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THERMAL DECOMPOSITIONS OF LANTHANUM AND LANTHANIDE SALTS OF SEBACIC ACID

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The conditions of thermal decomposition of La, Ce(III), Pr(III), Nd, Sm(III), Eu, Gd, Tb(III), Dy, Ho, Er, Tm, Yb and Lu sebacates have been studied. When heated in air atmosphere, the sebacates of La and lanthanides with general formula $Ln_2(C_{10}H_{16}O_4)_3 \cdot nH_2O$, where $n = 6$–24, lose some crystallization water molecules in one or two steps at 323–343 K and are then dehydrated and decomposed simultaneously to the oxides Ln_2O_3, CeO_2, Pr_6O_{11} and Tb_4O_7. The oxides are formed over the range of temperature 783 K (CeO_2) – 1073 K (Nd_2O_3).

Introduction

n-Octano-1,8-dicarboxylic acid, known as sebacic acid, is a crystalline solid sparingly soluble in water [1]. Sebacates of lanthanides are little known, but a survey of the literature does reveal some papers on these compounds.

Sebacates of lanthanides have been prepared as hydrated salts [2] sparingly soluble in water [3] by heating a solution of $LnCl_3$ with ammonium sebacate solution [2]. Whittemore and James [4] used sebacic acid for the quantitative determination of yttrium [5], whereas Smith and James [5] applied it to separate lanthanides from thorium (IV). Brzyska and Hubicki [6] prepared La, Ce(III), Pr(III), Nd, Sm(III) and Y sebacates, determined their solubilities in water and demonstrated the separation of a mixture of rare earths by the fractional precipitation of their sebacates. Azikov and Serebrennikov [7] prepared sebacates of La, Sm(III) and Lu and recorded their IR spectra. In previous work we examined the thermal decomposition

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of yttrium sebacate [8]. The sebacates of all the rare earth elements have not been studied systematically.

As a continuation of our research on the thermal decomposition of rare earth alkanodicarboxylates, we now report on the thermal decomposition of lanthanum and lanthanide sebacates during heating in static air atmosphere.

Experimental

Sebacates of La and lanthanides from Ce(III) to Lu (except Pm) were prepared by adding equivalent amounts of a 0.1 *M* solution of ammonium sebacate (*pH* 5.5–6.0) to a hot solution of the rare earth chloride (cerium(III) was used as nitrate). The precipitate formed was heated in the mother liquor at 343–353 K for 0.5 hr, and was then filtered off, washed with water to remove Cl^- and NH_4^+ ions and dried at 303 K to constant weight.

The contents of carbon and hydrogen were determined by elemental analysis. The rare earth content was determined by ignition of the salt to the oxide at 1073 K and from the TG curve. The content of water was determined from the TG curve and by heating the prepared salt isothermally at a definite temperature (Table 1).

The thermal stability and solid products of decomposition of the rare earth sebacates were studied. The measurements were made with a Q-1500D derivatograph recording TG, DTG and DTA curves. Samples of 100 mg were heated in static air in ceramic crucibles up 1273 K at a heating rate of 10 deg·min^{-1} with sensitivities TG – 100 mg, DTG – 500 μV, DTA – 500 μV. The products of decomposition were calculated on the basis of the TG curve weight losses and were verified by recording IR spectra and diffraction patterns.

The thermoanalytical curves of Ce(III), Pr(III), Tb(III), Dy, Ho, Tm and Yb sebacates heated at 473 K were additionally recorded.

Results and discussion

The sebacates of La and the lanthanides from Ce(III) to Lu (except Pm) were prepared as crystalline solids with colours characteristic of the Ln(III) ions. The prepared sebacates are hydrated salts with a metal to anion ratio of 2:3 and various degrees of hydration (Table 1). The number of crystallization water molecules ranges from 6 for samarium(III) sebacate to 24 for the gadolinium salt. From the thermal curves recorded for the prepared

