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THERMAL DECOMPOSITION OF THORIUM(IV) BENZENETRICARBOXYLATES PREPARED IN VARIOUS WAYS

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The thermal decompositions of thorium(IV) trimesinate and trimellitate, prepared under various conditions, have been studied. On heating benzenetricarboxylates of Th(IV) decompose in many stages. First, the hydrated complexes lose crystallization water in one, two or four stages, forming anhydrous comtlexes which decompose to ThO_2 with the intermediate formation of $ThOCO_3$. The dehydrations of the complexes are associated with strong endothermic effects, and the decompositions of the anhydrous complexes are accompanied by exothermic effects.

A search of the available literature shows that the benzenetricarboxylates of thorium(IV) have not been studied so far. Trimesinic (benzene-1,3,5-tricarboxylic) and trimellitic (benzene-1,2,4-tricarboxylic) acids have been used for the gravimetric determination of Th(IV) in mixtures of thorium + zirconium and thorium + hafnium [1]. Mukherji [1] studied the thermal stabilities of the prepared precipitates up to 1273 K publishing TG curves, but he did not study their compositions. As a continuation of our work on the thermal decompositions of thorium(IV) carboxylates [2], we now report the thermal decompositions of the above thorium(IV) benzenetricarboxylates, prepared under various conditions.

Experimental

Thorium(IV) trimesinates and trimellitates were prepared in double decomposition reactions by adding an aqueous solution of the benzenetricarboxylic acid or its ammonium salt to a solution of thorium(IV) nitrate at 328–333 K or 368–373 K. The precipitate formed was mixed in the mother liquor for 15 min, then filtered off, washed with water to remove NH_4^+ or NO_3^- ions, and dried at 303 K to constant weight. The conditions of preparation are given in Table 1.

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Table 1 Preparation conditions of Th(IV) benzenetricarboxylates

Complex	Th : L	Temperature, K		Reagents	Final pH
		of precipitation	of heating		
$Th_3(C_9H_3O_6)_4 \cdot 20H_2O$ 1,3,5	3 : 4	293	—	0.07 *M* ammonium trimesinate 0.1 *M* $Th(NO_3)_4$ 2 : 1	2.4
$Th_3(C_9H_3O_6)_4 \cdot 10H_2O$ 1,3,5	3 : 4	368–373	368–373	0.05 *M* trimesinic acid 0.05 *M* $Th(NO_3)_4$ 3 : 2	1.5
$Th_3(C_9H_3O_6)_4 \cdot 12H_2O$ 1,3,5	3 : 4	368–373	368–373	0.07 *M* ammonium trimesinate 0.05 *M* $Th(NO_3)_4$ 1 : 1	3.2
$Th(OH)(C_9H_3O_6) \cdot 4H_2O$ 1,2,4	1 : 1	293	—	0.1 *M* ammonium trimellitate 0.1 *M* $Th(NO_3)_4$ 2 : 1	3.3
$Th_3(C_9H_3O_6)_4 \cdot 12H_2O$ 1,2,4	3 : 4	328–333	353	0.1 *M* trimellitic acid 0.1 *M* $Th(NO_3)_4$ 2 : 1	1.4
$Th_4(OH)(C_9H_3O_6)_5 \cdot 18H_2O$ 1,2,4	4 : 5	368–373	368–373	0.07 *M* ammonium trimellitate 0.1 *M* $Th(NO_3)_4$ 2 : 1	2.6

The precipitates formed are white; they are sparingly soluble in water. Thorium(IV) trimesinates are crystalline solids, whereas the trimellitates are amorphous.

The contents of carbon and hydrogen in the prepared complexes were determined by elemental analysis, with V_2O_5 as oxidizing agent. The content of thorium(IV) was determined from the TG curves and by ignition of the complexes to ThO_2 at 1273 K. The water contents were determined from the TG curves and by isothermal heating of the samples at definite temperature. The analysis data are presented in Table 2.

