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THERMAL DECOMPOSITION OF Y, La AND LIGHT LANTHANIDE COMPLEXES OF HIPPURIC ACID

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The conditions of thermal decomposition of the hippurates of Y, La and the light lanthanides from Ce(III) to Gd have been studied. When heated, the Y, Ce(III), Pr and Gd complexes decomposed in two stages, those of La, Sm and Eu in three stages, and that of Nd in four stages, the oxides finally being formed. The complexes lost crystallization water to form anhydrous (Nd) or hydrated salts, and then decomposed to oxides directly (Y, Ce(III), Pr(III) and Gd) or with intermediate formation of $Ln_2O_2CO_3$ (La, Nd, Sm and Eu). The temperature of oxide formation varied periodically with the ionic potential in the lanthanide series.

Hippuric acid ($C_6H_5CONHCH_2COOH$) is a crystalline solid soluble in hot water and ethanol. It crystallizes with 4 molecules in an orthorhombic cell [1]. The benzene ring, the peptide part and the carboxyl groups are planar and twisted with respect to each other. The molecules are held together in 3 dimensions by one O—H...O and one N—H...O hydrogen-bond to the peptide oxygen atom. The salts of hippuric acid are little known. Hippurates of NH_4, Na [3], Mg, Ca, Sr, Ba, Cu(II), Ag(I), Zn, Pb(II), Co(II) and Ni(II) have been prepared as hydrated salts [2]. The anhydrous hippurate of Na has also been isolated [2]. The complexes of Zn(II) and Ni(II) with hippuric acid have been studied in aqueous and non aqueous media [4]. The polarographic behaviour of Zn(II) and Ni(II) in the presence of hippuric acid has been investigated [4], and the stability constants of the complex species formed were evaluated.

Chudnovych [5] prepared La and Ce(III) complexes with hippuric acid as hydrated salts with general formula $Ln(C_9H_8NO_3)_3 \cdot 4.5H_2O$. Complexes of other rare earth elements have not been studied.

The aim of the present work was to obtain Y, La and light lanthanide complexes of hippuric acid in the solid state and to examine their thermal decompositions during heating in an air atmosphere.

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Experimental

Hippurates of Y, La and the light lanthanides from Ce(III) to Gd were prepared by adding ammonium hippurate (pH 4.0) to a hot solution containing the rare earth chloride (cerium(III) was used as nitrate). The precipitate formed was heated in the mother liquor for 0.5 h, then filtered off, washed with water to remove ammonium ions and dried at 303 K to constant weight.

The contents of carbon, hydrogen and nitrogen were determined by elemental analysis. The contents of Y, La and light lanthanons were determined from the TG curves and by ignition of the complexes to the oxides Ln_2O_3 (Ln = Y, La, Nd, Sm, Eu and Gd), CeO_2 or Pr_6O_{11}. The content of water was determined from the TG curves and by isothermal heating of the complexes at defined temperature.

The analysis data are given in Table 1.

The results showed that the Y, La and light lanthanide hippurates were prepared as hydrates with a ratio of metal to ligand of 1 : 3, with the general formula $Ln(C_6H_5CONHCH_2COO)_3 \cdot nH_2O$, where $n = 4$–10.

Table 1 Analytical data

Complex	Metal, %		Carbon, %		Hydrogen, %		Nitrogen, %	
	found	calcd.	found	calcd.	found	calcd.	found	calcd.
$YL_3^* \cdot 10H_2O$	11.06	11.02	40.09	40.35	5.55	4.15	5.55	5.22
$LaL_3 \cdot 8H_2O$	17.00	17.05	40.98	39.86	4.95	4.43	5.05	5.13
$CeL_3 \cdot 6H_2O$	18.04	17.90	42.23	41.43	4.89	4.63	5.36	5.36
$PrL_3 \cdot 7H_2O$	17.26	17.38	41.70	40.46	4.50	4.52	5.89	5.24
$NdL_3 \cdot 5H_2O$	18.76	18.86	41.99	42.18	4.75	4.71	4.99	5.46
$SmL_3 \cdot 3H_2O$	19.83	19.49	42.96	42.78	4.84	4.78	5.01	5.54
$EuL_3 \cdot 6H_2O$	18.99	19.12	41.48	40.81	5.04	4.56	5.40	5.28
$GdL_3 \cdot 6H_2O$	19.52	19.66	40.65	40.54	4.21	4.53	5.78	5.25