Table 1 Analytical data

Complex	% Ln		% C		% H	
	Calc.	Found	Calc.	Found	Calc.	Found
$La_2(C_{10}H_{16}O_4)_3 \cdot 12H_2O$	25.26	25.23	32.73	32.90	6.54	6.66
$Ce_2(C_{10}H_{16}O_4)_3 \cdot 10H_2O$	26.26	26.04	33.76	34.12	6.37	6.35
$Pr_2(C_{10}H_{16}O_4)_3 \cdot 16H_2O$	23.96	23.84	30.61	30.80	6.80	6.70
$Nd_2(C_{10}H_{16}O_4)_3 \cdot 12H_2O$	25.98	26.06	32.41	32.44	6.48	6.84
$Sm_2(C_{10}H_{16}O_4)_3 \cdot 6H_2O$	29.63	29.00	35.47	35.30	5.91	6.29
$Eu_2(C_{10}H_{16}O_4)_3 \cdot 16H_2O$	25.37	25.56	30.07	30.12	6.68	6.98
$Gd_2(C_{10}H_{16}O_4)_3 \cdot 24H_2O$	23.25	22.98	26.61	27.12	7.09	7.62
$Tb_2(C_{10}H_{16}O_4)_3 \cdot 18H_2O$	25.47	25.84	28.85	29.10	6.73	6.92
$Dy_2(C_{10}H_{16}O_4)_3 \cdot 7H_2O$	30.74	30.67	34.05	34.60	5.86	6.12
$Ho_2(C_{10}H_{16}O_4)_3 \cdot 9H_2O$	30.04	30.07	32.79	32.90	6.01	6.59
$Er_2(C_{10}H_{16}O_4)_3 \cdot 16H_2O$	27.22	27.28	29.30	30.12	6.51	6.58
$Tm_2(C_{10}H_{16}O_4)_3 \cdot 18H_2O$	26.69	26.22	28.37	28.50	6.62	6.82
$Yb_2(C_{10}H_{16}O_4)_3 \cdot 7H_2O$	32.10	32.41	33.39	33.70	5.75	5.81
$Lu_2(C_{10}H_{16}O_4)_3 \cdot 7H_2O$	32.34	32.36	33.27	33.77	5.73	5.84

salts, the temperatures and solid products of decomposition were established and are presented in Tables 2 and 3 and in Figs 1–4.

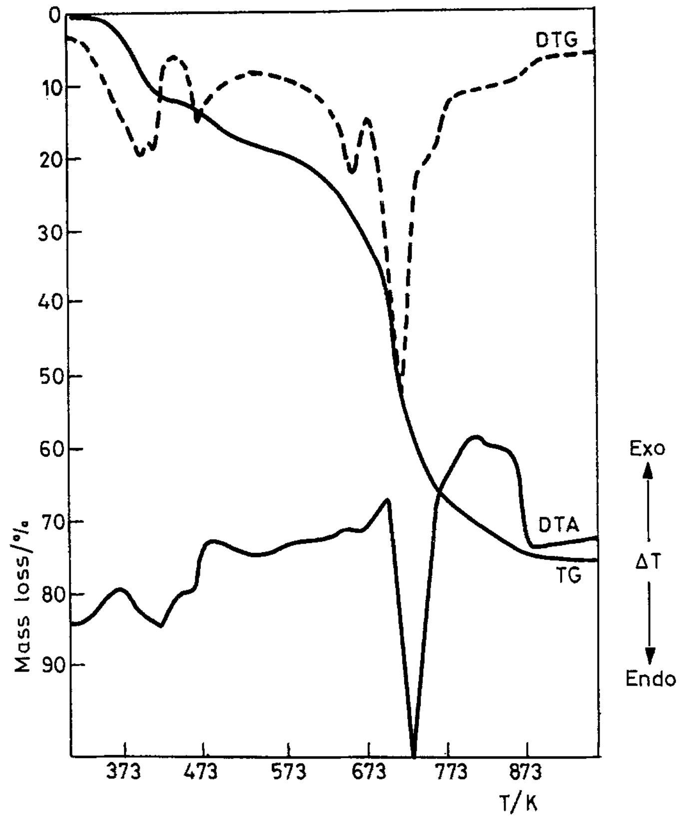

Fig. 1 TG, DTG and DTA curves of $Ce_2(C_{10}H_{16}O_4)_3 \cdot 10H_2O$

When heated in air, these salts decomposed in various way. The hydrated La, Nd and Lu sebacates lost some crystallization water molecules in two steps and then lost the residual water molecules during decomposition. The salts of La and Nd decomposed to the oxide Ln_2O_3 with intermediate formation of $Ln_2O_2CO_3$ (Table 3), whereas the Lu salt decomposed directly to Lu_2O_3.

