THERMAL DECOMPOSITION OF RARE EARTH ELEMENT ENANTHATES

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Abstract

The conditions of formation of Y, La and lanthanide (from Ce(III) to Lu) enanthates were worked out, their composition and their solubilities in water at 291 K were determined, and the conditions of their thermal decomposition were studied. They were prepared as crystalline solids with general formula $Ln(C_7H_{13}O_2)_3 \cdot nH_2O$, where $n = 2$–10. On heating, they decompose in two or three steps. They first lose some water molecules and then decompose to the oxides directly (salts of Y and heavy lanthanides) or via the intermediate formation of $Ln_2O_2CO_3$ (salts of La, Pr, Nd, Sm and Eu). Only yttrium enanthate dihydrate loses 2 water molecules on heating to form an anhydrous complex, which decomposes directly to Y_2O_3. The temperatures of dehydration are similar for all complexes (323–343 K), while the temperatures of oxide formation vary irregularly from 823 K for CeO_2 to 1078 K for La_2O_3.

Keywords: complexes, rare earth element salts of enanthic acid, derivatograph, IR, lanthanides

Introduction

Heptanoic acid, $CH_3(CH_2)_5COOH$, known as enanthic acid, is a liquid sparingly soluble in water (0.2 g/100 g H_2O). Its salts are little known. A search of the available literature shows that the conditions of preparation of the sodium [1], potassium [2], lithium [3], copper(II), silver(I), calcium [4], barium [4, 5], zinc(II), cadmium [4] and lead(II) [2] salts have been studied, and the properties of these salts have been determined. Brzyska [6] has prepared enanthates of light lanthanides and yttrium, and determined their solubilities in water. Cherchas [7] has studied the crystallographic structure of cerium(III) enanthate. Sklenskaya [8] has determined the stability constant of scandium(III) enanthate by potentiometry and has established the existence of the complex $Sc(C_7H_{13}O_2)^{2+}$. Salts of the heavy lanthanides have not been reported so far. The

thermoanalytical properties and IR spectra of rare earth element salts have not been studied either.

As a continuation of our work on the thermal decompositions of rare earth element carboxylates, we now report on the thermal decomposition of Y, La and lanthanide enanthates.

Experimental

The enanthates of Y, La and lanthanides from Ce(III) to Lu were prepared by adding a small excess of a 0.2 M solution of ammonium enanthate (pH 5.5–6.0) to a hot solution of rare earth element chloride (cerium(III) was used as nitrate). The precipitate formed was heated in the mother liquor at 343–353 K for 0.5 h, then filtered off, washed with destilled water to remove Cl^- and NH_4^+ ions, and dried at 303 K to constant mass.

The carbon and hydrogen contents in the prepared complexes were determined by elemental analysis. The rare earth element contents were determined from the TG curves and by ignition of the complexes at 1173 K to the oxides Ln_2O_3 (Ln = Y, La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb and Lu), CeO_2, Pr_6O_{11} or Tb_4O_7. The crystallization water contents were determined from the TG curves and by isothermal heating at definite temperature. The elemental analysis data are given in Table 1.

The IR spectra of enanthic acid, sodium enanthate and the prepared rare earth enanthates were recorded over the range 4000–400 cm^{-1} with a UR-20 spectrophotometer. The samples were prepared as KBr discs.

In order to establish the crystal structures of the prepared complexes, X-ray measurements were made on a DRON-2 diffractometer, using CuK_α radiation, through a powder method.

The solubilities in water of the prepared enanthates at 291 K were determined. The contents of rare earth element ions in the saturated solutions were determined by using the oxalate method.

Next, the thermal stabilities of the enanthates of Y, La and the lanthanides were studied via the TG, DTG and DTA curves. The measurements were made with a Q-1500D Paulik-Paulik-Erdey derivatograph. Alumina was used as reference material. Samples of 100 mg were heated to 1273 K in ceramic crucibles in an air atmosphere at a heating rate of 10 deg·min^{-1} with sensitivity TG = 100 mg, DTG = 500 μV, DTA = 500 μV. The intermediates were established from the TG curves and verified by recording the IR spectra.

