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THERMAL DECOMPOSITION OF RARE EARTH *p*-AMINOSALICYLATES IN AIR ATMOSPHERE

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The conditions of thermal decomposition of the *p*-aminosalicylates of Y, La and the lanthanides from Ce(III) to Lu have been studied. On heating, the hydrated complexes of La and the light lanthanides decompose to the oxides with the intermediate formation of $Ln_2[H_2N \cdot C_6H_3(O)COO]_3$. Only the complex of La decomposes to La_2O_3 through $La_2[H_2N \cdot C_6H_3(O)COO]_3$ and $La_2O_2CO_3$. The anhydrous complexes of the heavy lanthanides decompose directly to the oxides, whereas the anhydrous complex of Y decomposes to Y_2O_3 via $Y_2[H_2N \cdot C_6H_3(O)COO]_3$ formation. During heating, the hydrated complexes lose crystallization water and decompose simultaneously, and the endothermic effect of dehydration is masked by the strong exothermic effect of burning of the organic ligand.

p-aminopsalicylic acid, which has three functional groups (OH, NH_2 and COOH), forms a great number of complexes. In recent years, several studies have been made on the structure and the mode of coordination of d-electron element ions with *p*-aminosalicylic acid [1-4].

Pirkes [5] found that the coordination of neodymium(III) with *p*-aminosalicylic acid occurs through the carboxylic and amino groups simultaneously. Lapitskaya [6] reported on the compositions and some properties of the La-Nd *p*-aminosalicylates. We earlier determined the conditions of preparation of rare earth *p*-aminosalicylates, and studied their structures and the mode of metal-ligand coordination [7]. The rare earth *p*-aminosalicylates were prepared as complexes with general formula $Ln(C_7H_8NO_3)_3 \cdot nH_2O$, where $n = 3$ for La and Ce; $n = 2$ for Pr, Nd, Sm and Eu; and $n = 0$ for Gd - Lu and Y.

The aim of this work is to investigate the thermal decompositions of rare earth *p*-aminosalicylates during heating in air atmosphere.

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Experimental

The thermal stabilities and the solid products of decomposition of the *p*-aminosalicylates of Y, La and the lanthanides [from Ce(III) to Lu] were studied by heating these complexes to 1273 K in air atmosphere. The measurements were made on a Q-1500 derivatograph.

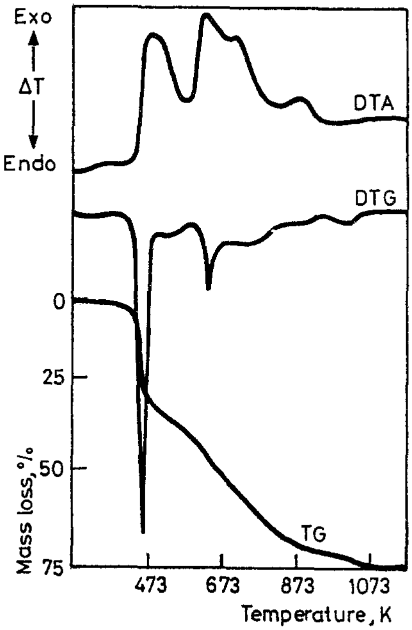

Fig. 1 The TG, DTG and DTA curves of $La(C_7H_6NO_3)_3 \cdot 3H_2O$

The TG, DTG and DTA curves were recorded. Samples of 100 mg were heated in platinum crucibles at a heating rate of 10 deg·min^{-1} with sensitivities T – 100 mg, DTG – 500 μV and DTA – 500 μV. The natures of the solid decomposition products were calculated from the weight losses in the TG curves and were confirmed by recording the IR spectra. The results obtained are presented in Figs 1-4 and in Tables 1 and 2.

