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THERMAL DECOMPOSITION OF RARE EARTH PYROMUCATES IN AIR ATMOSPHERE

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The conditions of thermal decomposition of Y, La and lanthanide (from Ce(III) to Lu) pyromucates have been studied. On heating, these complexes decompose in various ways: La, Pr, Nd and Sm pyromucates in four stages, Ce, Eu, Gd, Dy, Ho and Er pyromucates in three stages, and Tm, Yb, Lu and Y pyromucates in two stages, the oxides finally being formed. The hydrated complexes (from La to Er) lose crystallization water to form anhydrous salts. The anhydrous complexes of La, Pr, Nd and Sm decompose to oxides through the intermediate formation of unstable oxypyromucates and $Ln_2O_2CO_3$, whereas the anhydrous complexes of Ce(III), Eu, Gd, Dy, Ho, Er, Tm, Yb and Lu decompose to the oxides through the intermediate formation of oxypyromucates. The temperatures of dehydration and oxide formation change periodically with increasing atomic number in the lanthanide series.

Furan-2-carboxylic acid, known as pyromucic acid, is a crystalline solid sparingly soluble in cold water and soluble in alcohols [1]. The salts of pyromucic acid are little known. Pyromucates of Na, K, NH_4, Ca, Ba and Ag(I) have been prepared as anhydrous salts, and those of Cu(II) and Pb(II) as hydrates [1].

Pyromucates of La and light lanthanides have been prepared [2] as crystalline solids soluble in water. As a continuation of our work on the thermal decomposition of rare earth carboxylates [3–7], we now report the thermal decomposition of Y, La and lanthanide pyromucates.

Experimental

The pyromucates of Y. La and lanthanides from Ce(III) to Lu were prepared by adding equivalent amounts of a 0.5 *M* solution of ammonium pyromucate (pH 4.5–5.0) to a 0.1 *M* solution of rare earth nitrate and crystallizing in a water-bath at 323 K. The precipitated pyromucates of Y, La and lanthanides were filtered off, washed with methanol to remove ammonium ions, and dried at 303 K to constant weight.

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Table 1 Analytical data

Complex	% C		% H		% M	
	Calcd.	Found.	Calcd.	Found.	Calcd.	Found.
YL_3*	42.68	42.29	2.15	2.26	21.06	21.46
$LaL_3 \cdot 2H_2O$	35.45	35.87	2.57	3.13	27.33	27.43
$CeL_3 \cdot 2H_2O$	35.37	35.98	2.57	2.43	27.51	27.47
$PrL_3 \cdot 2H_2O$	35.31	34.81	2.57	2.73	27.62	27.99
$NdL_3 \cdot 3H_2O$	33.90	34.91	2.65	2.05	27.14	27.78
$SmL_3 \cdot 3H_2O$	33.51	34.28	2.62	2.23	28.06	28.24
$EuL_3 \cdot 3H_2O$	33.41	33.15	2.62	2.77	28.18	28.65
$GdL_3 \cdot 3H_2O$	33.08	32.88	2.59	2.81	28.88	29.06
$TbL_3 \cdot 3H_2O$	32.98	32.83	2.58	2.83	29.09	29.73
$DyL_3 \cdot 3H_2O$	32.77	32.40	2.57	3.07	29.56	29.38
$HoL_3 \cdot 3H_2O$	32.63	32.63	2.56	3.13	29.87	29.57
$ErL_3 \cdot 2H_2O$	33.58	33.06	2.44	2.43	31.17	30.96
TmL_3	35.88	35.62	1.81	2.04	33.64	34.16
YbL_3	35.59	35.08	1.79	1.81	34.18	34.25
LuL_3	35.25	35.34	1.78	1.82	34.43	34.35

The pyromucates of Y, La and lanthanides were prepared as crystalline solids soluble in water and sparingly soluble in methanol. The pyromucates of Y, La, Ce(III), Sm, Eu(III), Tb(III, Dy, Ho, Tm, Yb and Lu are cream-coloured, that of Pr is greenish, that of Nd is pink, and that of Er is pale-pink.

The carbon and hydrogen contents were determined by elemental analysis. The rare earth content was determined by ignition to the oxide Ln_2O_3 (Ln = La, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu or Y), 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 closely to the values required by theory. These pyromucates were hydrated complexes with a metal to ligand ratio of 1 : 3. The pyromucates of La, Ce(III), Pr and Er were prepared as dihydrates, those of intermediate lanthanides from Nd to Ho as trihydrates, and those of Tm, Yb, Lu and Y as anhydrous salts. These pyromucates were also prepared as monocrystals. Monocrystals of La and all lanthanide pyromucates have the same composition as the polycrystals, but monocrystalline yttrium pyromucate was prepared as the trihydrate and the polycrystalline complex as the anhydrous salt.