Table 1 Analytical data and solubility of Y, La and lanthanide enanthates

Complex	% Ln		% C		% H		Solubility / 10^{-4} mol·dm^{-3}
	calcd.	found	calcd.	found	calcd.	found	
$Y(C_7H_{13}O_2)_3 \cdot 2H_2O$	17.36	17.40	49.21	49.24	8.39	8.23	7.58
$La(C_7H_{13}O_2)_3 \cdot 6H_2O$	21.91	21.70	39.75	39.70	8.04	8.00	5.84
$Ce(C_7H_{13}O_2)_3 \cdot 4H_2O$	23.38	23.40	42.06	42.00	7.84	7.90	4.60
$Pr(C_7H_{13}O_2)_3 \cdot 7H_2O$	21.54	21.40	38.53	38.50	8.10	8.10	4.04
$Nd(C_7H_{13}O_2)_3 \cdot 7H_2O$	21.94	22.00	38.34	38.20	8.06	8.00	4.00
$Sm(C_7H_{13}O_2)_3 \cdot 8H_2O$	22.04	22.00	36.95	36.90	8.06	8.10	3.83
$Eu(C_7H_{13}O_2)_3 \cdot 5H_2O$	24.16	24.00	40.06	40.03	7.79	7.80	3.42
$Gd(C_7H_{13}O_2)_3 \cdot 10H_2O$	21.71	21.70	34.79	34.60	8.14	8.20	3.42
$Tb(C_7H_{13}O_2)_3 \cdot 9H_2O$	22.44	22.50	35.59	35.60	8.05	8.00	3.46
$Dy(C_7H_{13}O_2)_3 \cdot 5H_2O$	25.41	25.40	39.40	40.00	7.66	7.70	1.96
$Ho(C_7H_{13}O_2)_3 \cdot 9H_2O$	23.10	23.10	35.29	35.20	7.98	8.00	4.97
$Er(C_7H_{13}O_2)_3 \cdot 10H_2O$	22.78	22.70	34.31	34.50	8.03	8.20	3.38
$Tm(C_7H_{13}O_2)_3 \cdot 5H_2O$	26.19	26.20	38.98	39.10	7.58	7.70	4.45
$Yb(C_7H_{13}O_2)_3 \cdot 2H_2O$	29.02	29.00	42.28	42.20	7.21	7.25	1.97
$Lu(C_7H_{13}O_2)_3 \cdot 7H_2O$	25.43	25.20	36.62	36.60	7.70	7.50	4.62

The data on the thermal decompositions of the rare earth enanthates were evaluated from the thermal curves, and are presented in Tables 2 and 3, and, for example, in Figs 1 and 2.

Results and discussion

The enanthates of Y, La and the lanthanides from Ce(III) to Lu were prepared as solids with colours characteristic of the Ln^{3+} ions. They were sparingly soluble in water (Table 1); their solubilities are of the order of 10^{-4} mol·dm^{-3}, and decrease with increasing atomic number in the light lanthanide series, whereas they change irregularly in the heavy lanthanide series. They rare earth element enanthates were prepared as complexes with a metal to organic ligand ratio of 1:3 and different degrees of hydration (Table 1). The number of crystallization water molecules changes from 2 for the yttrium salt to 10 for gadolin-

Table 2 Absorption bands of v_{as} COO$^-$ and v_s COO$^-$ of Na, Y, La and lanthanide enanthates

Complex	v_{as} COO$^-$	Δv_{as} COO$^-$	v_s COO$^-$	Δv_s COO$-$	$v_{as} - v_s$ COO$-$
NaL*·nH$_2$O	1570, 1560		1450, 1425		127.5
YL$_3$·2H$_2$O	1555	– 10	1460	22.5	95
LaL$_3$·6H$_2$O	1540	– 25	1450	12.5	90
CeL$_3$·4H$_2$O	1550, 1540	– 20	1460, 1450	17.5	90
PrL$_3$·7H$_2$O	1550, 1540	– 20	1455, 1450	15.0	92.5
NdL$_3$·7H$_2$O	1550, 1540	– 20	1460, 1450	17.5	90
SmL$_3$·8H$_2$O	1550, 1540	– 20	1470, 1460	27.5	80
EuL$_3$·5H$_2$O	1555, 1540	– 17.5	1470, 1460	27.5	82.5
GdL$_3$·10H$_2$O	1555, 1540	– 17.5	1470, 1460	27.5	82.5
TbL$_3$·9H$_2$O	1555	– 10	1455	17.5	100
DyL$_3$·5H$_2$O	1555	– 10	1455	17.5	100
HoL$_3$·9H$_2$O	1550	– 15	1455	17.5	95
ErL$_3$·10H$_2$O	1555	– 10	1450	12.5	105
TmL$_3$·5H$_2$O	1555	– 10	1460	22.5	95
YbL$_3$·2H$_2$O	1550	– 15	1450	12.5	100
LuL$_3$·7H$_2$O	1555	– 10	1455	17.5	100