The hydrated sebacates of Ce(III), Gd, Tb(III), Dy, Ho, Er, Tm and Yb decomposed in two steps. In the first step, at 333 K, they lost some crystallization water molecules and then decomposed directly to the oxides Ln_2O_3, CeO_2 and Tb_4O_7. The hydrated sebacates of Pr(III), Sm(III) and Eu(III) lost

Table 2 Data on thermal decomposition of La and lanthanide sebacates

Complex	Temperature range of dehydration / K	Loss of weight / %		Loss of H_2O	Temperature range of decomposition / K	Loss of weight / %		Temperature of oxide formation / K	Activation energy of dehydration / $J\cdot mol^{-1}$
		Calc.	Found	mole		Calc.	Found		
$La_2L_3^x\cdot 12H_2O$	333 – 423	5.2	4.9	3	568 – 1033	67.73	67.5	1033	340
	473 – 558	3.2	3.3	2					
$Ce_2L_3\cdot 10H_2O$	343 – 413	5.0	4.8	3	603 – 783	65.99	66.4	783	299
$Pr_2L_3\cdot 16H_2O$	343 – 403	9.2	9.1	6	583 – 903	68.39	68.2	903	341
$Nd_2L_3\cdot 12H_2O$	343 – 433	8.1	8.1	5	573 – 1073	65.18	66.0	1073	407
	473 – 553	5.3	4.9	3					
$Sm_2L_3\cdot 6H_2O$	333 – 413	8.8	8.8	5	468 – 983	62.30	63.0	983	346
$Eu_2L_3\cdot 16H_2O$	333 – 413	12.2	12.0	8	493 – 943	66.00	66.7	943	516
$Gd_2L_3\cdot 24H_2O$	333 – 423	10.6	10.8	8	463 – 963	70.00	70.8	963	390
$Tb_2L_3\cdot 18H_2O$	323 – 483	12.9	12.8	9	523 – 1053	65.60	66.0	1053	467
$Dy_2L_3\cdot 7H_2O$	333 – 448	9.6	9.8	6	523 – 973	61.40	61.3	973	532
$Ho_2L_3\cdot 9H_2O$	333 – 433	8.2	8.8	5	543 – 963	61.5	61.4	963	478
$Er_2L_3\cdot 16H_2O$	333 – 443	11.7	12.0	8	523 – 913	64.7	64.5	913	418
$Tm_2L_3\cdot 18H_2O$	333 – 493	12.7	12.8	9	583 – 933	65.0	65.1	933	425
$Yb_2L_3\cdot 7H_2O$	343 – 413	9.8	9.6	6	593 – 873	60.8	61.0	873	393
$Lu_2L_3\cdot 7H_2O$	343 – 388	6.7	6.8	4	593 – 833	59.1	59.6	833	269
	463 – 573	3.6	3.8	2					

L^x – $C_{10}H_{16}O_4$

Table 3 Intermediate products of decomposition of La and lanthanide sebacates

Complex	Intermediate products of decomposition			Final products of decom-position	Exothermic peaks / K	Endothermic peaks / K	DTG peaks / K
$La_2L_3 \cdot 12H_2O$	$La_2L_3 \cdot 9H_2O$	$La_2L_3 \cdot 7H_2O$	$La_2O_2CO_3$	La_2O_3	683, 798	418, 488, 783	783
$Ce_2L_3 \cdot 10H_2O$	$Ce_2L_3 \cdot 7H_2O$	–	–	CeO_2	693, 773	403, 733	723
$Pr_2L_3 \cdot 16H_2O$	$Pr_2L_3 \cdot 10H_2O$	–	$Pr_2O_2CO_3$	Pr_6O_{11}	693, 823	413, 723	723
$Nd_2L_3 \cdot 12H_2O$	$Nd_2L_3 \cdot 7H_2O$	$Nd_2L_3 \cdot 4H_2O$	$Nd_2O_2CO_3$	Nd_2O_3	753, 853	433, 573, 783	773
$Sm_2L_3 \cdot 6H_2O$	$Sm_2L_3 \cdot H_2O$	–	$Sm_2O_2CO_3$	Sm_2O_3	673, 883	413, 783	783
$Eu_2L_3 \cdot 16H_2O$	$Eu_2O_3 \cdot 8H_2O$	–	$Eu_2O_2CO_3$	Eu_2O_3	573, 823	433, 773	773
$Gd_2O_3 \cdot 24H_2O$	$Gd_2L_3 \cdot 16H_2O$	–	–	Gd_2O_3	703, 813	423, 723	723
$Tb_2L_3 \cdot 18H_2O$	$Tb_2L_3 \cdot 9H_2O$	–	–	Tb_4O_7	573, 853	423, 733	733
$Dy_2L_3 \cdot 7H_2O$	$Dy_2L_3 \cdot H_2O$	–	–	Dy_2O_3	573, 833	428, 743	723
$Ho_2L_3 \cdot 9H_2O$	$Ho_2L_3 \cdot 4H_2O$	–	–	Ho_2O_3	573, 833	428, 773	773
$Er_2L_3 \cdot 16H_2O$	$Er_2L_3 \cdot 8H_2O$	–	–	Er_2O_3	633, 833	413, 723	723
$Tm_2L_3 \cdot 18H_2O$	$Tm_2L_3 \cdot 9H_2O$	–	–	Tm_2O_3	603, 823	423, 643	593
$Yb_2L_3 \cdot 7H_2O$	$Yb_2L_3 \cdot H_2O$	–	–	Yb_2O_3	763, 883	413, 683	683
$Lu_2L_3 \cdot 7H_2O$	$Lu_2L_3 \cdot 3H_2O$	$Lu_2L_3 \cdot H_2O$	–	Lu_2O_3	623, 733	383, 463, 663	663

