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THERMAL DECOMPOSITION OF Y, La AND LIGHT LANTHANIDE FERULATES

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The conditions of thermal decomposition of Y, La and light lanthanide ferulates have been studied. On heating, these complexes decomposed in various ways; lanthanum ferulate in four stages, Ce(III) ferulate in three stages, and the ferulates of Y, Pr(III), Nd, Sm, Eu(III) and Gd in two stages, the oxides finally being formed. The complexes lose crystallization water to form anhydrous or hydrated salts, and are then decomposed directly to oxides. Only lanthanum ferulate decomposes to the oxide with intermediate formation of $La_2O_2CO_3$. The temperatures of oxide formation change periodically with the decrease in the ionic potential in the lanthanide series.

In recent years several studies have been made on rare earth complexes with carboxylic acids and their thermal decomposition [1–8]. The aim was the understanding of the decomposition mechanism and the nature of the decomposition products. The salts of ferulic acid have received little attention. Hlasewitz and Barth [9] prepared the ferulates of potassium and silver(I) as anhydrous salts and that of ammonium as the monohydrate, with a yellow colour. A search of the available literature showed that ferulates of rare earth have not been studied so far. As a continuation of our work on the thermal decomposition of rare earth carboxylates [10–14], we now report the thermal decomposition of Y, La and light lanthanide ferulates.

Experimental

Ferulates of Y, La, Ce(III), Pr(III), Nd, Sm, Eu(III) and Gd were prepared by double decomposition, equivalent amounts of a 0.1 *M* solution of ammonium ferulate (pH 5) being added to a hot solution containing the rare earth nitrate. The precipitate formed was heated in the mother liquor for 0.5 h at 333–343 K, and was then filtered off, washed with hot water to remove nitrate ions and dried at 303 K to constant mass. The ferulates of Y, La, Ce(III), Sm, Eu(III) were obtained as yellow microcrystals; the Pr salt was green, and the Nd salt pink.

The contents of carbon and hydrogen were determined by elemental analysis. The rare earth content was determined by ignition to the oxides Ln_2O_3 (Ln = La, Nd, Sm, Eu, Gd), CeO_2 or Pr_6O_{11} at 1173 K. The elemental analysis data are presented in Table 1. In most cases the experimental results approximate losely to the

Table 1

Analytical data

Complex	% Metal		% Carbon		% Hydrogen	
	Found	Calcd.	Found	Calcd.	Found	Calcd.
$Y(C_{10}H_9O_4)_3 \cdot 4.5\ H_2O$	11.86	11.81	48.07	48.07	4.84	4.11
$La(C_{10}H_9O_4)_3 \cdot 3\ H_2O$	17.98	18.08	46.60	46.60	4.56	4.62
$Ce(C_{10}H_9O_4)_3 \cdot 5.5\ H_2O$	17.10	17.10	44.01	43.36	4.64	4.37
$Pr(C_{10}H_9O_4)_3 \cdot 3\ H_2O$	18.91	18.90	46.53	48.03	4.56	4.96
$Nd(C_{10}H_9O_4)_3 \cdot 4\ H_2O$	18.15	18.10	45.28	45.44	4.43	4.30
$Sm(C_{10}H_9O_4)_3 \cdot 5.5\ H_2O$	18.39	18.40	43.46	44.08	4.62	4.82
$Eu(C_{10}H_9O_4)_3 \cdot 6\ H_2O$	18.10	18.00	42.88	42.47	4.68	4.40
$Gd(C_{10}H_9O_4)_3 \cdot 2\ H_2O$	20.30	19.93	44.63	44.80	4.95	4.90

values required by theory. The ferulates of Y, La and light lanthanides were prepared as hydrated salts with general formula

$$Ln(C_{10}H_9O_3)_3 \cdot n\ H_2O, \text{ where } n = 2-6.$$

The IR spectra of ferulic acid and the obtained ferulates were recorded over the range 4000–400 cm^{-1} with an OD-102 spectrophotometer. Analysis of the IR spectra confirmed the data obtained from elemental analysis.

In order to establish the crystalline structures of the complexes of Y, La and light lanthanides, X-ray measurements were taken on a DRON-2 diffractometer, using Ni-filtered CuKα radiation, by means of the powder Debye–Scherrer method. The recorded diffractograms showed that La, Ce(III), Pr(III), Nd and Sm ferulates are crystalline. They are characterized by low symmetry and large unit cells. The ferulates of La and Ce(III) are isostructural. The ferulates of Pr(III), Nd and Sm have various structures. The complexes of Y, Eu and Gd are amorphous.

Next, the thermal stabilities of the ferulates of Y, La and light lanthanides were studied by using TG, DTA and DTG techniques. The measurements were made with an OD-102 Paulik–Paulik–Erdey derivatograph (MOM, Hungary) with sensitivities TG – 200 mg, DTA – 1/20, DTG – 1/10. Alumina was used as reference material. Two series of measurements were made. The samples were heated in ceramic crucibles in air at heating rates of 9 and 5.5 deg $\cdot$ min^{-1}.