* L – $C_6H_{13}COO^-$
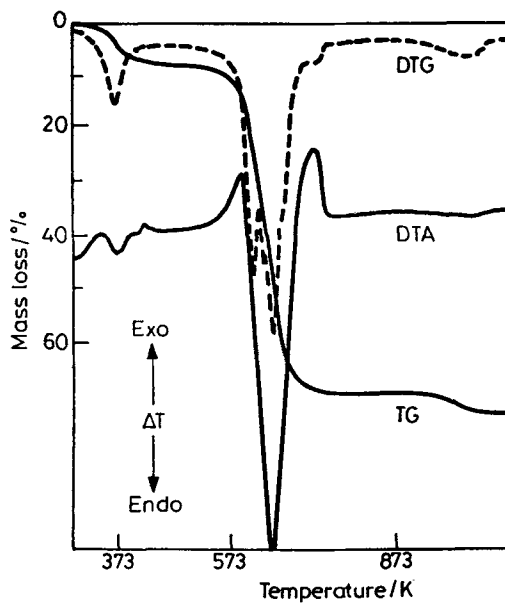
Fig. 1 TG, DTG and DTA curves of $La(C_6H_{13}COO)_3 \cdot 6H_2O$
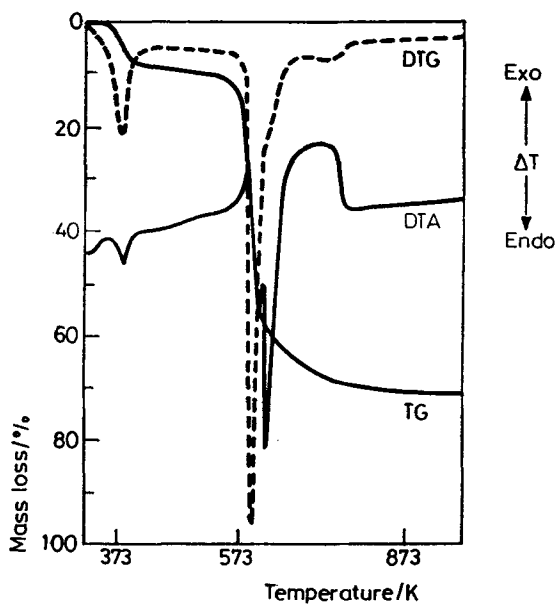
Fig. 2 TG, DTG and DTA curves of $Dy(C_6H_{13}COO)_3 \cdot 5H_2O$

ium. The recorded diffractograms show that the prepared salts are crystalline solids isostructural in the La, Ce, Pr series and in the Y, Nd-Lu series.

The IR spectra (Table 2) of the prepared complexes are similar. The absorption bands with maxima at 3440–3330 cm^{-1} and 1630–1610 cm^{-1} confirmed the presence of crystallization water. The IR spectra display the absorption bands of asymmetric and symmetric vibrations of the OCO$^-$ group at 1555–1540 cm^{-1} and 1470–1450 cm^{-1}, respectively, and the metal-oxygen bond at 660–650 cm^{-1} and 460–420 cm^{-1}. In the IR spectra of the Ce(III), Pr(III), Nd, Sm(III), Eu(III) and Gd salts, the absorption bands of the asymmetric and symmetric vibrations of the OCO$^-$ group are split (Table 2), similarly as in the IR spectrum of the sodium salt. On the basis of the shifts of v_{as}OCO to lower frequencies and of v_sOCO to higher values as compared with those for the sodium salt, it is possible to say that the carboxylate ion is chelated in a bidentate manner. The magnitude of the split, $\Delta v = v_{as}-v_s$ ($\Delta v = 80$–105 cm^{-1}), shows a higher degree of covalency of the OCO$^-$---Ln^{3+} bond than that of the corresponding bond in the sodium salt ($\Delta v = 127.5$ cm^{-1}). The higher values of Δv in the IR spectra of Y and the heaviest lanthanide salts ($\Delta v = 95$–105 cm^{-1}) in comparison with those for the light lanthanide salts ($\Delta v = 80$–90 cm^{-1}) can be caused by asymmetrization of the OCO$^-$---Ln^{3+} bond. The trend for the bidentate structures to undergo symmetrization and equalization of the bond lengths is connected with the decreasing Δv values [9] and may be connected with the change in the OCO bond angle. In this way, it is possible to suggest that the chelating bond OCO$^-$---Ln^{3+} is more symmetric in the salts of La and the light lanthanides than in those of Y and the heavy lanthanides. For a full explanation of the character of the OCO$^-$---Ln^{3+} bond, it is necessary to determine the crystallographic and molecular structures of the monocrystalline salts.