Table 2 Analytical data

Thorium(IV) Complexes		Th, %		C, %		H, %	
name	formula	calcd.	found	calcd.	found	calcd.	found
Trimesinate	$Th_3(C_9H_3O_6)_4 \cdot 20H_2O$	36.93	36.91	22.94	22.90	2.78	2.58
Trimesinate	$Th_3(C_9H_3O_6)_4 \cdot 10H_2O$	40.83	40.42	25.36	25.41	1.89	1.88
Trimesinate	$Th_3(C_9H_3O_6)_4 \cdot 12H_2O$	39.99	39.72	24.84	25.20	2.08	2.40
Trimellitate	$Th(OH)(C_9H_3O_6) \cdot 4H_2O$	43.92	43.59	20.46	20.88	2.29	2.61
Trimellitate	$Th_3(C_9H_3O_6)_4 \cdot 12H_2O$	39.99	39.72	24.84	25.23	2.08	2.42
Trimellitate	$Th_4(OH)(C_9H_3O_6)_5 \cdot 18H_2O$	40.27	40.07	23.45	23.35	2.27	2.58

The results show that the thorium(IV) trimesinate prepared under various conditions was isolated as a hydrated complex with a thorium to ligand ratio of 3 : 4, but with various degrees of hydration. Thorium(IV) trimellitate was obtained as a complex with a thorium to ligand ratio of 3 : 4, or as a basic complex with a thorium to ligand ratio of 1 : 1 or 4 : 5.

The IR and X-ray spectra of these benzenetricarboxylic acids and the prepared complexes were recorded over the range 4000–400 cm^{-1}. Analysis of the IR spectra confirmed the results of elemental analysis.

The thermal stabilities of the thorium(IV) trimesinates and trimellitates were studied by means of TG, DTG and DTA techniques. The measurements were made with a Q-1500 D derivatograph at a heating rate of 10 $deg \cdot min^{-1}$, with a sensitivity TG = 200 mg. The samples were heated in Pt crucibles in air up to 1273 K. From the thermal curves of the benzenetricarboxylates, the temperatures and solid products of decomposition were evaluated and are presented in Tables 3 and 4. The solid products of decomposition were confirmed by recording their IR spectra.

Table 3 Temperature data of dehydration of Th(IV) benzenetricarboxylates

Complex	Temperature range of dehydration, K	Peak temperature, K		Loss of weight, %		Loss of H_2O molecules
		of DTG	of DTA	calcd.	found	
$Th_3L_4^* \cdot 20H_2O$ 1,3,5	343–563	408	418	19.12	18.80	20
$Th_3L_4 \cdot 10H_2O$ 1,3,5	338–403	393	393	5.28	5.20	5
	403–443	423	428	2.11	2.00	2
	443–523	458	458	2.11	2.00	2 } 10
	523–593	563	563	1.06	1.20	1
$Th_3L_4 \cdot 12H_2O$ 1,3,5	348–433	393	403	6.21	6.40	6 } 12
	433–543	483	483	6.21	6.00	6
$Th(OH)L \cdot 4H_2O$ 1,2,4	348–563	403	413	13.64	13.20	4
$Th_3L_4 \cdot 12H_2O$ 1,2,4	333–533	393	393	12.42	12.80	12
$Th_4(OH)L_5 \cdot 18H_2O$ 1,2,4	343–563	403	413	14.07	13.60	18

L* C $H_3(COO)_3^{3-}$ 1,3,5, 1,2,4 – position of COO^- group

Table 4 Temperature data of decomposition of Th(IV) benzenetricarboxylates

Complex	Temperature, K		Peak temperature, K		Loss of weight, %		Temperature of oxide formation, K
	of dehydration	of decomposition	of DTG,	of DTA,	calcd.	found	
$Th_3L_4 \cdot 20H_2O$ 1,3,5	343–563	753–923	803 863	863 893	57.98	58.00	923
$Th_3L_4 \cdot 10H_2O$ 1,3,5	338–593	693–893	763 853	783 863	53.54	54.00	893
$Th_3L_4 \cdot 12H_2O$ 1,3,5	348–543	693–873	763 853	773 853	54.50	54.80	873
$Th(OH)L \cdot 4H_2O$ 1,2,4	348–563	673–873	773 853	793 863	50.01	50.40	883
$Th_3L_4 \cdot 12H_2O$ 1,2,4	333–533	673–893	763 853	773 853	54.50	54.80	893
$Th_4(OH)L_5 \cdot 18H_2O$ 1,2,4	343–563	693–893	753 853	793 853	54.18	54.40	893

Results

When these benzenetricarboxylates of thorium(IV) are heated in air, they decompose in several steps. On heating, the complexes are stable up to 333–353 K. In the temperature range 333–593 K, they are dehydrated to anhydrous compounds. Thorium(IV) trimesinate, $Th_3(C_9H_3O_6)_4 \cdot 10H_2O$, is dehydrated in four steps, and $Th_3(C_9H_3O_6)_4 \cdot 12H_2O$ (Fig. 1) in two steps. The other complexes are dehydrated in one step. The dehydration processes are accompanied by a strong endothermic effects. On heating, the anhydrous benzenetricarboxylates of thorium(IV) decompose to ThO_2 with the intermediate formation of $ThOCO_3$. The decomposition of the anhydrous complexes begins at 753–803 K, and that of $ThOCO_3$ to ThO_2 at 853–863 K. The burning of the organic ligand is accompanied by a strong exothermic effect. ThO_2 is formed at 873–923 K. The temperatures of ThO_2 formation during the decompositions of these benzenetricarboxylates are similar to those reported earlier [1, 2]. However, the precipitates obtained by Mukherji [1] decomposed at temperatures higher than 773 K, so they were more stable than the complexes described in this work.

