

THERMAL DECOMPOSITION OF RARE EARTH ELEMENT SUBERATES IN AIR ATMOSPHERE

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The condition of thermal decomposition of La, Ce(III), Pr(III), Nd, Sm, Eu(III), Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu suberates were studied. The suberates of Ce(III), Sm, Eu(III), Ho, Tm, Yb and Lu heated lose crystallization water. Anhydrous Sm and Eu(III) suberates decompose to oxides with intermediate formation $\text{Ln}_2\text{O}_2\text{CO}_3$, whereas suberates of other lanthanides decompose directly to oxides. Suberates of La, Pr(III), Nd, Gd, Tb, Dy and Er lose some water molecules and then decompose directly to oxides. Only La complex decomposes to La_2O_3 via the intermediate formation $\text{La}_2\text{O}_2\text{CO}_3$.

Complexes of rare earth elements of suberic acid $(\text{CH}_2)_6(\text{COOH})_2$ are little known. Ryabchikov and Terentyeva [1] have prepared rare earth suberates as solids sparingly soluble in water. Brzyska and Hubicki [2] have determined solubility of La, Ce(III), Pr, Nd and Sm suberates in water and used fractional precipitation of suberates for their separation. The yttrium suberate was prepared as hexahydrate, its IR and X spectra were recorded and thermal decomposition was studied [3]. Thermal decomposition of other rare earth element suberates have not been studied.

As a continuation of our work on the thermal decomposition of rare earth carboxylates [4-6], we now report the thermal decomposition of the La and lanthanide suberates in air atmosphere.

Experimental

The suberates of La and lanthanide from Ce(III) to Lu (except Pm) were prepared by adding equivalent amounts of a 0.1 M solution of ammonium suberate (*pH* 5.5) to a hot solution of rare earth element chlorides

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(cerium(III) was used as nitrate). The precipitate formed was filtered off, washed with water to remove NH_4^+ ions and dried at 300 K to constant weight.

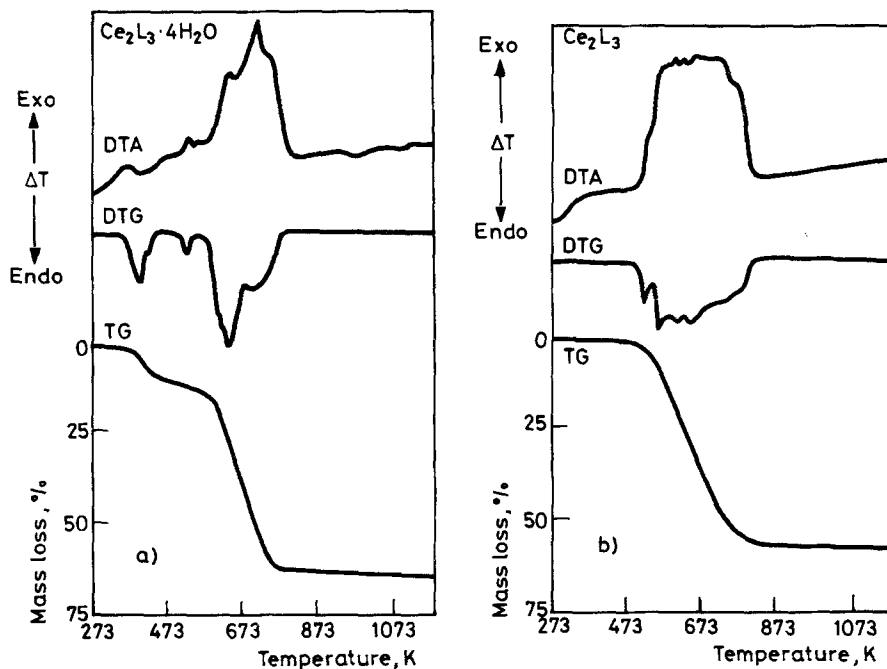


Fig. 1 TG, DTG and DTA curves of a) $\text{Ce}_2(\text{C}_8\text{H}_{12}\text{O}_4)_3 \cdot 4\text{H}_2\text{O}$; b) $\text{Ce}_2(\text{C}_8\text{H}_{12}\text{O}_4)_3$