some water molecules and then decomposed to the oxides Ln_2O_3 and Pr_6O_{11} with intermediate formation of $Ln_2O_2CO_3$.

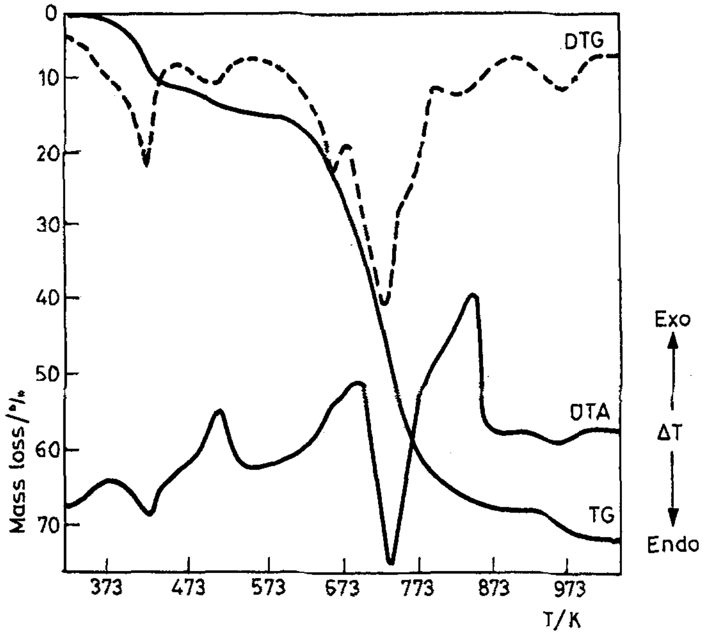

Fig. 2 TG, DTG and DTA curves of $Nd_2(C_{10}H_{16}O_4)_3\cdot 12H_2O$

The activation energy of the dehydration reaction, calculated according to the Chuchas and Jezerskaya method [9], ranged from 269 $J\cdot mol^{-1}$ for the Lu salt to 532 $J\cdot mol^{-1}$ for the Dy salt (Table 2) and varied irregularly in the lanthanide series.

The dehydration and simultaneous decomposition were accompanied by strong endothermic effects, and the combustion of the organic ligand by an exothermic effect. The DTA curves exhibited strong endothermic effects connected with a dehydration process, dehydration and simultaneous decomposition of the salt and decomposition of $Ln_2O_2CO_3$, and exothermic effects connected with combustion of the organic ligand. The thermoanalytical curves of the Ce(III), Pr(III), Tb(III), Dy, Ho, Tm and Yb salts heated isothermally to constant weight at 473 K were also recorded (Figs 3b and 4b). The results obtained confirmed the data obtained from the fundamental thermal curves.