From the thermal curves, the data on the thermal decomposition of the ferulates were evaluated and are presented in Table 2, where ΔT_1 is the temperature range corresponding to the endothermic loss of some molecules of crystallization water, ΔT_2 is the temperature range corresponding to decomposition of the complex and deflagration of the carbon residue until the formation of oxide and T_p is the temperature of the peak in the DTA curve.

Table 2

Data on decomposition of Y, La and light lanthanide ferulates

Complex*	ΔT_1, K	T_p, K	Loss of weight %		Loss of H_2O, mole	ΔT_2, K	Loss of weight %	
			Calcd.	Found			Calcd.	Found
$YL_3 \cdot 5\ H_2O$	313–383	373	8.4	8.0	2.5	463–928	84.4	85.0
$LaL_3 \cdot 3\ H_2O$	333–373	373	2.3	2.5	1	573–1043	78.9	79.0
	373–573	433	7.0	7.0	2			
$CeL_3 \cdot 5.5\ H_2O$	333–363	363	3.3	3.0	1.5	533–883	77.0	78.0
	373–523	423	6.6	6.5	3			
$PrL_3 \cdot 3\ H_2O$	353–533	433	7.0	6.5	2	533–948	78.0	78.0
$NdL_3 \cdot 4\ H_2O$	333–533	433	4.4	5.0	2	533–1033	74.5	75.5
$SmL_3 \cdot 5.5\ H_2O$	373–533	433	5.4	5.5	2.5	503–873	79.0	79.0
$EuL_3 \cdot 6\ H_2O$	323–513	373	6.4	6.0	3	533–938	79.0	79.0
$GdL_3 \cdot 2\ H_2O$	333–513	373	4.7	5.0	2	553–973	77.0	77.0

* $L^- = C_{10}H_9O_4^-$

Results

The results demonstrated that the ferulates of rare earths decompose in various ways (Figs 1–4. These curves were taken using 5.5 deg · $\min^{-1}$ heating rate). Lanthanum ferulate decomposes in four stages. Its hydrated complex undergoes dehydration in two stages, these processes being connected with two endothermic effects. Next, the heated complex decomposes to the oxide, with the intermediate formation of $La_2O_2CO_3$.

Ce(III) ferulate decomposes in three stages. The dehydrated compound is dehydrated in two stages and then, during heating, the anhydrous salt decomposes directly to CeO_2. The ferulates of Y, Pr(III), Nd, Sm and Eu(III) first lose some molecules of crystallization water, and next the hydrated salts decompose to oxides. During heating the hydrate of gadolinum ferulate loses crystallization water to form the anhydrous salt, which then decomposes to Gd_2O_3.

From the TG curve the temperatures of oxide formation (T_k) were determined at heating rates of 9 and 5.5 K · $\min^{-1}$. The results obtained are presented in Table 3.

Table 3

Temperature of rare earth oxide formation

V \ T_k, K	La	Ce	Pr	Nd	Sm	Eu	Gd	Y
9°/min	1173	1063	1113	1153	1083	1133	1133	993
5.5°/min	1043	883	948	1033	823	958	973	928
ΔT_k	130	180	165	120	150	175	160	65

