

Short Communications

THERMAL DECOMPOSITIONS OF LIGHT LANTHANIDE ACONITATES

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The conditions of thermal decomposition of Y, La, Ce(III), Pr, Nd, Sm, and Gd aconitates have been studied. On heating, the aconitate of Ce(III) loses crystallization water to yield anhydrous salt, which then is transformed into oxide CeO_2 . The aconitates of Y, Pr, Nd, Sm, Eu and Gd decompose in three stages. First, aconitates undergo dehydration to form the anhydrous salts, which next decompose to $\text{Ln}_2\text{O}_2\text{CO}_3$. In the last one the thermal decomposition of $\text{Ln}_2\text{O}_2\text{CO}_3$ to Ln_2O_3 is accompanied by endothermic effect. Dehydration of aconitate of La undergoes in two stages. The anhydrous complex decomposes to $\text{La}_2\text{O}_2\text{CO}_3$; this subsequently decomposes to La_2O_3 .

Currently, much work is being done on the thermal decompositions of Y, La and lanthanide carboxylates [1–7] to understand the mechanisms of decomposition and the nature of the decomposition products. Motas [8] has studied the thermal decompositions of La and Ce(III) aconitates. A search of the available literature showed that the thermal decompositions of aconitates of other lanthanide elements have not been studied so far. As a continuation of our work on the thermal decompositions of lanthanide carboxylates [9–11], we now report the thermal decompositions of Y, La and the light lanthanide aconitates.

Experimental

Aconitates of Y, La, Ce(III), Pr(III), Nd, Sm, Eu and Gd were prepared by adding equivalent quantities of 0.1 M ammonium aconitate to a hot solution containing the lanthanide chloride. The solid formed was heated for 0.5 h in the mother liquor, filtered off, washed with hot water and dried at 303 K to constant mass. The aconitates of Y, La and the light lanthanides were prepared in crystalline form, with the colours characteristic for the Ln^{3+} ions.

The carbon and hydrogen contents were determined by elemental analysis. The Y, La and light lanthanide contents were determined by ignition of the salts to the oxides at 1173 K. The elemental analysis data are given in Table 1.

The results showed that the aconitates of Y, La and the light lanthanides are hydrated salts. The aconitates of La and Ce(III) were obtained as trihydrates, those

Table 1
Analytical data

Compound	Metal %		Carbon %		Hydrogen %	
	calc.	found	calc.	found	calc.	found
$\text{YC}_6\text{H}_3\text{O}_6 \cdot 2.5 \text{H}_2\text{O}$	29.15	19.76	23.61	23.23	2.62	2.38
$\text{LaC}_6\text{H}_3\text{O}_6 \cdot 3 \text{H}_2\text{O}$	38.17	38.34	19.78	19.22	2.47	2.83
$\text{CeC}_6\text{H}_3\text{O}_6 \cdot 3 \text{H}_2\text{O}$	38.37	38.80	19.71	18.71	2.46	2.59
$\text{PrC}_6\text{H}_3\text{O}_6 \cdot 2\text{H}_2\text{O}$	40.50	39.00	20.69	19.40	2.01	2.04
$\text{NdC}_6\text{H}_3\text{O}_6 \cdot 2.5 \text{H}_2\text{O}$	40.03	40.05	19.98	20.25	2.22	2.27
$\text{SmC}_6\text{H}_3\text{O}_6 \cdot 2.5 \text{H}_2\text{O}$	41.03	41.50	19.65	19.90	2.18	2.21
$\text{EuC}_6\text{H}_3\text{O}_6 \cdot 2 \text{H}_2\text{O}$	42.33	42.20	20.05	20.30	1.95	1.98
$\text{GdC}_6\text{H}_3\text{O}_6 \cdot 2 \text{H}_2\text{O}$	43.17	42.90	19.76	18.76	1.92	2.12

of Pr, Eu and Gd as dihydrates, and those of Y, Nd and Sm with 2.5 moles of crystallization water.

The IR spectra of aconitic acid and the complexes were recorded over the range 4000–400 cm^{-1} . Analysis of the IR spectra confirms the elemental analysis data.

The thermal stabilities of Y, La and the light lanthanide aconitates were studied by TG, DTG and DTA techniques. The measurements were made with an OD-102 derivatograph at a heating rate of 9°/min, at the sensitivities TG – 200 mg, DTA – 1/20, DTG – 1/10. From the recorded TG, DTG and DTA curves two are pre-

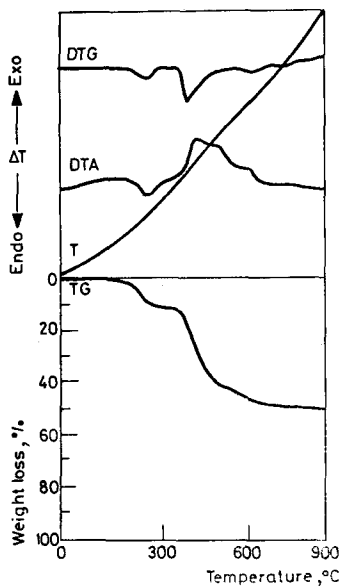


Fig. 1. TG, DTG and DTA curves of $\text{YC}_6\text{H}_3\text{O}_6 \cdot 2.5 \text{H}_2\text{O}$