The IR spectra of pyromucic acid and the prepared rare earth pyromucates were recorded over the range 4000–400 cm^{-1} with a UR-20 spectrophotometer. Analysis of the IR spectra confirmed the data obtained from elemental analysis.

In order to establish the crystalline structure of the Y, La and lanthanide complexes, X-ray measurements were made on a DRON-2 diffractometer, using CuK_α radiation, through powder and monocrystal methods.

Table 2 Data on decomposition of Y, La and lanthanide pyromucates

Complex	Temperature range of dehydration, K	Loss of weight		Loss of H_2O mole	Temperature range of decomposition, K	Residue of weight		Temperature of oxide** formation, K
		% calcd.	% found			% calcd.	% found	
$LaL_3^* \cdot 2H_2O$	378–478	7.09	7.0	2	573–1023	32.06	31.8	1023
$CeL_3 \cdot 2H_2O$	353–453	7.07	7.0	2	553–1073	33.79	33.4	1073
$PrL_3 \cdot 2H_2O$	373–453	7.06	7.0	2	483–1063	33.37	33.0	1063
$NdL_3 \cdot 3H_2O$	348–523	10.17	9.9	3	548–1038	31.65	32.4	1038
$SmL_3 \cdot 3H_2O$	353–413	10.05	10.0	3	548–1013	32.43	32.5	1013
$FuL_3 \cdot 3H_2O$	363–413	10.02	10.2	3	513–1083	32.63	32.3	1083
$GdL_3 \cdot 3H_2O$	353–423	9.92	10.0	3	583–1013	33.29	32.9	1013
$TbL_3 \cdot 3H_2O$	363–413	9.89	10.0	3	573–1213	33.49	33.5	1213
$DyL_3 \cdot 3H_2O$	368–403	9.83	9.5	3	478–1013	33.92	33.4	1013
$HoL_3 \cdot 3H_2O$	368–403	9.79	10.0	3	568–1033	34.21	33.5	1033
$ErL_3 \cdot 2H_2O$	343–393	6.72	7.5	2	488–1013	35.65	35.4	1013
TmL_3					513– 993	38.42	38.1	993
YbL_3					523–1033	38.92	38.5	1033
LuL_3					603–1063	39.15	38.7	1063
YL_3					603–1063	26.75	26.5	1063