L^* – $C_9H_8NO_3$

The IR spectra of hippuric acid and the isolated hippurates were recorded over the range 4000–400 cm^{-1} with an UR-20 Spectrophotometer. Analysis of the IR spectra confirmed the data obtained from the elemental analyses. The IR spectra of Y, La and light lanthanide hippurates are similar to one another. The absorption bands of asymmetrical and symmetrical vibrations of the carboxyl ion occur at 1570–1550 cm^{-1} and 1405–1395 cm^{-1}, respectively. The broad absorption band at 3400–3380 cm^{-1} and the sharp band at 1630 cm^{-1} confirm the presence of crystallization water in the complexes. The bands due to metal–oxygen bonds are observed at 380–550 cm^{-1}, and the bands of N—H bands at 1405–1395 cm^{-1} and

1260–1240 cm^{-1}. In order to confirm the crystalline structure of the prepared complexes, X-ray measurements were made on a DRON-2 diffractometer, using Ni-filtered CuK$_\alpha$ radiation, by means of the powder Debye–Scherrer method. The recorded diffractograms showed that all prepared complexes were crystalline compounds. They are characterized by low symmetry and large unit cells. They have various structures.

The thermal stabilities of the Y, La and light lanthanide hippurates were studied by using TG, DTG and DTA techniques. The measurements were made with an OD-102 Paulik–Paulik–Erdey derivatograph (MOM, Hungary) with sensitivities TG = 100 mg, DTG = 1/5 and DTA = 1/10. The samples were heated in platinum crucibles in an air atmosphere at heating rate of 10 deg·min^{-1}, up to 1173 K.

From the thermal curves, the data on the thermal decompositions of the prepared hippurates were evaluated, and are presented in Tables 2 and 3. The solid products were calculated from the TG curves, and verified by recording the IR and X spectra.

Table 2 Temperature data of dehydration of Y, La and light lanthanide hippurates

Complex	Temperature range of dehydration, K	Peak temperature of DTG, K	Endothermic peaks, K	Loss of weight %		Loss of H_2O molecules
				found	calcd.	
$YL_3 \cdot 10H_2O$	363–433	418	413	9.0	9.00	4
$LaL_3 \cdot 8H_2O$	363–413	403	403	9.0	8.80	4
$CeL_3 \cdot 6H_2O$	343–413	403	403	9.0	9.21	4
$PrL_3 \cdot 7H_2O$	343–413	403	403	9.0	8.99	4
$NdL_3 \cdot 5H_2O$	343–413	398	398	7.0	7.03	3
	513–563	563	563	12.0	11.72	2
$SmL_3 \cdot 4H_2O$	353–403	393	403	7.0	7.14	3
$EuL_3 \cdot 6H_2O$	353–423	413	413	9.0	9.06	4
$GdL_3 \cdot 6H_2O$	363–423	413	413	9.0	9.01	4

Results

The results demonstrated that the hippurates of Y, La and the light lanthanides are stable up to 343–363 K and then decompose in two, three or four stages (Figs 1–5). The hippurates of Y, Ce(III), Pr(III) and Gd decompose in two steps. Their hydrated complexes lose 4 water molecules in the temperature range 363–433 K to the accompaniment of a strong endothermic effect, and next decompose directly to Y_2O_3, CeO_2 and Pr_6O_{11} in the temperature range 513–1143 K. The beginning of decomposition is connected with a weak endothermic effect. The burning of the