The content of carbon and hydrogen in prepared complexes was determined by elemental analysis by using V_2O_5 as oxidizing agent. The content of rare earth element was determined from TG curve. The content of water was determined from TG curve and by isothermal heating of complexes at definite temperature. For confirming the composition of complexes their IR spectra were recorded over the range of $4000\text{--}400\text{ cm}^{-1}$.

The thermal stability of rare earth element suberates was determined by heating their samples of 100 mg in air atmosphere in platine crucibles to 1273 K at a heating rate of 10 deg. min^{-1} . The measurements were carried out with a Q - 1500D derivatograph. From the thermal curves of La and lanthanide suberates, the temperature of thermal decomposition were evaluated and presented in Tables 3 and 4. As examples, the TG, DTG and DTA curves of Ce(III), Nd, Tm and Er suberates are given in Figs 1a - 4a.

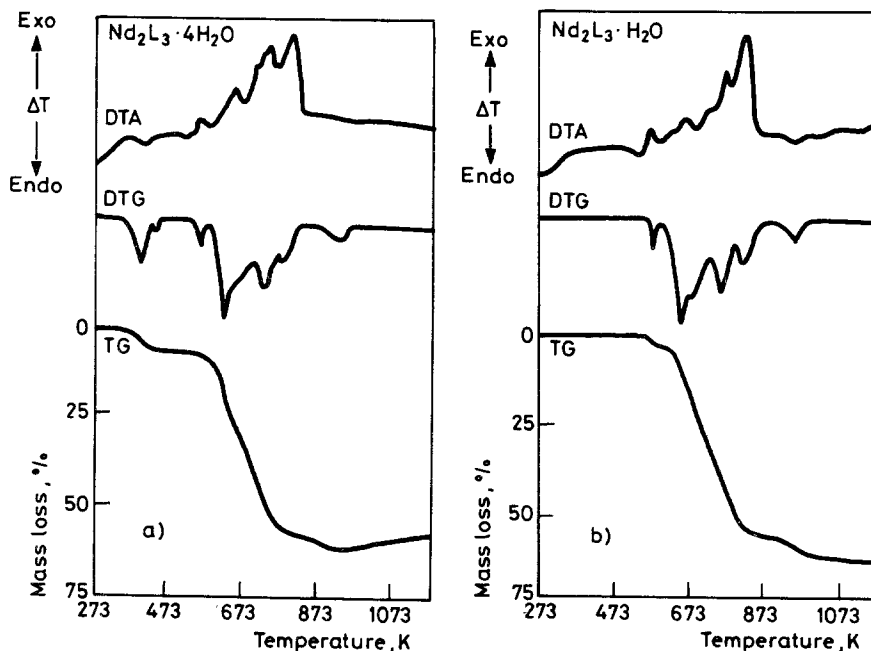


Fig. 2 TG, DTG and DTA curves of a) $\text{Nd}_2(\text{C}_8\text{H}_{12}\text{O}_4)_3 \cdot 4\text{H}_2\text{O}$; b) $\text{Nd}_2(\text{C}_8\text{H}_{12}\text{O}_4)_3 \cdot \text{H}_2\text{O}$

The thermal curves of prepared suberates heated isothermally at 473 K were recorded, too (Figs 1b - 4b). The natures of the solid decomposition products were calculated from the weight loss in TG curve and were confirmed by the IR spectra.

