Journal of Thermal Analysis, Vol. 23 (1982) 231–234

THERMAL DECOMPOSITIONS OF HEAVY LANTHANIDE ACONITATES

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(Received July 27, 1981)

The conditions of thermal decomposition of Tb(III), Dy, Ho, Er, Tm, Yb and Lu aconitates have been studied. On heating, the aconitates of heavy lanthanides lose crystallization water to yield anhydrous salts, which are then transformed into oxides. The aconitate of Tb(III) decomposes in two stages. First, the complex undergoes dehydration to form the anhydrous salt, which next decomposes directly to Tb_4O_7. The aconitates of Dy, Ho, Er, Tm, Yb and Lu decompose in three stages. On heating, the hydrated complexes lose crystallization water, yielding the anhydrous complexes; these subsequently decompose to Ln_2O_3 with intermediate formation of $Ln_2O_2CO_3$.

The salts of aconitic acid have been comparatively little investigated. Motas [1] has obtained La, Ce(III) and Th(IV) aconitates and studied their thermal decompositions. Brzyska and Ożga [2] have prepared aconitates of Y, La and light lanthanides. A search of the available literature showed that aconitates of the heavy lanthanides have not been studied so far. As a continuation of our work on the thermal decompositions of lanthanide carboxylates [3–6] we now report the thermal decompositions of heavy lanthanide aconitates.

Experimental

Aconitates of Tb(III), Dy, Ho, Er, Tm, Yb and Lu were prepared by adding an equivalent quantity of 0.1 *M* ammonium aconitate (pH 5–5.5) to a hot solution containing the heavy lanthanide chloride (the solution of ammonium aconitate was prepared by dissolving aconitic acid in an equivalent quantity of ammonia solution). The precipitate formed was heated in the mother liquor for 0.5 h, and was then filtered off, washed with hot water to remove chloride ion and dried at 303 K to constant mass. The aconitates of the heavy lanthanides were prepared in macrocrystalline form with the colours characteristic for the Ln^{3+} ions.

The carbon and hydrogen contents were determined by elemental analysis. The heavy lanthanide content was determined by ignition of the salt to the oxide Ln_2O_3 (Ln = Dy, Ho, Er, Tm, Yb, Lu) or Tb_4O_7 at 1173 K. The elemental analysis data are presented in Table 1. In most cases the experimental result approximates closely to the value required by theory.

Table 1

Analytical data

Compound	Metal, %		Carbon, %		Hydrogen, %	
	calc.	found	calc.	found	calc.	found
$TbC_6H_3O_6 \cdot 2\,H_2O$	43.43	43.02	19.67	19.60	1.91	2.00
$DyC_6H_3O_6 \cdot 2\,H_2O$	43.97	44.00	19.48	20.11	1.89	2.02
$HoC_6H_3O_6 \cdot 2\,H_2O$	44.34	43.98	19.35	19.72	1.88	1.99
$ErC_6H_3O_6 \cdot 2\,H_2O$	44.69	44.42	19.23	18.84	1.87	1.87
$TmC_6H_3O_6 \cdot 2\,H_2O$	44.99	45.00	19.13	19.20	1.86	1.90
$YbC_6H_3O_6 \cdot 2\,H_2O$	45.53	45.04	18.94	18.47	1.84	2.06
$LuC_6H_3O_6 \cdot 2\,H_2O$	45.80	45.90	18.84	19.00	1.83	1.79

The results revealed that the aconitates of Tb, Dy, Ho, Er, Tm, Yb and Lu were hydrated salts with general formula $LnC_6H_3O_6 \cdot 2\,H_2O$.

IR spectra of aconitic acid and the complexes were recorded over the range 4000–400 cm^{-1} with an OD-102 spectrophotometer. Analysis of the IR spectra confirms the elemental analysis data.