The thermal studies permit the suggestion that the crystallization water molecules are bonded in various ways. The water molecules lost at 333 K are

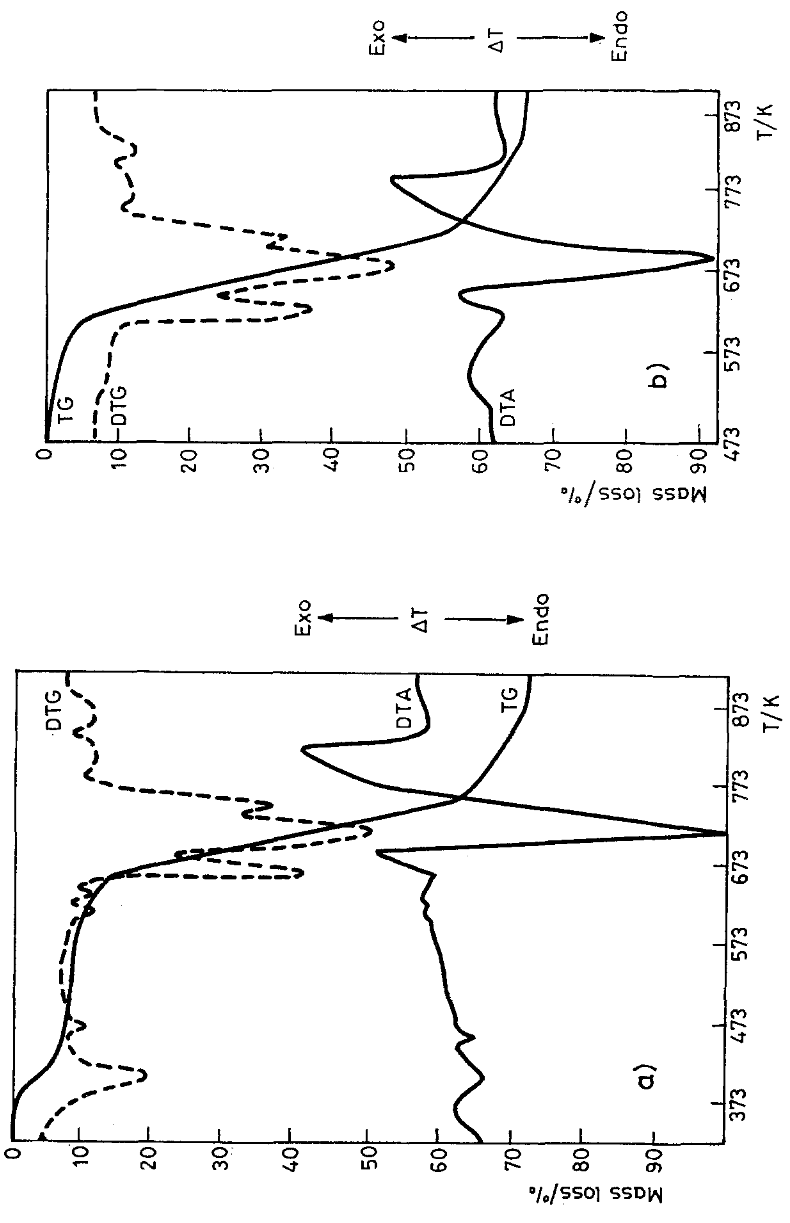

Fig. 3 TG, DTG and DTA curves of *a*) $Pr_2(C_{10}H_{16}O_4)_3 \cdot 16H_2O$ *b*) $Pr_2(C_{10}H_{16}O_4)_3 \cdot 10H_2O$