* L — $C_5H_3O_3$

** Ln_2O_3 (Ln — La, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) CeO_2, Pr_6O_{11}

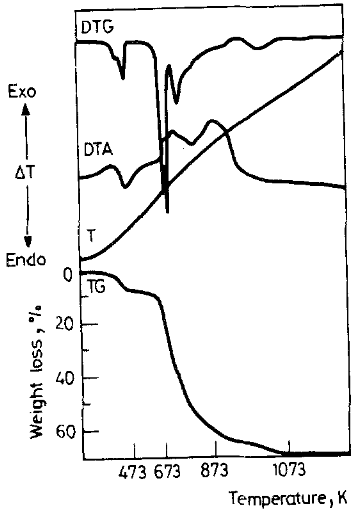

Fig. 1 TG, DTG and DTA curves of $La(C_5H_3O_3)_3 \cdot 2H_2O$

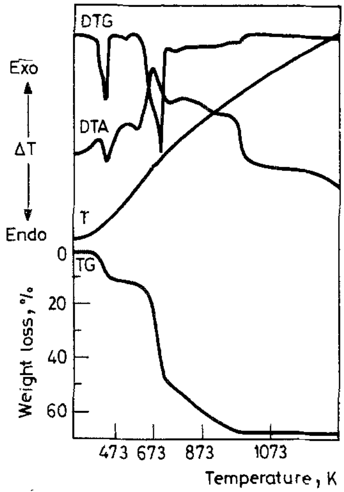

Fig. 2 TG, DTG and DTA curves of $Ce(C_5H_3O_3)_3 \cdot 2H_2O$

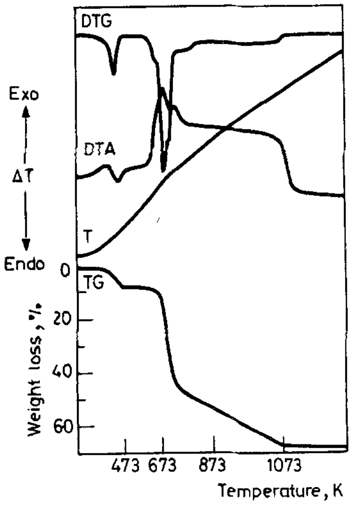

Fig. 3 TG, DTG and DTA curves of $Gd(C_5H_3O_3)_3 \cdot 3H_2O$

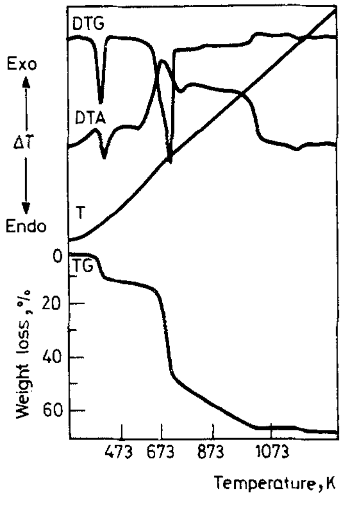

Fig. 4 TG, DTG and DTA curves of $Tb(C_5H_3O_3)_3 \cdot 3H_2O$

The recorded diffractograms showed that the Y, La and lanthanide complexes are crystalline. They are characterized by low symmetry and large unit cells. All prepared complexes crystallize in the monoclinic system.

Next, the thermal stabilities of the pyromucates of Y, La and lanthanides from Ce(III) to Lu were studied by TG, DTA and DTG. The measurements were made

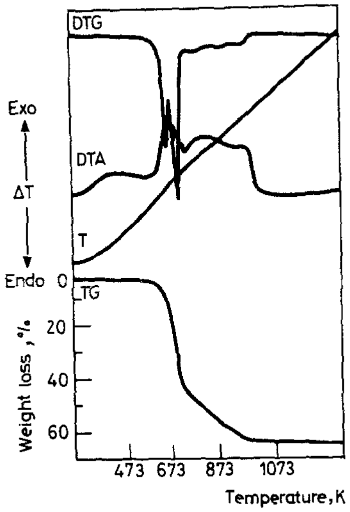

Fig. 5 TG, DTG and DTA curves of $Tm(C_5H_3O_3)_3$

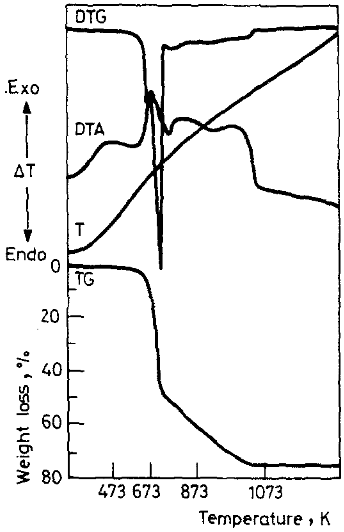

Fig. 6 TG, DTG and DTA curves of $Y(C_5H_3O_3)_3$

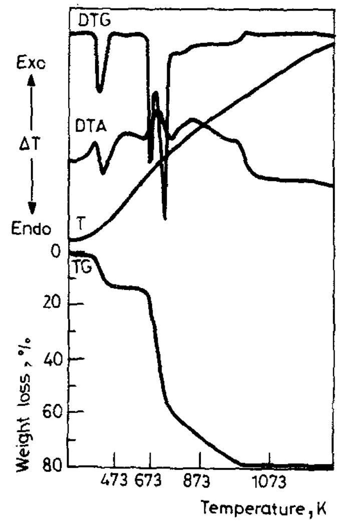

Fig. 7 TG, DTG and DTA curves of $Y(C_5H_3O_3)_3 \cdot 3H_2O$ monocrystal

with an OD–102 Paulik–Paulik–Erdey derivatograph. Alumina was used as reference materials. The samples were heated in ceramic crucibles in air at heating rates of 10 deg·min^{-1}.

From the thermal curves, the data on the thermal decomposition of the rare earth pyromucates were evaluated and are presented in Table 2 and Figs 1–7.

Results and discussion

The results indicate that the rare earth pyromucates decompose in various way (Figs 1–6). The hydrated pyromucates of the rare earths from La to Er undergo dehydration in one step, accompanied by a strong endothermic effect. Dehydration takes place at 343–393 K. The ranges of dehydration temperatures of rare earth Pyromucates are presented in Fig. 8. These were found to change periodically with increasing atomic number, and for the light lanthanons they are higher than for the heavy ones. The anhydrous complexes of La, Pr, Nd and Sm (Fig. 1) decompose to oxides (Ln_2O_3 or Pr_6O_{11}) with the intermediate formation of very unstable oxypyromucates (LnOL) and oxycarbonates ($Ln_2O_2CO_3$).