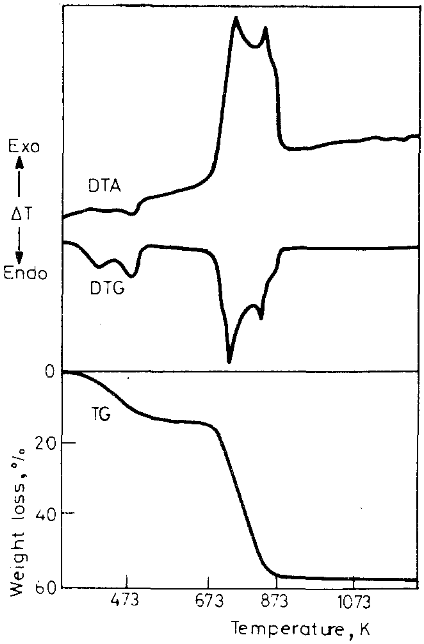

Fig. 1 TG, DTG and DTA curves of $Th_3(C_9H_3O_6)_4 \cdot 12H_2O$ (1,3,5)

This crystalline structure of ThO_2 formed on the decomposition of these benzenetricarboxylates was studied. The debyegrams indicate that the structure of the oxides is the same as that of ThO_2 obtained on the decomposition of Th(IV) oxalate.

The obtained results suggest the following general decomposition process for these benzenetricarboxylates:

$$Th_3L_4\cdot nH_2O \xrightarrow{333\text{–}593\ K} Th_3L_4 \xrightarrow{673\text{–}863\ K} ThOCO_3 \xrightarrow{T>873\ K} ThO_2$$

where $n = 10$, 12 or 20, and $L = C_6H_3(COO)_3^{3-}$, or:

$$\begin{array}{lllllll} Th(OH)L\cdot 4H_2O & \xrightarrow{343\text{–}563\ K} & Th(OH)L & \xrightarrow{673\text{–}853\ K} & ThOCO_3 & \xrightarrow{T>873\ K} & ThO_2 \\ Th_4(OH)L_5\cdot 18H_2O & & Th_4(OH)L_5 & & & & \end{array}$$

(the water molecules are lost in one or several steps).

It is possible that the intermediate is not pure $ThOCO_3$, but a mixture of $ThOCO_3+Th(CO_3)_2+C$ or $ThOCO_3+Th(CO_3)_2+ThO_2+C$.

The results show that the thermal decompositions of these thorium(IV) benzenetricarboxylates are similar to those of Th(IV) isophthalate Th(IV), terephthalate [2] and $Th(C_2O_4)_2\cdot 6H_2O$ [3].

References

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Zusammenfassung — Thorium-(IV)-trimesinat und -trimellinat wurden unter verschiedenen Bedingungen gefertigt und ihre thermische Zersetzung untersucht. Beim Erhitzen zersetzen sich Benzyltricarboxylate von Th(IV) in mehreren Stufen. Als erstes geben die hydrierten Komplexe in ein, zwei oder vier Schritten Kristallwasser ab. Die dehydrierten Komplexe zersetzen sich über das Zwischenprodukt $ThOCO_3$ zu ThO_2. Die Dehydrierung der Komplexe ist mit starken endothermischen Effekten verbunden, während die Zersetzung der dehydrierten Komplexe von exothermen Effekten begleitet wird.

Резюме — Изучено термическое разложение солей четырехвалентного тория с тримезиновой и тримеллитовой кислотами, полученных в различных условиях. При нагревании бензотрикарбоксилаты тория разлагаются в несколько стадий. Сначала гидраты солей теряют кристаллизационную воду в одну, две или четыре стадии, давая безводные соли, разлагающиеся затем до оксида четырехвалентного тория с образованием промежуточного соединения $ThOCO_3$. Дегидратация солей сопровождается сильными эндотермическими эффектами, а разложение безводных солей — экзотермическими эффектами.