When heated in air atmosphere to 1273 K the rare earth element enanthates decompose in various ways (Tables 2 and 3). For example, the thermal curves of the La and Dy salts are given in Figs 1 and 2. The prepared complexes are stable up to 323–343 K, but subsequently lose 2–4 water molecules, to the accompaniment of a strong endothermic effect, to form hydrates containing less crystallization water. Only yttrium enanthate is transformed into the anhydrous salt. The rare earth enanthates are dehydrated in one step, with the exception of thulium enanthate, which is dehydrated in two steps. The temperatures of dehydration remain practically unchanged with increase in the atomic number of the metal and the ionic potential $\varnothing$. When heated, anhydrous yttrium enanthate decomposes directly to Y$_2$O$_3$ in the temperature interval 523–923 K. The hydrated

Table 3 Thermoanalytical data of Y, La and lanthanide enanthates

| Complex | Temperature range of dehydration / K | Loss of weight / % | | Loss of H_2O molecules | Temperature range of decomposition / K | Loss of weight / % | | Temperature of oxide formation T_k / K |
		calcd.	found			calcd.	found	
$YL_3^*\cdot 2H_2O$	333–393	7.5	7.0	2	523–923	76.5	76.2	923
$LaL_3\cdot 6H_2O$	323–423	8.0	8.5	3	538–1073	72.5	71.9	1073
$CeL_3\cdot 4H_2O$	323–418	6.2	6.0	2	518–823	72.0	71.9	823
$PrL_3\cdot 7H_2O$	338–413	8.0	8.2	3	563–908	72.0	71.6	908
$NdL_3\cdot 7H_2O$	328–413	8.0	8.2	3	563–1028	72.0	72.1	1028
$SmL_3\cdot 8H_2O$	343–433	10.4	10.5	4	523–1033	72.0	71.4	1033
$EuL_3\cdot 5H_2O$	323–413	8.8	8.6	3	473–973	69.0	68.7	973
$GdL_3\cdot 10H_2O$	323–423	10.2	10.0	4	593–948	71.9	72.2	948
$TbL_3\cdot 9H_2O$	323–408	10.4	10.2	4	523–983	70.5	70.7	983
$DyL_3\cdot 5H_2O$	323–413	8.2	8.4	3	593–893	68.8	68.3	893
$HoL_3\cdot 9H_2O$	323–443	9.8	10.1	4	513–973	70.4	70.5	973
$ErL_3\cdot 10H_2O$	323–413	10.0	9.8	4	533–913	71.6	71.1	913
$TmL_3\cdot 5H_2O$	323–413	8.5	8.3	3	513–958	67.8	67.5	958
$YbL_3\cdot 2H_2O$	333–383	3.1	3.0	1	543–913	65.2	64.8	913
	448–523	3.2	3.2	1				
$LuL_3\cdot 7H_2O$	323–418	10.5	10.4	4	608–923	68.0	67.7	923

* $L - C_7H_{13}O_2$

Table 4 Intermediate products of thermal decomposition of Y, La and lanthanide enanthates

Complex	Intermediate products of decomposition	Final product of decomposition	Exothermic effects / K	Endothermic effects / K	Peak temperatures of DTG / K
$YL_3 \cdot 2H_2O$*	–	Y_2O_3	333, 593, 753	373, 623, 643	373, 643
$LaL_3 \cdot 3H_2O$	$La_2O_2CO_3$	La_2O_3	348, 633, 748	373, 653, 678	373, 678
$CeL_3 \cdot 4H_2O$	–	CeO_2	343, 593, 743	373, 653, 668	373, 653
$PrL_3 \cdot 7H_2O$	$Pr_2O_2CO_3$	Pr_6O_{11}	338, 633, 738	378, 653, 683	378, 643
$NdL_3 \cdot 7H_2O$	$Nd_2O_2CO_3$	Nd_2O_3	343, 613, 733	373, 613, 733	373, 648
$SmL_3 \cdot 8H_2O$	$Sm_2O_2CO_3$	Sm_2O_3	343, 613, 763	373, 633, 658	373, 633
$EuL_3 \cdot 5H_2O$	$Eu_2O_2CO_3$	Eu_2O_3	323, 593, 743	373, 623, 658	373, 623
$GdL_3 \cdot 10H_2O$	–	Gd_2O_3	343, 623, 723	393, 633, 663	373, 383, 633
$TbL_3 \cdot 9H_2O$	–	Tb_4O_7	343, 613, 773	373, 628, 663	373, 383, 623
$DyL_3 \cdot 5H_2O$	–	Dy_2O_3	333, 623, 728	373, 633, 658	373, 633
$HoL_3 \cdot 9H_2O$	–	Ho_2O_3	323, 613, 723	373, 633, 663	373, 633
$ErL_3 \cdot 10H_2O$	–	Er_2O_3	353, 623, 723	373, 633, 668	373, 633
$TmL_3 \cdot 5H_2O$	–	Tm_2O_3	333, 603, 753	363, 603, 658	363, 628
$YbL_3 \cdot 2H_2O$	–	Yb_2O_3	363, 563, 603, 723	483, 583, 653	363, 483, 653
$LuL_3 \cdot 7H_2O$	–	Lu_2O_3	343, 633, 718	373, 633, 673	373, 383, 643