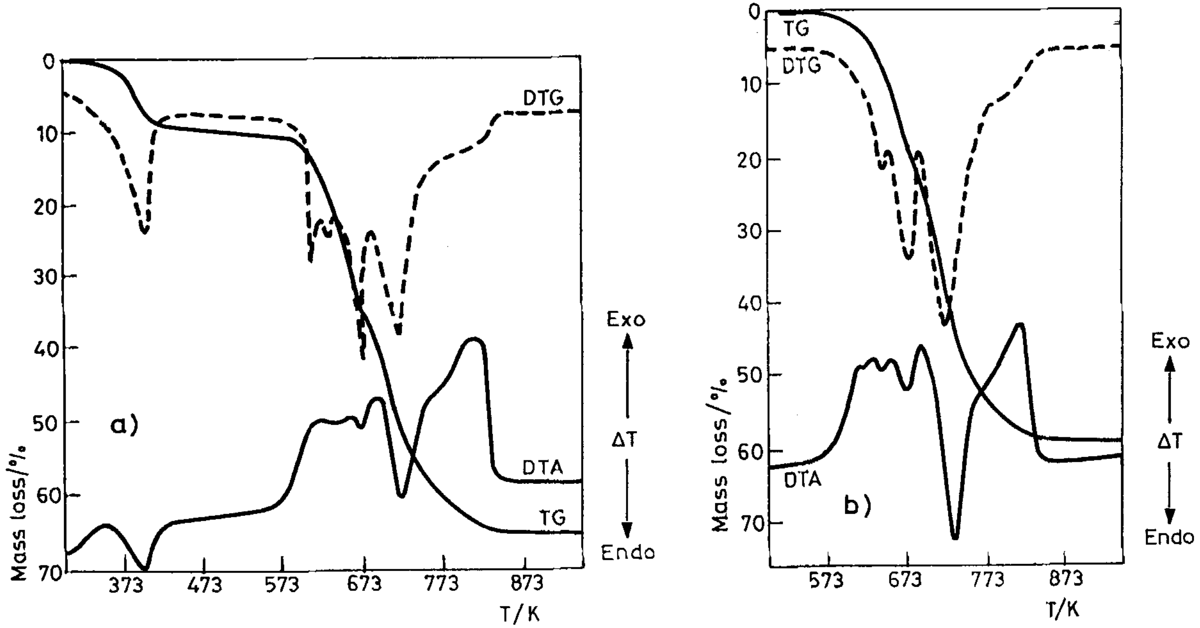

Fig. 4 TG, DTG and DTA curves of *a*) $Yb_2(C_{10}H_{16}O_4)_3 \cdot 7H_2O$ *b*) $Yb_2(C_{10}H_{16}O_4)_3 \cdot H_2O$

weakly bonded and are outer sphere water molecules, whereas the water molecules lost during decomposition are inner sphere molecules.

The temperatures of the beginning of rare earth sebacate decomposition (T_o), the temperatures of oxide formation (T_k) and the atomic numbers Z of the lanthanides are presented in Fig. 5.

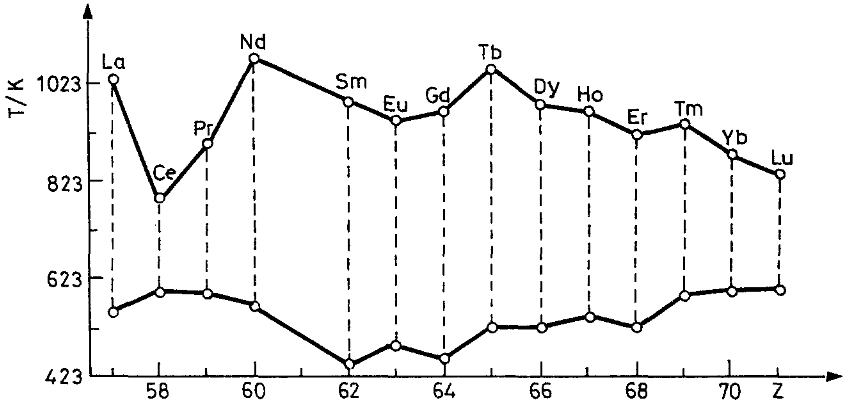

Fig. 5 Relationship between T_o, T_k and atomic number Z

These temperatures change periodically in the lanthanide series with increase of the atomic number. Cerium(III) sebacate is the most stable ($T = 603$ K), whereas samarium(III) sebacate is the least stable ($T = 468$ K).

The sebacates of La, Pr(III), Nd, Sm(III) and Eu(III) decompose to the oxides via $Ln_2O_2CO_3$, whereas the sebacates of Ce(III), Gd, Tb(III), Dy, Ho, Er, Tm, Yb and Lu decompose to the oxides directly. The sebacates of La, Nd and Tb display the higest temperatures of oxide formation (1033–1073 K), and Ce(III) sebacate the lowest one (783 K). The sebacates of the other rare earth elements decompose at 833–983 K.

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Zusammenfassung — Bei Erhitzen in Luft wurde die thermische Zersetzung der Sebazate von La, Ce(III), Pr(III), Nd, Sm(III), Eu, Gd, Tb(III), Dy, Ho, Er, Tm, Yb und Lu untersucht. Die Sebazate von La und der Lanthanoide mit der allgemeinen Formel $Ln_2(C_{10}H_{16}O_4)_3 \cdot nH_2O$ mit $n = 6–24$ verlieren Kristallwasser in ein oder zwei Schritten bei 323–343 K und werden anschließend dehydratiert und gleichzeitig in die Oxide Ln_2O_3, CeO_2, Pr_6O_{11} und Tb_4O_7 zersetzt. Die Oxide werden im Temperaturbereich 783 K (CeO_2) bis 1073 K (Nd_2O_3) gebildet.