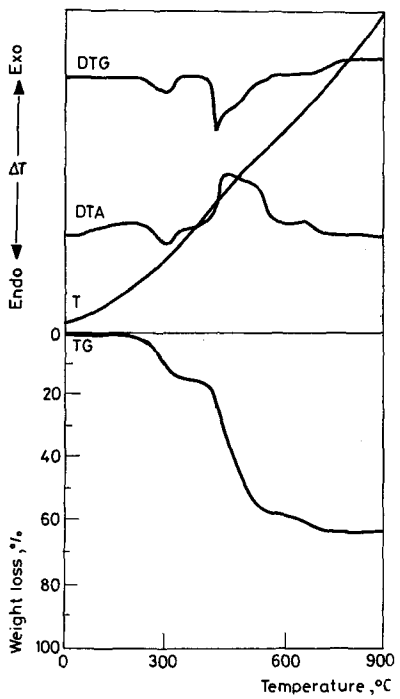

Fig. 1. TG, DTG and DTA curves of $TbC_6H_3O_6 \cdot 2\,H_2O$

Table 2

Temperature data on thermal decompositions of heavy lanthanide aconitates

Complex	ΔT_1, K	Loss of weight, %		ΔT_2, K	Loss of weight, %		T_k, K
		calc.	found		calc.	found	
$TbC_6H_3O_6 \cdot 2\,H_2O$	443–548	11.0	10.5	623–913	48.9	49.5	913
$DyC_6H_3O_6 \cdot 2\,H_2O$	443–548	10.9	10.5	613–973	49.5	50.0	973
$HoC_6H_3O_6 \cdot 2\,H_2O$	453–553	10.8	10.3	648–998	49.2	49.5	998
$ErC_6H_3O_6 \cdot 2\,H_2O$	443–538	10.7	10.2	633–978	49.0	50.0	978
$TmC_6H_3O_6 \cdot 2\,H_2O$	443–548	10.7	10.0	633–1013	48.7	49.5	1013
$YbC_6H_3O_6 \cdot 2\,H_2O$	453–543	10.5	10.0	633–948	48.2	48.0	948
$LuC_6H_3O_6 \cdot 2\,H_2O$	433–553	10.5	10.0	653–1013	48.0	48.0	1013

X-ray diffraction patterns of the aconitates were taken on a DRON-2 diffractometer, using CuK_α radiation. The measurements were made by means of the powder Debye-Scherrer method. The results indicate that these complexes are isostructural.

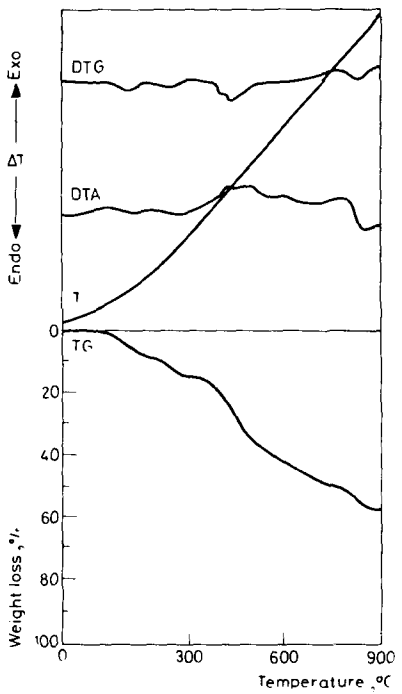

Fig. 2. TG, DTG and DTA curves of $DyC_6H_3O_6 \cdot 2\,H_2O$

The thermal stabilities of the aconitates of Tb(III), Dy, Ho, Er, Tm, Yb and Lu, were studied by TG, DTA and DTG techniques. The measurements were made with the OD-102 derivatograph (Paulik–Paulik–Erdey) at a heating rate of 9°/min, at the sensitivities TG – 200 mg, DTG – 1/10 and DTA – 1/20. The samples were heated in air in ceramic crucibles. Alumina was used as reference material.

From the curves recorded for the aconitates of the heavy lanthanides, the temperatures of thermal decomposition were evaluated and are presented in Table 2, where ΔT_1 is the temperature range (K) corresponding to the endothermic loss of 2 molecules of crystallization water, ΔT_2 is the temperature range (K) corresponding to the decomposition of the anhydrous salt and deflagration of the carbon residue until the formation of oxide, and T_K is the temperature of oxide formation.

The aconitate of Tb(III) is found to decompose in two stages. (Fig. 1) In the first step, at 443–548 K, the complex undergoes dehydration to the accompaniment of a strong endothermic effect, and the anhydrous aconitate then decomposes directly to the oxide Tb_4O_7 in the temperature range 623–915 K. The aconitates of Dy, Ho, Er, Tm, Yb and Lu are found to decompose in three stages. (Fig. 2) On heating, the hydrated complexes lose crystallization water at 443–553 K, yielding the anhydrous complexes, which subsequently decompose to Ln_2O_3 with intermediate formation of $Ln_2O_2CO_3$. The thermal decomposition of $Ln_2O_2CO_3$ to Ln_2O_3 is accompanied by an endothermic effect. The oxides are formed in the temperature range 913–1013 K.

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