Results and discussion

When heated, the *p*-aminosalicylates of Y, La and the lanthanides decompose in various ways. The hydrated *p*-aminosalicylates of La(III),

Table 1 Temperature range of decomposition of Y, La and lanthanide *p*-aminosalicylates in air atmosphere

Complex	ΔT, K	Weight loss, % Calcd.	Weight loss, % Found	T_k, K	Peak temp. of DTG, K	DTA exothermic peaks, K
$LaL_3^x \cdot 3H_2O$	443 – 1043	74.91	74.8	1043	473, 643	538, 658, 741, 908
$CeL_3 \cdot 3H_2O$	339 – 703	73.54	73.6	703	463	528, 568
$PrL_3 \cdot 2H_2O$	433 – 873	73.12	73.6	873	468, 463	538, 668, 728
$NdL_3 \cdot 2H_2O$	418 – 953	73.57	74.0	953	468, 453	538, 665, 863
$SmL_3 \cdot 2H_2O$	363 – 973	72.87	72.8	973	383, 463, 483	493, 593, 723
$EuL_3 \cdot 2H_2O$	353 – 1136	72.68	72.8	1136	378, 443	$693 - 1123^{xx}$
GdL_3	323 – 1048	70.46	70.8	1048	373, 448	$503 - 1013^{xx}$
TbL_3	343 – 1038	70.27	69.6	1038	383, 463	$523 - 1023^{xx}$
DyL_3	333 – 1028	69.86	68.0	1028	383, 458	$493 - 1003^{xx}$
HoL_3	333 – 1033	69.59	69.2	1033	383, 463	$513 - 1023^{xx}$
ErL_3	328 – 1023	69.38	69.6	1023	383, 448	$513 - 993^{xx}$
TmL_3	333 – 1048	69.08	69.6	1048	388, 463	$503 - 1023^{xx}$
YbL_3	323 – 1018	68.70	68.8	1018	378, 473	$513 - 1003^{xx}$
LuL_3	328 – 1023	68.48	68.8	1023	378, 463	$503 - 1013^{xx}$
YL_3	323 – 938	79.2	78.4	938	383, 473	508, 563, 715

$^xL^-$ - $[NH_2C_6H_3(OH)COO]^-$

ΔT -temperature range of decomposition

T_k - temperature of oxide formation

xx - temperature range of exothermic effect (plateau)

Ce(III), Pr(III) and Nd(III) are stable up to 363-443 K and then decompose in two or three steps. The complexes of Pr(III), Nd(III) and Sm(III) decompose to unstable $Ln_2(C_7H_5NO_3)_3$, which next undergo direct decomposition to the oxides Ln_2O_3 or Pr_6O_{11}. The *p*-aminosalicylate of La(III) decomposes first to $La_2(C_7H_5NO_3)_3$, and then to La_2O_3 via the intermediate formation of $La_2O_2CO_3$, which is stable at 928-963 K. The trihydrated *p*-aminosalicylate of Ce(III) and the dihydrated complex of Eu(III) are stable to 353-393 K and then decompose directly to the oxides CeO_2 and Eu_2O_3. In the DTA curves of the hydrated *p*-aminosalicylates of La and the light lanthanides from Ce(III) to Eu(III), the endothermic effect characteristic of the dehydration process is not observed. In these cases, the dehydration reaction occurs simultaneously with the decomposition, and the endothermic effect connected with the dehydration reaction is masked by the exothermic effect accompanying the burning of the organic ligand.

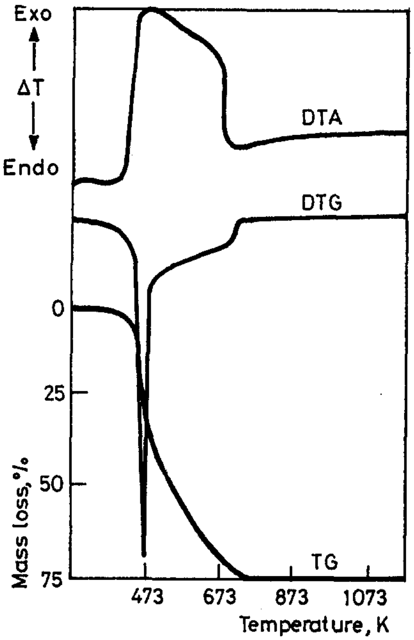

Fig. 2 The TG, DTG and DTA curves of $Ce(C_7H_6NO_3)_3 \cdot 3H_2O$

The anhydrous *p*-aminosalicylates of the heavy lanthanides (from Gd to Lu) are stable up to 323-343 K and then decompose directly to the oxides Ln_2O_3 or Tb_4O_7 over the temperature range 1018-1048 K. In the DTA cur-