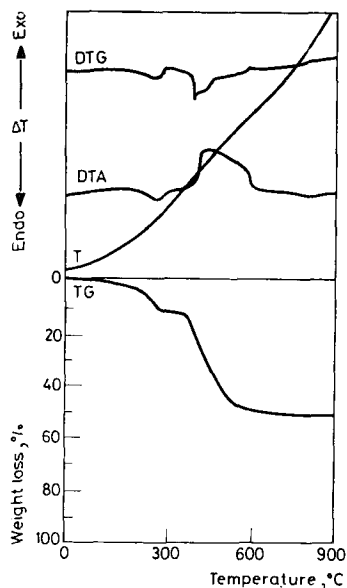


Fig. 2. TG, DTG and DTA curves of $\text{LaC}_6\text{H}_3\text{O}_6 \cdot 3 \text{H}_2\text{O}$

sented in Figs 1 and 2. The temperatures of thermal decomposition of the complexes were evaluated from the curves and are given in Table 2, where ΔT_1 is the temperature range (K) corresponding to the endothermic loss of the given number of crystallization water molecules, ΔT_2 is the temperature range (K) corresponding to decomposition of the anhydrous salt and deflagration of the carbon residue until the formation of oxide and T_k is the temperature (K) of oxide formation.

Table 2

Temperature data on thermal decompositions of Y, La and light lanthanide aconitates

Compound	ΔT_1 , K	Loss of weight, %		ΔT_2 , K	Loss of weight, %		T_k , K
		calc.	found		calc.	found	
$\text{YC}_6\text{H}_3\text{O}_6 \cdot 2.5 \text{H}_2\text{O}$	443–543	12.5	13.0	653–1023	62.8	63.0	1023
$\text{LaC}_6\text{H}_3\text{O}_6 \cdot 3 \text{H}_2\text{O}$	333–653	15.0	16.0	653–1113	53.8	54.5	1113
$\text{CeC}_6\text{H}_3\text{O}_6 \cdot 3 \text{H}_2\text{O}$	333–553	14.8	15.0	553–853	52.9	53.2	833
$\text{PrC}_6\text{H}_3\text{O}_6 \cdot 2 \text{H}_2\text{O}$	333–513	10.3	10.0	573–1053	50.6	51.0	1053
$\text{NdC}_6\text{H}_3\text{O}_6 \cdot 2.5 \text{H}_2\text{O}$	453–583	12.5	12.0	583–973	53.4	54.0	973
$\text{SmC}_6\text{H}_3\text{O}_6 \cdot 2.5 \text{H}_2\text{O}$	453–563	11.0	11.0	623–1023	52.4	52.5	1023
$\text{EuC}_6\text{H}_3\text{O}_6 \cdot 2 \text{H}_2\text{O}$	438–573	11.2	11.0	573–953	52.3	52.0	953
$\text{GdC}_6\text{H}_3\text{O}_6 \cdot 2 \text{H}_2\text{O}$	463–553	11.1	10.5	653–1023	50.3	51.0	1023

The results demonstrate that the aconitates of Pr, Nd, Sm, Eu and Gd decompose in three stages. In the first step, at 333–583 K, the aconitates undergo dehydration with an accompanying endothermic effect, and the anhydrous complexes then decompose to oxides in the temperature range 553–1113 K, with intermediate formation of $\text{Ln}_2\text{O}_2\text{CO}_3$. The thermal decomposition of $\text{Ln}_2\text{O}_2\text{CO}_3$ to Ln_2O_3 is accompanied by an endothermic effect. The aconitates of Ce(III) is found to decompose in two stages. On heating the trihydrated complex undergoes dehydration at 333–533 K, yielding the anhydrous salt, which decomposes directly to CeO_2 .

The aconitate of La decomposes in four stages. During heating, its dehydration occurs in two stages, and the anhydrous complex then decomposes to La_2O_3 with intermediate formation of $\text{La}_2\text{O}_2\text{CO}_3$. The thermal decomposition of $\text{La}_2\text{O}_2\text{CO}_3$ to La_2O_3 is accompanied by an endothermic effect.

References

1. W. W. GOSTISHCHEV and W. K. VALCEV, *Zh. Neorgan Khim.* 25 (1980) 2278.
2. C. N. PUPLIKOVA, Ł. N. NECKŁADNOVA and H. V. ZARECKIJ, *Zh. Neorgan Khim.*, 25 (1980) 481.
3. A. M. PASSOS FELICISSIMO and E. GLESBRACHT, *Ann. Acad. Brasil. Sci.*, 48 (1976) 437.
4. S. M. GUBASCHOVA, N. A. SKORIK and W. W. SEREBRENNIKOV, *Zh. Neorgan Khim.*, 47 (1977) 2641.
5. S. B. PIRKES, T. A. KOROVSKAJA and S. W. KURBATOVA, *Zh. Neorgan Khim.* 23 (1978) 390.
6. O. N. PUPLIKOVA, Ł. N. NEOKŁADNOVA, O. P. USOVA and H. H. ZARECKIJ, *Zh. Neorgan Khim.*, 48 (1978) 186.
7. Ł. M. VDOVINA, Ł. N. BONDAREVA and P. A. TARABANOVSKAJA, *Izv. Uchebn. zavedenii Khim. i Khim. Tekhnol.*, 20 (1977) 315.
8. M. MOTAS, *Annale Sciintifice de Universitatii "Al. I. Cuza" Din Iass. sec. I, c. chimie* 16 (1970) 19.
9. W. BRZYSKA and R. KURPIEL, *Zeszyty Nauk. Politech. Ślaskiej, Chemia Z.*, 93 (1980) 181.
10. W. BRZYSKA and L. SZUBARTOWSKI, *Zeszyty Nauk. Politech. Ślaskiej, Chemia Z.*, 93 (1980) 175.
11. J. KOWALEWICZ and W. BRZYSKA, *Folia Scientiarum Societatis Lublinensis*, 22 (1980) 13