Table 3 Thermal data of decomposition of Y, La and light lanthanide hippurates

Complex	Temperature range of decomposition, K	Peak temperature of DTG, K	Loss of weight, %		Endothermic peaks, K	Exothermic peaks, K	Temperature of oxide formation, K
			found	Calcd			
$YL_3 \cdot 10H_2O$	533– 973	563, 833	86.0	85.59	583	833	973
$LaL_3 \cdot 8H_2O$	533–1143	563, 793	80.0	80.07	573	733, 823	1143
$CeL_3 \cdot 6H_2O$	493– 883	563	78.0	78.01	573	713, 823	883
$PrL_3 \cdot 7H_2O$	513– 933	553, 773	79.0	78.76	583	818	933
$NdL_3 \cdot 5H_2O$	563– 953	763	78.0	78.11	—	843	953
$SmL_3 \cdot 4H_2O$	493– 973	563, 813	77.0	76.56	573	823	973
$EuL_3 \cdot 6H_2O$	493– 913	553, 773	78.0	77.86	573	713, 813	913
$GdL_3 \cdot 6H_2O$	503– 953	563	77.5	77.33	573	823	953

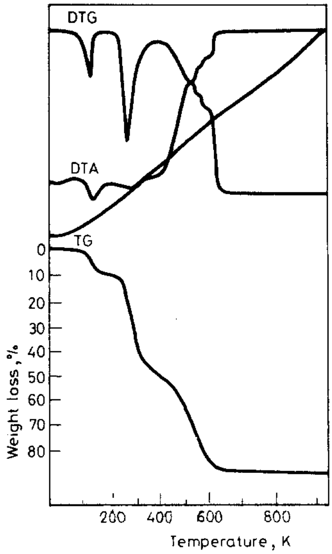

Fig. 1 TG, DTG and DTA curves of $Y(C_6H_5CONHCH_2COO)_3 \cdot 10H_2O$

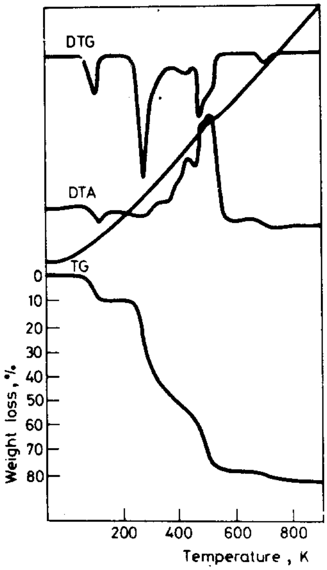

Fig. 2 TG, DTG and DTA curves of $La(C_6H_5CONHCH_2COO)_3 \cdot 8H_2O$

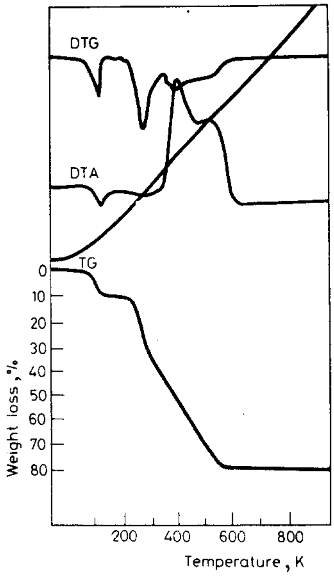

Fig. 3 TG, DTG and DTA curves of $Ce(C_6H_5CONHCH_2COO)_3 \cdot 6H_2O$

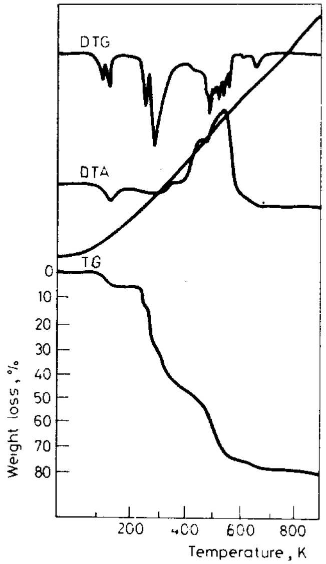

Fig. 4 TG, DTG and DTA curves of $Nd(C_6H_5CONHCH_2COO)_3 \cdot 5H_2O$

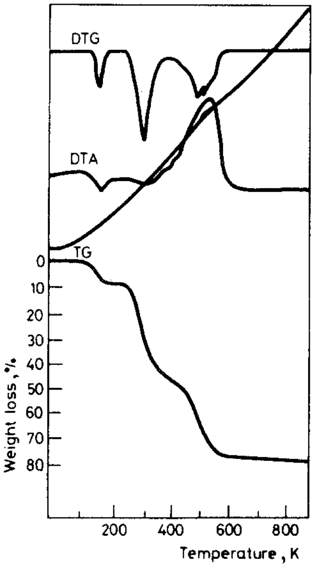

Fig. 5 TG, DTG and DTA curves of $Gd(C_6H_5CONHCH_2COO)_3 \cdot 6H_2O$

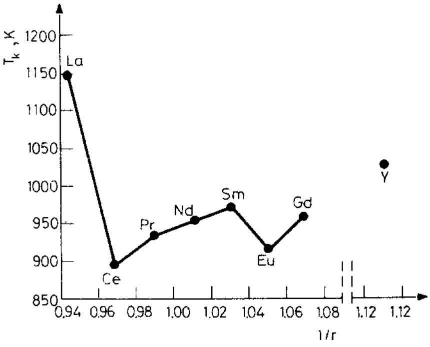

Fig. 6 Relationship between T_k and $1/r_{Ln}$ Goldschmidt's value

organic ligand is accompanied by a strong exothermic effect. The hippurates of La, Sm and Eu decompose in three steps. They lose some water molecules endothermally to yield hydrates, which then lose the remaining water molecules and are decomposed to oxides at 913–1043 K, with the intermediate formation of $Ln_2O_2CO_3$.

The pentahydrate of neodymium hippurate is dehydrated in two steps, first forming the anhydrous complex, which then decomposes to Nd_2O_3 with the intermediate formation of $Nd_2O_2CO_3$.