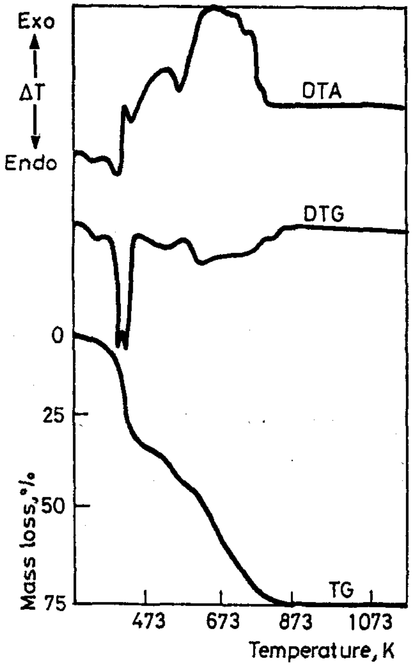

Fig. 3 The TG, DTG and DTA curves of $Sm(C_7H_6NO_3)_3 \cdot 2H_2O$

ves, the precision effect connected with the decomposition of the complexes and the burning of the organic ligand are not observed as for the *p*-aminosalicylates of the light lanthanides. The DTA curves have a plateau over the broad temperature range 493-1023 K.

Table 2 Temperature range of formation of stable and unstable intermediate products of Y, La and lanthanide *p*-aminosalicylate decomposition

Ln	$Ln_2(C_7H_5O_3N)_3$			$Ln_2O_2CO_3$		
	T, K	Calcd., %	Found %	*T*, K	Calcd., %	Found %
Y	678	42.12	38.4			
La	633	43.70	42.4	928–965	71.5	70.4
Pr	633	41.97	42.0			
Nd	633	41.75	42.8			
Sm	663	41.34	41.2			

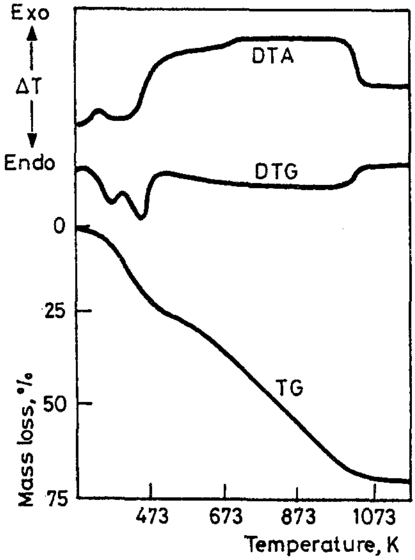

Fig. 4 The TG, DTG and DTA curves of $Ho(C_7H_6NO_3)_3$

On heating, anhydrous Y(III) *p*-aminosalicylate forms an unstable intermediate product with a metal to ligand ratio of 2 : 3, as do the complexes of La(III) and the light lanthanides. The initial temperature of decomposition of Y(III) *p*-aminosalicylate (323 K) is near the decomposition temperatures of the heavy lanthanide *p*-aminosalicylates, whereas the temperature of Y_2O_3 formation (938 K) is near the temperature of neodymium oxide formation (953 K).

