Journal of Thermal Analysis, Vol. 32 (1987) 55–59

THERMAL DECOMPOSITION OF THORIUM(IV) BENZENEDICARBOXYLATES IN AIR ATMOSPHERE

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(Received July 18, 1985)

The conditions of thermal decomposition of Th(IV) benzenedicarboxylates have been studied. On heating, thorium(IV) phthalate and isophthalate are dehydrated and the anhydrous complexes decompose to ThO_2 with intermediate formation of a mixture of $ThOCO_3$ and carbon.

Th(IV) terephthalate obtained at room temperature loses crystal water and then decomposes directly to ThO_2, while the complex isolated from a hot solution on heating is first dehydrated, and the anhydrous complex is decarboxylated and then decomposed to ThO_2 with the intermediate formation of $ThOCO_3$.

The activation energies of dehydration have been calculated for the Th(IV) benzenedicarboxylates.

The salts of thorium(IV) with benzenecarboxylic acids are little known. In recent years studies have been made on the preparation of Th(IV) complexes with phthalic acid [1–4]. Kovalenko and Kozachenko [4] studied the thermal decomposition of dihydrated thorium(IV) phthalate on heating to 708 K. Their studies were complete, and only a DTA curve was published. A search of the available literature showed that thorium(IV) isophthalate and terephthalate have not been studied so far. As a continuation of our work on the thermal decomposition of *d* and *f* electron element carboxylates [5–7], we now report on the thermal decomposition of thorium(IV) benzenedicarboxylates.

Experimental

Benzenedicarboxylates of thorium(IV) were prepared by adding equivalent amounts of a 0.2 *M* aqueous solution of ammonium benzenedicarboxylate (pH 4.5) to a hot solution containing thorium(IV) nitrate (0.1 *M*). The precipitate formed was heated in the mother liquor for 15 min at 353–363 K, filtered off,

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washed with hot water to remove ammonium ions and dried at 303 K to constant weight.

The terephthalate of Th(IV) was also prepared in a double decomposition reaction by adding ammonium terephthalate to a solution containing $Th(NO_3)_4$ at room temperature (291 K).

The phthalate and isophthalate of thorium(IV) were prepared as white solids and the terephthalate as a cream-coloured one. Benzenedicarboxylates obtained from hot solution are crystalline compounds, and thorium(IV) terephthalate obtained at room temperature is an amorphous one. All compounds are sparingly soluble in water.

The contents of carbon and hydrogen were determined by elemental analysis, using V_2O_5 as oxidizing agent. The thorium content was determined by ignition of the compounds to ThO_2 at 1173 K and from the TG curve. The water content was determined by isothermal heating at definite temperatures and from the TG curve. The elemental analysis data are presented in Table 1.

Table 1 Analytical data

Thorium(IV) complexes		%, Th		%, C		%, H	
Name	Formula	calcd.	found.	calcd.	found.	calcd.	found.
phthalate	$Th(C_8H_4O_4)_2 \cdot 2H_2O$	38.92	38.68	32.23	32.42	2.03	1.80
isophthalate	$Th(C_8H_4O_4)_2 \cdot 2H_2O$	38.92	39.02	32.23	32.01	2.03	1.76
terephthalate	$Th_3(OH)_5 \cdot (C_8H_4O_4)_2(C_8H_5O_4)_3 \cdot 5H_2O$	41.07	41.13	28.34	28.25	2.26	1.82
terephthalate	$Th_5(OH)_{14}(C_8H_4O_4)_3 \cdot 7H_2O$	57.53	57.65	14.29	14.14	2.00	2.05

The results showed that thorium(IV) phthalate and isophthalate were isolated as dihydrates with a metal to ligand ratio of 1 : 2. Kovalenko and Kozachenko [4] prepared Th(IV) phthalate as the dihydrate too.

Thorium(IV) terephthalates prepared under various conditions have different compositions.

Thorium(IV) terephthalate prepared at 353–363 K was isolated as the pentahydrate with a metal to ligand ratio of 3 : 5, and that obtained at room temperature as the heptahydrate with a metal to ligand ratio of 5 : 3.

The IR spectra of benzenedicarboxylic acids and their Th(IV) complexes are recorded over the range 4000–400 cm^{-1}. Analysis of the IR spectra confirmed the results of elemental analysis.

The thermal stabilities of Th(IV) phthalate, isophthalate and terephthalates were studied by the use of TG, DTG and DTA techniques. The measurements were made with a Q 1500D derivatograph at a heating rate of 10 deg $\cdot$ min^{-1}. The samples