* $L - C_6H_{13}COO^-$

salts of the other elements undergo dehydration and decomposition simultane-
ously in the temperature interval 473–1028 K. The enanthates of La, Pr(III),
Nd, Sm(III) and Eu(III) decompose to Ln_2O_3 or Pr_6O_{11} with intermediate for-
mation of $Ln_2O_2CO_3$. When heated, the salts of Y, Ce(III) and the heavy lantha-
nides from Gd to Lu decompose directly to Ln_2O_3, CeO_2 or Tb_4O_7. The
temperatures of oxide formation T_k vary irregularly with increasing ionic poten-
tial $\varnothing$ and atomic number Z of the lanthanides (Fig. 3). The rare earth oxides
are formed at 893–983 K, except those of La, Nd and Sm, which are formed at
1028–1073 K, and that of Ce, at 823 K. The dehydration and decomposition of
the salts, and the decomposition of $Ln_2O_2CO_3$, are endothermic processes,
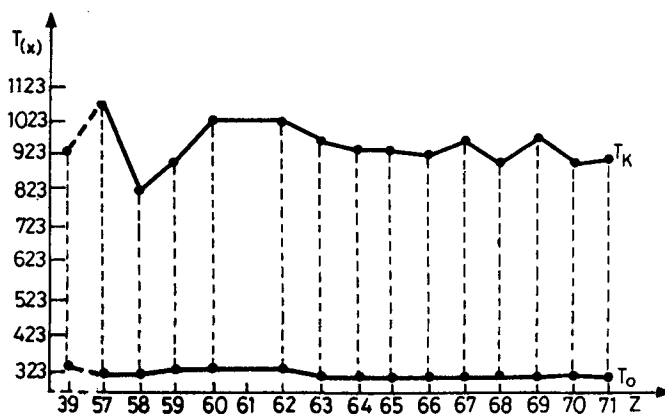whereas the ignition of the organic ligand and deflagration carbon is exother-
mic.

Fig. 3 Relationship between T_0, T_k and Z for rare earth enanthates

The crystallization water in the prepared salts is bonded in different ways.
The water molecules lost at 323–343 K are outer sphere water, and those lost
during decomposition are in the inner sphere. Only yttrium enanthate dihydrate
contains merely outer sphere water.

Yttrium enanthate has properties similar to those of the heavy lanthanide
salts: temperature of decomposition (Table 3), solubility and crystallographic
structure. It crystallizes with 2 water molecules, as does the ytterbium complex.
Yttrium complexes are in most cases similar to heavy lanthanide complexes,
this being connected with the values of ionic radius and potential $\varnothing$.

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Zusammenfassung — Es wurden die Bedingungen für die Bildung von Y-, La- und Lanthanoiden- (von Ce(III) bis Lu) Oenanthaten ausgearbeitet, ihre Zusammensetzung und Wasserlöslichkeit bei 291 K bestimmt und die Umstände ihrer thermischen Zersetzung untersucht. Sie wurden als kristalline Feststoffe mit der allgemeinen Formel $Ln(C_7H_{13}O_2)_3 n H_2O$ (mit $n = 2$–10) dargestellt. Beim Erhitzen zersetzen sie sich in zwei oder drei Schritten. Zuerst verlieren sie einige Wassermoleküle und zersetzen sich dann direkt zu Oxiden (Salze von Y und schweren Lanthanoiden) oder aber über die Bildung des Zwischenproduktes $Ln_2O_2CO_3$ (Salze von La, Pr, Nd, Sm und Eu). Nur Yttriumoenanthat-Dihydrat gibt beim Erhitzen zwei Moleküle Wasser ab und bildet einen wasserfreien Komplex, der sich direkt in Y_2O_3 zersetzt. Die Dehydratationstemperaturen sind für alle Komplexe ähnlich (323–343 K), während die Temperatur für die Oxidbildung sehr unterschiedlich ist und von 823 K (CeO_2) bis 1078 K (La_2O_3) reicht.