The scheme of the thermal decompositions of the rare earth element *p*-aminosalicylates can be presented as follows:

$$LaL_3 \cdot 3H_2O \rightarrow La_2L_3^{-x} \rightarrow La_2O_2CO_3 \rightarrow La_2O_3$$

$$LnL_3 \cdot nH_2O \rightarrow Eu_2O_3 \quad \text{and} \quad CeO_2$$

for Ln = Eu and Ce

$$LnL_3 \cdot nH_2O \rightarrow Ln_2L_3^{-x} \rightarrow Ln_2O_3 \quad \text{and} \quad Pr_6O_{11}$$

for Ln = Nd, Sm and Pr

$$\mathrm{LnL_3} \rightarrow \mathrm{Ln_2O_3} \quad \text{and} \quad \mathrm{Tb_4O_7}$$

$$\text{for} \quad \mathrm{Ln} = \mathrm{Gd\text{-}Lu}$$

$$\mathrm{YL_3} \rightarrow \mathrm{Y_2L_3^{-x}} \rightarrow \mathrm{Y_2O_3}$$

$$\mathrm{L^{-x}} \rightarrow [\mathrm{H_2N{\cdot}C_6H_3(O)COO}]^{2-}$$

The results obtained indicate that the anhydrous *p*-aminosalicylates of Y and the heavy lanthanides (from Gd to Lu) are less stable than the hydrated complexes of La(III) and the light lanthanides.

The initial temperatures of decomposition of the lanthanide *p*-aminosalicylates (Fig. 5) decrease from Pr(III) to Gd(III), whereas these from Tb(III) to Lu(III) have very similar values, which suggests that the metal - ligand bonds in the heavy lanthanide *p*-aminosalicylates have similar energies.

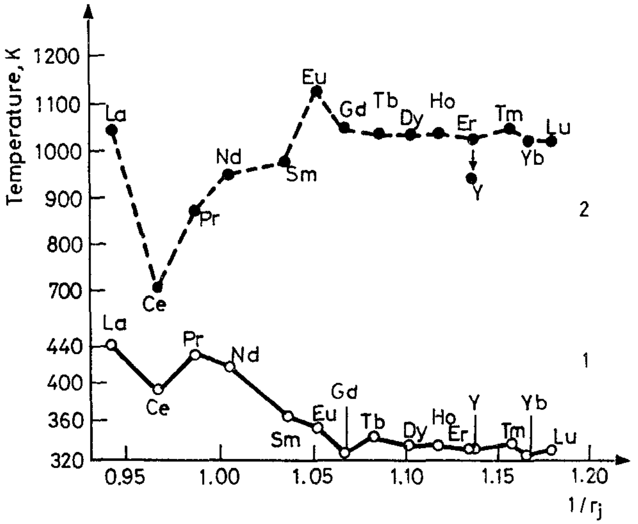

Fig. 5 Relationship between: 1 - temperature of decomposition, 2 - temperature of oxide formation and 1/rj (Galdsmidt's valus)

The temperatures of formation of oxides on decomposition of the rare earth element *p*-aminosalicylates increase from Ce(III) to Eu(III), while those from Gd(III) to Lu(III) have similar values. The thermal stabilities of the rare earth *p*-aminosalicylates are lower than those of the corresponding salicylates [8], which is connected with the presence of the amine group on the benzene ring.

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Zusammenfassung — Es wurden die Bedingungen für die thermische Zersetzung der *p*-Aminosalicylate von Y, La und der Lanthanoide von Ce(III) bis Lu untersucht. Beim Erhitzen zersetzen sich die hydratierten Komplexe von La und der leichteren Lanthanoide unter Bildung des Zwischenproduktes $Ln_2[H_2NC_6H_3(O)COO]_3$ in ihre Oxide. Nur der Komplex mit La zersetzt sich zu La_2O_3 über die Zwischenstufen $La_2[H_2NC_6H_3(O)COO]_3$ und $La_2O_2CO_3$. Die wasserfreien Komplexe der schweren Lanthanoide zersetzen sich direkt in die Oxide, während sich der wasserfreie Komplex von Y über die Bildung von $Y_2[H_2NC_6H_3(O)COO]_3$ in Y_2O_3 zersetzt. Beim Erhitzen verlieren die hydratierten Komplexe ihr Kristallwasser und zersetzen sich gleichzeitig, der endotherme Effekt der Dehydratation wird durch den starken exothermen Effekt der Verbrennung der organischen Liganden überdeckt.