Results and discussion

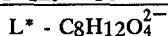
The suberates of La, Ce(III), Pr(III), Nd, Sm, Eu(III), Gd, Dy, Ho, Er, Tm, Yb and Lu were prepared as crystalline solid with the colour characteristic for Ln^{3+} ions. Prepared suberates are compounds of low symmetry and with large unit cells. They were found to be complexes having formula: $\text{Ln}_2(\text{C}_8\text{H}_{12}\text{O}_4)_3 \cdot n\text{H}_2\text{O}$, where $n = 3$ for Eu(III), Ho, Tm; $n = 4$ for Ce(III), Nd, Sm, Yb; $n = 5$ for Pr(III), Gd, Er; $n = 6$ for La, Dy and $n = 7$ for Tb(III). All prepared complexes are sparingly soluble in water. Their solubility is of the order $10^{-5} \text{ mol} \cdot \text{dm}^{-3}$. The suberates of La and Lu are

diamagnetic, whereas the complexes of remaining lanthanides are paramagnetic.

The rare earth suberates heated in air atmosphere decompose in two or three steps. The hydrated suberates of rare earth elements are dehydrated at 328-463 K, but then in the temperature range 473-1208 K the organic anion is decomposed and the rare earth oxides are formed.

Table 1 Analytical data

Complex	C, %		H, %		Rare earth elements, %	
	calcd.	found	calcd.	found	calcd.	found
La ₂ L ₃ *.6H ₂ O	35.92	35.97	5.36	5.24	30.78	31.03
Ce ₂ L ₃ .4H ₂ O	33.18	33.41	5.10	5.12	32.25	31.99
Pr ₂ L ₃ .5H ₂ O	32.45	32.11	5.22	5.41	31.72	31.78
Nd ₂ L ₃ .4H ₂ O	32.87	32.21	5.06	5.08	32.89	32.92
Sm ₂ L ₃ .4H ₂ O	32.38	31.85	4.98	5.12	33.89	33.91
Eu ₂ L ₃ .3H ₂ O	32.96	32.73	4.84	5.21	34.75	34.88
Gd ₂ L ₃ .5H ₂ O	31.29	30.87	5.03	5.05	34.14	34.35
Tb ₂ L ₃ .7H ₂ O	30.01	30.20	5.25	4.93	33.09	32.99
Dy ₂ L ₃ .6H ₂ O	30.35	29.65	5.09	5.06	34.22	34.50
Ho ₂ L ₃ .3H ₂ O	32.01	32.05	4.70	5.22	36.63	36.63
Er ₂ L ₃ .5H ₂ O	30.63	30.75	4.93	5.01	35.54	35.33
Tm ₂ L ₃ .3H ₂ O	31.73	31.88	4.66	4.93	37.19	37.13
Yb ₂ L ₃ .4H ₂ O	30.80	30.85	4.75	5.07	37.03	37.20
Lu ₂ L ₃ .3H ₂ O	31.32	31.30	4.59	4.07	38.01	37.99



When heated, the prepared complexes are dehydrated in different ways. Suberates of Ce(III), Sm, Eu(III), Ho, Tm, Yb and Lu heated lose all crystallization water molecules (Table 2) undergoing to anhydrous complexes. Suberates of La, Pr(III), Nd, Gd, Tb, Dy and Er lose some water molecules and the remaining coordination water molecules are lost simultaneously with decomposition of complexes. The dehydration of complexes accompanied by an endothermic effect. The process undergoes the most quickly at 393-423 K. The results obtained from TG curve recorded for prepared suberates heated isothermally at 473 K confirm these suggestions. During heating above 473 K rare earth suberates (anhydrous or hydrated) are decomposed to oxides Ln₂O₃, CeO₂, Pr₆O₁₁ and Tb₄O₇, which are formed in the range 788-1203 K. The burning of organic ligand is connected with strong exothermic effect. Suberates of La, Nd, Sm and Eu(III) decompose to oxides with intermediate formation of Ln₂O₂CO₃. The suberates of other