The water molecules in the prepared complexes are bonded in various ways, probably involving outer and inner sphere water.

From the TG curves, the temperatures of oxide formation (T_k) were determined. It was found that La_2O_3 has the highest temperature of formation (1143 K), while CeO_2 has the lowest one (883 K). It can be seen in Fig. 6 that the temperatures of oxide formation vary periodically in the lanthanide series, which is connected with the periodic change in quantum number L.

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Zusammenfassung — Die Bedingungen der thermischen Zersetzung der Hippurate von Y, La und der leichten Lanthanide von Ce(III) bis Gd wurden untersucht. Beim Aufheizen zersetzen sich die Komplexe von Y, Ce(III), Pr und Gd in zwei Schritten, die von Sm und Eu in drei Schritten und der von Nd in vier Schritten zu den Oxiden. Die Komplexe verlieren Kristallwasser unter Bildung wasserfreier (Nd) oder hydratisierter Salze und zersetzen sich dann direkt (Y, Ce(III), Pr(III), Gd) oder über $Ln_2O_2CO_3$ (Ln, Nd, Sm, Eu) zu den Oxiden. Die Temperatur der Oxidbildung verändert sich periodisch mit abnehmenden Ionenpotential in der Lanthanidenreihe.

Резюме — Изучены условия термического разложения гиппуратов иттрия, лантана и легких лантаноидов от церия до гадолиния. Комплексы иттрия, церия, празеодима и гадолиния при нагревании разлагаются в две стадии, лантана, самария и европия — в три стадии, а неодима — в четыре стадии, образуя оксиды в качестве конечных продуктов разложения. Первоначально комплексы теряют кристаллизационную воду, давая гидраты или безводную соль в случае неодима, а затем непосредственно разлагаются до оксидов (иттрий, церий, празеодим и гадолиний) или же с образованием промежуточного продукта $Ln_2O_2CO_3$ (лантан, неодим, самарий и европий). Температура образования оксидов изменяется периодически с уменьшением ионного потенциала в ряду лантаноидов.