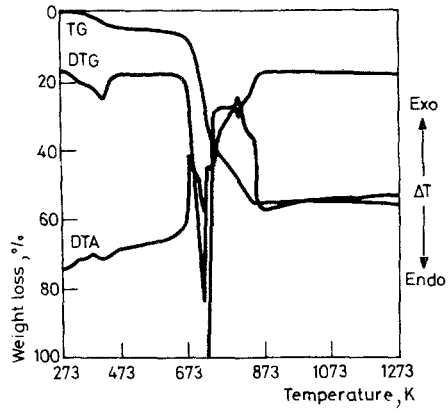

Fig. 1 TG, DTG and DTA curves of Th(IV) phthalate

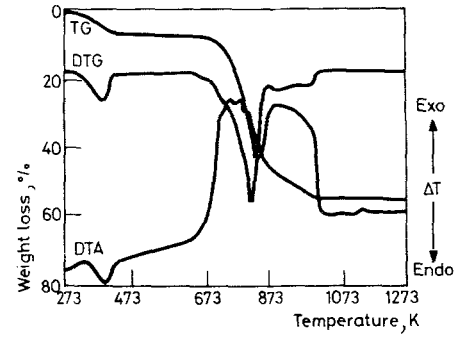

Fig. 2 TG, DTG and DTA curves of Th(IV) isophthalate

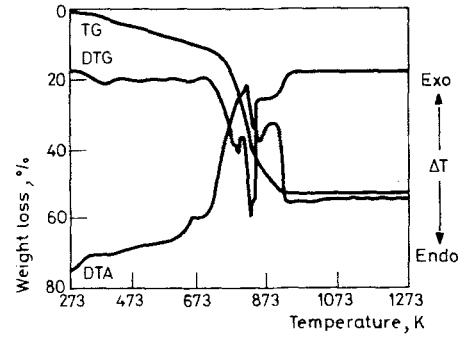

Fig. 3 TG, DTG and DTA curves of Th(IV) terephthalate:
$Th_3(OH)_5(C_8H_4O_4)_2(C_8H_5O_2)_3 \cdot 5H_2O$

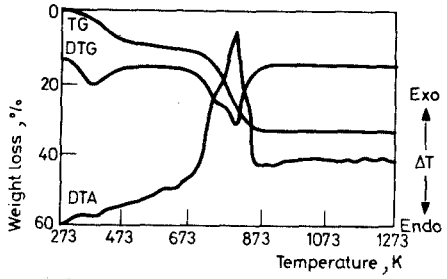

Fig. 4 TG, DTG and DTA curves of Th(IV) terephthalate: $Th_5(OH)_{14}(C_8H_4O_4)_3 \cdot 7H_2O$

were heated to 1273 K in air atmosphere in platinum crucibles. The recorded TG, DTG and DTA curves are given in Figs 1–4. The products of decomposition were confirmed by heating preparations isothermally at a definite temperature and recording the IR spectra and loss of weight.

Results

The benzenedicarboxylates of thorium(IV) decompose in various ways. On heating, the phthalate and isophthalate dehydrate in the temperature range 343–453 K to the accompaniment of a strong endothermic effect, and the anhydrous complexes next decompose to ThO_2 with the intermediate formation of a mixture of $ThO(CO_3)$ and carbon. The decomposition and burning of the organic ligand are associated with two exothermic effects.

Thorium(IV) terephthalate prepared at room temperature $Th_5(OH)_{14}(C_8H_4O_4)_3 \cdot 7H_2O$ decomposes in two steps on heating. The hydrate is dehydrated in and endothermic process in the temperature range 333–543 K and the anhydrous basic complex next decomposes directly to ThO_2.

The decomposition of thorium(IV) terephthalate isolated at 353–363 K proceeds in several steps. During heating, the pentahydrated complex is dehydrated in an endothermic process, next decarboxylated to $Th_3(OH)_5(C_8H_4O_4)_2 \cdot (C_7H_5O_2)_3$, and then decomposed to ThO_2 with the intermediate formation of $ThOCO_3$.

Table 2 Activation energy of dehydration

Complex	E, kJ·mol^{-1}
$Th(C_8H_4O_4)_2 \cdot 2H_2O$ (1.2)	35.7
$Th(C_8H_4O_4)_2 \cdot 2H_2O$ (iso) (1.3)	44.2
$Th_3(OH)_5(C_8H_4O_4)_2(C_8H_5O_4)_3 \cdot 5H_2O$ (1.4)	24.4
$Th_5(OH)_{14}(C_8H_4O_4)_3 \cdot 7H_2O$ (1.4)	35.3

Dehydration of thorium benzenedicarboxylates occurs in the temperature range 343–453 K. The anhydrous complexes are stable up to 643–723 K. On heating in air, they finally yield ThO_2, which forms at 853–913 K in the decomposition of the isophthalates.

From the TG and DTA curves the activation energy of dehydration was calculated [8] (Table 2). The activation energies of the phthalate and the terephthalate prepared at room temperature have similar values. The dehydration reaction of thorium(IV) isophthalate has the highest activation energy.

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Zusammenfassung — Die Bedingungen der thermischen Zersetzung von Th(IV)-benzendicarboxylaten wurde untersucht. Thorium(IV)-phthalat und -isophthalat werden beim Erhitzen zunächst dehydratisiert, danach zersetzen sich die wasserfreien Komplexe über ein intermediär auftretendes Gemisch von $ThOCO_3$ und Kohlenstoff zu ThO_2. Bei Raumtemperatur erhaltenes Th(IV)-terephthalat verliert Wasser und zersetzt sich dann direkt zu ThO_2, während der aus einer heißen Lösung isolierte Komplex nach der als erster Schritt verlaufenden Dehydratisierung zunächst decarboxyliert wird und sich dann über $ThOCO_3$ als Zwischenprodukt zu ThO_2 zersetzt. Die Aktivierungsenergien der Dehydratisierung der Th(IV)-benzendicarboxylate wurden berechnet.

Резюме — Изучены условия термического разложения бензолдикарбоксилатов четырехвалентного тория. Фталат и изофталат тория дегидратируются при нагревании, а образующиеся при этом безводные соли разлагаются до ThO_2 с образованием смеси $ThOCO_3$ и углерода в качестве промежуточных продуктов. Терефталат тория, полученный при комнатной температуре, теряет кристаллизационную воду, а затем прямо разлагается до ThO_2. Эта же соль, выделенная из горячего раствора, при нагревании сначала дегидратируется, после чего безводная соль декарбоксилируется, а затем уже разлагается до ThO_2 с образованием $ThOCO_3$ в качестве промежуточного продукта. Для всех изученных солей вычислены энергии активации процесса дегидратации.