Table 2 Temperature data of dehydration of rare earth element suberates

Compounds	Temperature range of dehydration K	Loss of weight, %		Loss of H ₂ O molecules n	Endothermic peaks, K
		calcd.	found		
La ₂ L ₃ .6H ₂ O	345 - 463	7.98	8.4	4	411
Ce ₂ L ₃ .4H ₂ O	355 - 463	8.29	8.4	4	408
Pr ₂ L ₃ .5H ₂ O	328 - 453	4.06	4.2	2	403
Nd ₂ L ₃ .4H ₂ O	348 - 465	6.15	6.8	3	408
Sm ₂ L ₃ .4H ₂ O	365 - 461	8.09	8.0	4	421
Eu ₂ L ₃ .3H ₂ O	348 - 453	6.18	6.7	3	413
Gd ₂ L ₃ .5H ₂ O	355 - 463	7.82	8.0	4	423
Tb ₂ L ₃ .7H ₂ O	373 - 453	7.50	7.9	4	415
Dy ₂ L ₃ .6H ₂ O	371 - 458	7.59	8.0	4	423
Ho ₂ L ₃ .3H ₂ O	355 - 461	6.00	6.4	3	418
Er ₂ L ₃ .5H ₂ O	351 - 471	7.66	8.1	4	415
Tm ₂ L ₃ .3H ₂ O	353 - 438	5.95	6.4	3	398
Yb ₂ L ₃ .4H ₂ O	345 - 428	7.71	7.6	4	395
Lu ₂ L ₃ .3H ₂ O	333 - 431	5.87	6.4	3	393

Table 2 Temperature data of dehydration of rare earth element substrates

Complexes	Stability of oxycarbonates		Residue of weight, %		Exothermic peak K	Formation of oxide K	Residue of weight, %	
	K		calcd.	found			calcd.	found
La ₂ L ₃ .6H ₂ O	838-891		40.98	41.2	788	1073	36.10	36.40
Ce ₂ L ₃ .4H ₂ O					715	773	39.62	39.20
Pr ₂ L ₃ .5H ₂ O					800	893	38.32	38.40
Nd ₂ L ₃ .4H ₂ O	818-833		43.38	43.60	798	951	38.37	38.40
Sm ₂ L ₃ .4H ₂ O	828-841		44.22	44.00	794	933	39.17	39.20
Eu ₂ L ₃ .3H ₂ O	795-813		45.29	45.20	743	903	40.24	40.40
Gd ₂ L ₃ .5H ₂ O					783	918	39.35	39.60
Tb ₂ L ₃ .7H ₂ O					748	1108	38.92	38.80
Dy ₂ L ₃ .6H ₂ O					775	991	39.28	39.60
Ho ₂ L ₃ .3H ₂ O					761	836	41.96	41.96
Er ₂ L ₃ .5H ₂ O					733	893	40.64	40.40
Tm ₂ L ₃ .3H ₂ O					711	863	42.47	42.40
Yb ₂ L ₃ .4H ₂ O					731	848	42.16	42.40
Lu ₂ L ₃ .3H ₂ O					715	813	43.23	43.20

Table 4. Temperature data of decomposition of rare earth element suberates heated at 473 K in air atmosphere

Complex	Stability of oxycarbonates K	Residue of weight, %		Exothermic peak, K	Formation of oxide, K	Residue of weight, %	
		calcd.	found			calcd.	found
$\text{La}_2\text{L}_3 \cdot 2\text{H}_2\text{O}$	833-913	44.54	44.80	793	1098	39.24	39.60
Ce_2L_3	-	-	-	671	788	43.20	43.60
$\text{Pr}_2\text{L}_3 \cdot 3\text{H}_2\text{O}$	-	-	-	808	893	39.94	40.00
$\text{Nd}_2\text{L}_3 \cdot \text{H}_2\text{O}$	848-861	47.26	47.20	808	961	40.88	40.80
$\text{Er}_2\text{L}_3 \cdot \text{H}_2\text{O}$	-	-	-	751	843	44.01	44.00
Tm_2L_3	-	-	-	729	833	45.16	45.20