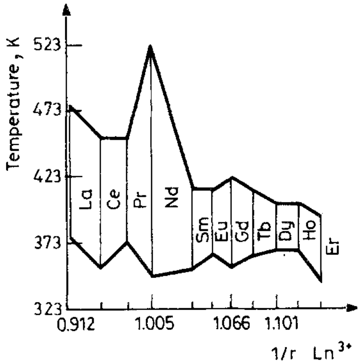

Fig. 8 Relationship between range of dehydration temperatures and $1/r_M$ (Goldschmidt's value)

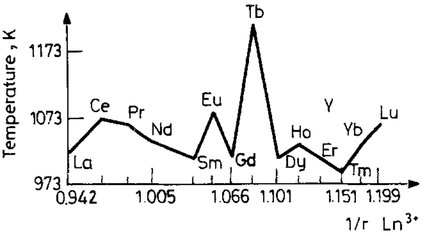

Fig. 9 Relationship between T_k and $1/r_M$ (Goldschmidt's value)

The anhydrous pyromucates of lanthanides from Gd to Lu, Ce(III) and Y decompose to oxides (Ln_2O_3 or CeO_2) with the intermediate formation of very unstable oxypyromucates (Figs 2–6). The oxypyromucates of rare earths from La to Gd are formed at 733 K, or those from Tb to Ho at 753 K, those of Er, Tm and Y at 773 K, and those of Yb and Lu at 793 K.

During heating, terbium pyromucate decomposes at 1053 K to Tb_4O_7, which at 1213 K decomposes further to Tb_2O_3 in an endothermic reaction. The rare earth oxides are formed at 933–1073 K, except for Tb_2O_3, which is formed at 1213 K (Table 2, Fig. 9). The temperatures of oxide formation change periodically with increasing atomic number and decreasing ionic radius in the lanthanide series. The double-double effect has been observed.

Polycrystalline yttrium pyromucate was prepared as the anhydrous salt stable to 603 K. At higher temperatures it decomposes Y_2O_3 with intermediate formation of the oxypyromucate (Fig. 6). Monocrystalline yttrium pyromucate was prepared as the trihydrate. On heating, the hydrate loses crystallization water to form the anhydrous salt, which then decomposes to Y_2O_3 as the polycrystalline complex (Fig. 7).

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Zusammenfassung — Die Bedingungen der thermischen Zersetzung der Pyromucate von Y, La und den Lanthaniden (Ce(III) bis Lu) wurden untersucht. Beim Erhitzen zersetzen sich die Komplexe auf verschiedene Weise: die Pyromucate von La, Pr, Nd und Sm in 4 Schritten, die von Ce, Eu, Gd, Dy, Ho d Er in 3 Schritten und die von Tm, Yb, Lu und Y in nur 2 Schritten. Endprodukte der Zersetzung sind die Oxide, Die hydratisierten Komplexe von La bis Er verlieren Kristallwasser unter Bildung der wasserfreien Salze. Die wasserfreien Komplexe von La, Pr, Nd und Sm zersetzen sich zu Oxiden über instabile Oxypyromucate und $Ln_2O_2CO_3$ als Zwischenprodukte, bei der Zersetzung der wasserfreien Komplexe von Ce(III), Eu, Gd, Dy, Ho, Er, Tm, Yb und Lu werden Oxypyromucate als Zwischenprodukte gebildet. Die Temperaturen der Dehydratisierung und Oxidbildung schwanken periodisch mit ansteigender Atomzahl in der Lanthanidenreihe.

Резюме — Изучены условия термического разложения иттрий, лантан и лантанидных (от церия до лютеция) солей пирослизёвой кислоты. При нагревании соли разлагаются различными путями: соли лантана, празеодима, неодима и самария разлагаются в четыре стадии, соли церия, европия, гадолиния, диспрозия, гольмия и эрбия — в три стадии, а соли тулия, иттербия, лютеция и иттрия — в две стадии с образованием окислов в качестве конечных продуктов реакции. Гидраты солей от лантана до эрбия теряют кристаллизационную воду, давая безводные соли. Безводные соли лантана, празеодима, неодима и самария разлагаются до окислов через промежуточную стадию образования неустойчивых солей оксипирослизёвой кислоты и $Ln_2O_2CO_3$. Безводные соли остальных лантанидов разлагаются до окислов через промежуточную стадию образования только солей оксипирослизёвой кислоты. Температуры дегидратации и образования окислов изменяются периодически с увеличением атомного числа в рядах лантанидов.