed on the DTA curves as exothermic plateaux without a maximum.

From the results obtained, it is possible to suggest that water of crystallization is bonded in different ways: with anion, in the space lattice bonded by hydrogen bonds with anion, and the water of coordination which is

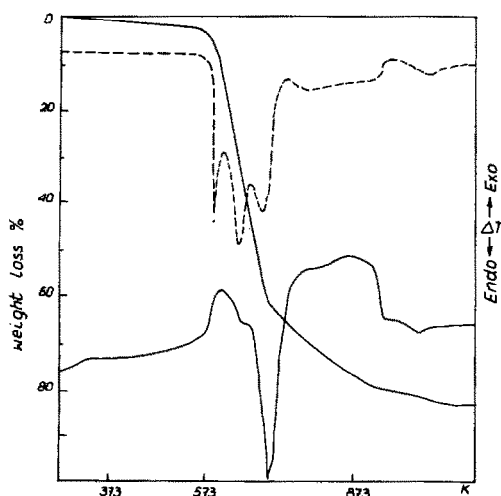


Fig. 7. TG, DTG and DTA curves of $\text{La}(\text{C}_{15}\text{H}_{14}\text{O}_2\text{N})_3 \cdot 4\text{H}_2\text{O}$.

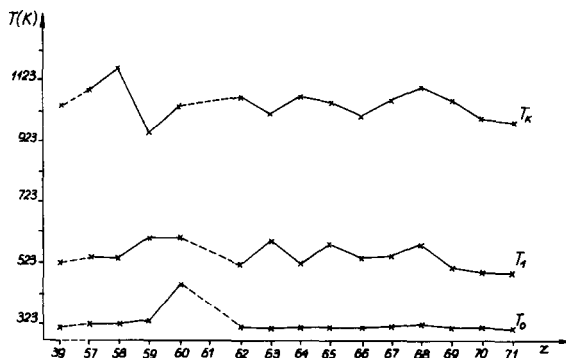


Fig. 8. Relationship between temperatures of dehydration (T_0), decomposition (T_1) and oxide formation (T_k) and the atomic number z of the metal.

bonded strongly with the metal ion. Only complexes of samarium(III), gadolinium(III), dysprosium(III), thulium(III) and lutetium(III) become anhydrous when heated. The complexes of the remaining lanthanides do not form anhydrous compounds upon heating.

The temperatures of dehydration (T_0), decomposition (T_1) of the yttrium and lanthanide mephenamates, and temperatures of oxide formation (T_k) in the lanthanide series are presented in Fig. 8.

Comparing the temperatures of commencement of complex dehydration (T_0) it is apparent that they are similar to each other (about 313 K) which indicates that the stabilities of hydrated complexes are similar, except the complex of neodymium(III) which is stable up to 458 K.

The decomposition of hydrated complexes begins at temperature T_1 of 503–563 K, and anhydrous complexes start to decompose at 503–523 K. The temperatures of oxide formation (T_k) change irregularly with increasing atomic number z of the metal (Fig. 8). The temperature of CeO_2 formation is the highest (1153 K) whereas the temperature of Pr_6O_{11} formation is the lowest (953 K). This is a rarely observed phenomenon, because in most cases the temperature of CeO_2 formation is the lowest.

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