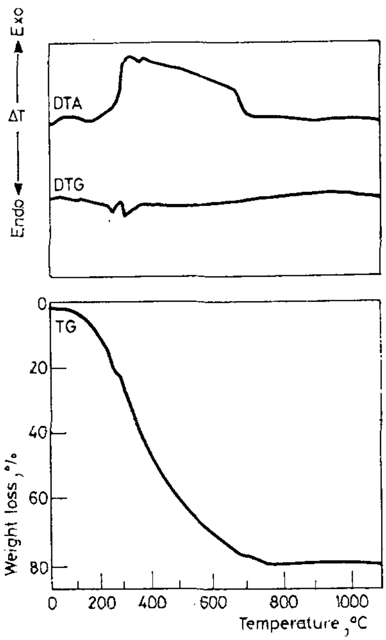

Fig. 1. TG, DTG and DTA curves of $La(C_{10}H_9O_4)_3 \cdot 3\ H_2O$

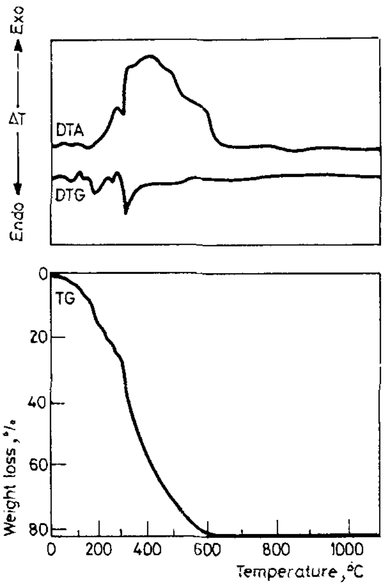

Fig. 2. TG, DTG and DTA curves of $Ce(C_{10}H_9O_4)_3 \cdot 5.5\ H_2O$

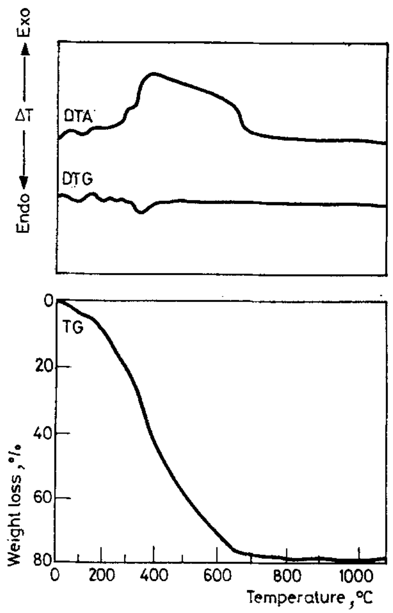

Fig. 3. TG, DTG and DTA curves of $Eu(C_{10}H_9O_4)_3 \cdot 6\,H_2O$

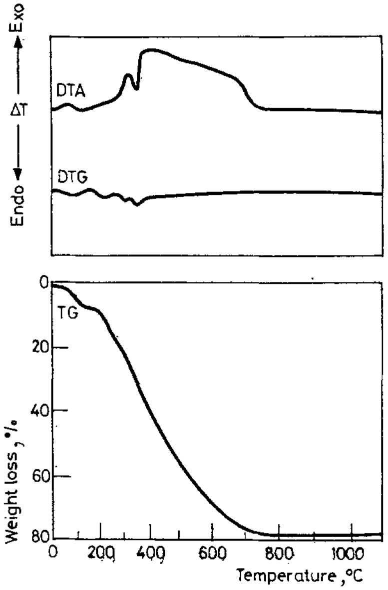

Fig. 4. TG, DTG and DTA curves of $Gd(C_{10}H_9O_4)_3 \cdot 2\,H_2O$

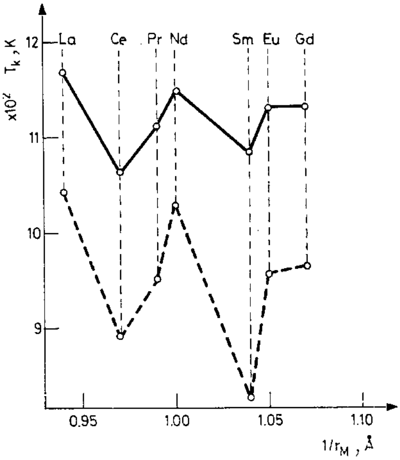

Fig. 5. Relationship between T_k and $1/r_M$ (Goldschmidt's value)

From these data it was found that La_2O_3 has the highest temperature of formation while CeO_2 has the lowest one. The temperature of oxide formation depends on the rate of heating of the sample. At the heating rate of 9 $K \cdot min^{-1}$ the temperatures of oxide formation are lower than those at the heating rate of 5.5 $K \cdot min^{-1}$.

It can be seen from Fig. 5 that the temperatures of oxide formation change periodically.

The double – double effect has been observed; this is very often found in the lanthanide series, and is connected with the periodic change of the quantum number *L* and with the magnitude of the splitting term.

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ZUSAMMENFASSUNG — Es wurden die Bedingungen der Zersetzung der Y-, La- und leichten Lanthanidferulate untersucht. Die erhaltenen Komplexe werden beim Erhitzen auf verschiedene Weise zersetzt. Lanthanferulat wird über vier, Ce(III)-Ferulat über drei und die Ferulate von Y, Pr(III), Nd, Sm, Eu(III) und Gd über zwei Zwischenstufen in das entsprechende Oxid überführt. Aus den Komplexen entstehen zunächst unter Verlust von Kristallwasser wasserfreie oder hydratisierte Salze, die dann direkt zu den Oxiden abgebaut werden. Nur Lanthanferulat wird über eine intermediäre Verbindung des Typs $M_2O_2CO_3$ zum Oxid abgebaut. Die Bildungstemperaturen der Oxide ändern sich periodisch mit abnehmenden Ionenpotential in der Lanthanidenreihe.

Резюме — Изучены условия термического разложения ферулатов Y, La и легких лантанидов. При нагревании эти соли разлагаются различным образом. Ферулат лантанида разлагается в четыре стадии, ферулат трехвалентного церия — в три стадии, а ферулаты Y, Pr(III) Nd, Sm, Eu(III) и Gd — в две стадии с образованием окислов. Комплексы теряют кристаллизационную воду, образуя безводные или гидратные соли, которые затем уже разлагаются до окислов. Только ферулат лантана разлагается до окисла с образованием промеждуточного продукта $La_2O_2CO_3$. Температуры образования окислов изменяются периодически с уменьшением ионизационных потенциалов лантанидных элементов.