lanthanides decompose directly to oxides. The shape of DTA and DTG curves of La, Ce(III), Pr and Nd suberates differ from the shape of these curves for other complexes. Suberates of La, Ce(III), Pr(III) and Nd are characterized by very quickly loss of weight at 563 K for La, 525 K - for Ce(III), 535 K for Pr(III) and 568 K for Nd and on the DTA curves the very sharp peak is observed. However, the formed products are very unstable and it is impossible to identify them. On the DTA curve of Nd suberate is an endothermic peak at 528 K indicating the melting of complex.

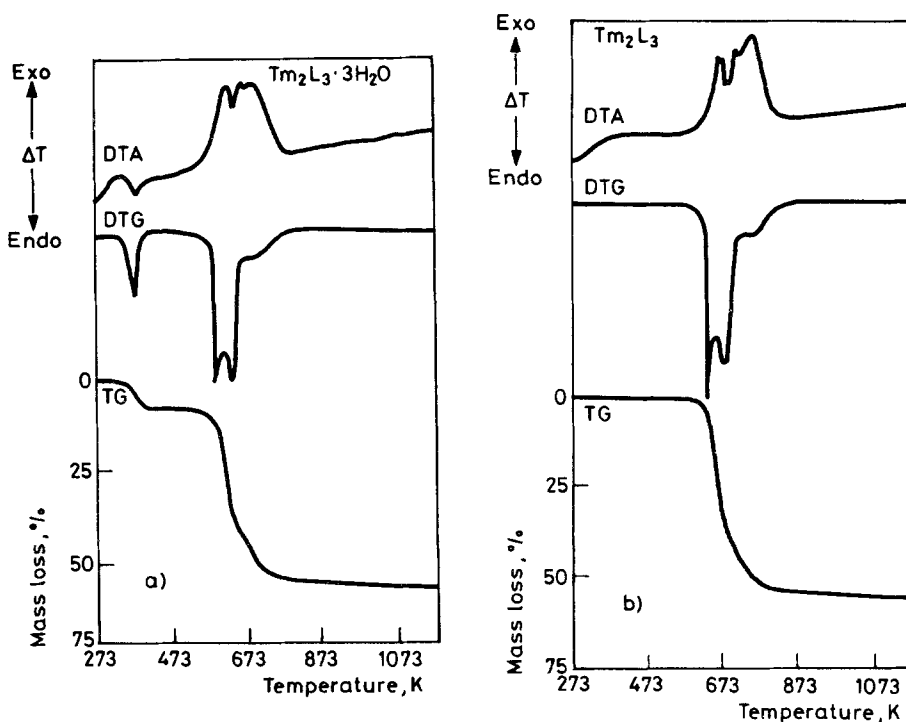


Fig. 3 TG, DTG and DTA curves of a) $Tm_2(C_8H_{12}O_4)_3 \cdot 3H_2O$; b) $Tm_2(C_8H_{12}O_4)_3$

The temperature of oxide formation changes irregularly in the lanthanide series with increasing of the atomic number. The temperature of CeO_2 formation has the lowest value, whereas this of Tb_4O_7 - the highest one.

In comparison with the temperatures of endothermic peaks (DTA) of dehydration for suberates in lanthanide series it is possible to suggest that the bonding of crystallization water molecules are the strongest in hydrates of Sm-Er, and the weakest - in hydrates of Tm and Yb.

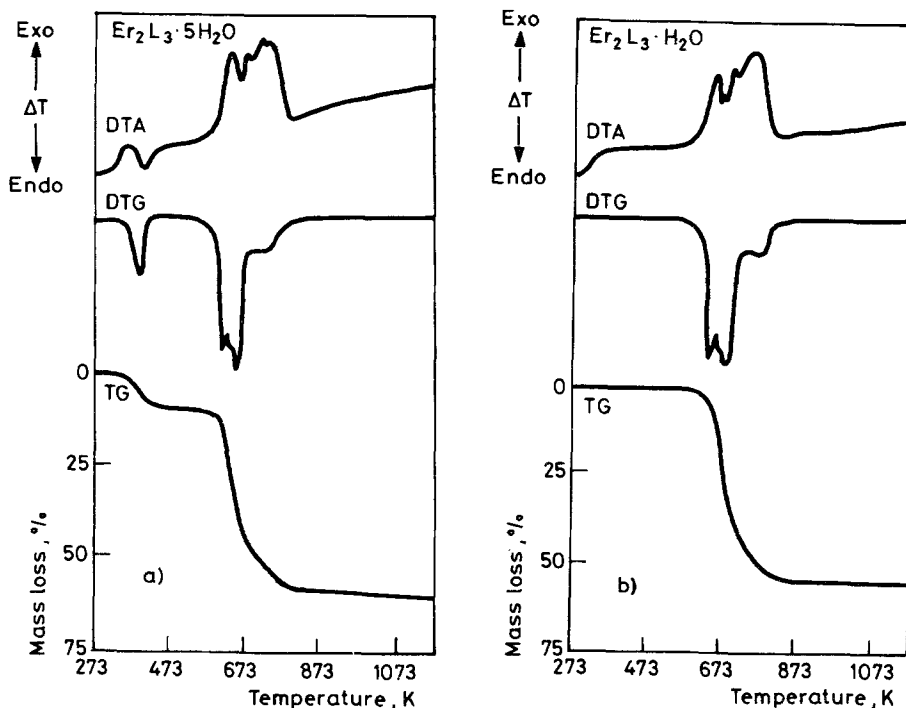


Fig. 4 TG, DTG and DTA curves of a) $\text{Er}_2(\text{C}_8\text{H}_{12}\text{O}_4)_3 \cdot 5\text{H}_2\text{O}$; b) $\text{Er}_2(\text{C}_8\text{H}_{12}\text{O}_4)_3 \cdot \text{H}_2\text{O}$

References

- 1 D. I. Riabchikov, E. A. Terentieva, *Izv. Akad. Nauk SSSR*, 44 (1949) 55.
- 2 W. Brzyska, W. Hubicki, *Ann. Univ. M. Curie Skłodowska, Lublin, Sect. AA XXIII* (1967) 7.
- 3 W. Brzyska, W. Ozga, *Pol. J. of Chem.* - in press.
- 4 W. Brzyska, R. Kurpiel-Gorgol, *J. Thermal Anal.* 32 (1987) 671.
- 5 W. Brzyska, Z. Rzaczyńska, *J. Thermal Anal.* 32 (1987) 1355.
- 6 W. Ferenc, W. Brzyska, *Monatshefte für Chemie* 118 (1987) 1087.

Zusammenfassung — Es wurden die Umstände der thermischen Zersetzung von La-, Ce(III)-, Pr(III)-, Nd-, Sm-, Eu(III)-, Gd-, Tb-, Dy-, Ho-, Er-, Tm-, Yb- und Lu-suberat untersucht. Bei Erhitzen verlieren Ce(III)-, Sm-, Eu(III)-, Ho-, Tm-, Yb- und Lu-suberat Kristallwasser. Wasserfreies Sm- bzw. Eu(III)-suberat zersetzt sich über das Zwischenprodukt der Zusammensetzung $\text{Ln}_2\text{O}_2\text{CO}_3$ zum Oxid, während sich die Suberate der anderen Lanthanoide direkt zu den Oxiden zersetzen. La-, Pr(III)-, Nd-, Gd-, Tb-, Dy- und Er-suberat geben einige Moleküle Kristallwasser ab und zersetzen sich dann direkt zu den Oxiden. Nur der Lanthan komplex zersetzt sich zu La_2O_3 über das Zwischenprodukt $\text{La}_2\text{O}_2\text{CO}_3$.