

THERMAL DECOMPOSITION OF THORIUM(IV) COMPLEXES WITH BENZENECARBOXYLIC ACIDS IN AIR ATMOSPHERE

III. Thorium(IV) complexes with methylbenzoic and benzenedicarboxylic acids

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(Received April 13, 1992; in revised form March 5, 1993)

Abstract

The conditions and products of thermal decomposition of thorium(IV) complexes with general formula $\text{Th}(\text{R}-\text{C}_6\text{H}_4\text{COO})_4$ (where $\text{R} = 2\text{-CH}_3, 3\text{-CH}_3, 4\text{-CH}_3$), $\text{Th}(\text{OH})_2(4\text{-CH}_3\text{C}_6\text{H}_4\text{COO})_2 \cdot \text{H}_2\text{O}$ and $\text{Th}(\text{OH})_2(\text{R}-\text{C}_6\text{H}_4\text{COO})_2 \cdot n\text{H}_2\text{O}$ (where $\text{R} = 2\text{-COO}, 3\text{-COO}, n = 2$; $\text{R} = 4\text{-COO}, n = 1$) were studied. Anhydrous thorium(IV) complexes decompose in two steps. On heating, tetra(2-methylbenzoato)-thorium(IV) decomposes to yield ThO_2 through the intermediate ThOCO_3 , whereas tetra(3-methylbenzoato)thorium(IV) and tetra(4-methylbenzoato)thorium(IV) decompose to ThO_2 through oxocomplexes. Hydrated thorium(IV) complexes are dehydrated in one step and then anhydrous complexes decompose to ThO_2 . Di [1,2-(benzene)dicarboxylato]dihydroxythorium(IV) decomposes directly to ThO_2 , whereas the 1,3- and 1,4-isomers through the intermediate thorium(IV) oxocarbonates.

Keywords: complexes, thorium(IV) complexes

Introduction

The thorium(IV) salts of methylbenzoic acids are little known. There are only some papers on thorium(IV) complexes with 2-methylbenzoic acid [1-3]. Wendlandt [1] prepared tetra-(2-methylbenzoato)thorium(IV) and determined its thermal stability and temperature of ThO_2 formation from the TG curve Singh [2] described di(2-methylbenzoato)oxothorium(IV). A search of the available literature showed that thorium(IV) complexes with 3-methylbenzoic and 4-methylbenzoic acids have not been studied so far.

The salts of thorium(IV) with 1,2-benzenedicarboxylic acid with a metal to organic ligand ratio of 1:2 have been known for many years [4-13]. Kovalenko

and Kozachenko [5], Singh [7], Brzyska and Karasinski [13] studied the thermal decomposition of bis[1,2-(benzene)dicarboxylato]thorium(IV) dihydrate. Bilinski *et al.* [9, 10] studied the system of thorium(IV) nitrate - potassium phthalate by using turbidimetric method and stated the existence of [1,2-(benzene)dicarboxylato]dihydroxothorium(IV). They studied the precipitate formed by using IR and NMR spectroscopy. The thermal decomposition of polynuclear thorium(IV) complexes with 1,4-(benzene)dicarboxylic acid have been studied, too [13].

In this work we present the thermal decomposition of thorium(IV) complexes with the general formula $\text{Th}(\text{R}-\text{C}_6\text{H}_4\text{COO})_4$ (where $\text{R}=2\text{-CH}_3$, 3-CH_3 and 4-CH_3), $\text{Th}(\text{OH})_2(4\text{-CH}_3\text{C}_6\text{H}_4\text{COO})_2\cdot\text{H}_2\text{O}$ and $\text{Th}(\text{OH})_2(\text{R}-\text{C}_6\text{H}_4\text{COO})_2\cdot n\text{H}_2\text{O}$ ($\text{R}=2\text{-COO}^-$, $n=2$; 3-COO^- ; $n=2$; 4-COO^- , $n=1$).

Experimental

The preparation of tetra(2-methylbenzoato)thorium(IV) and [1,2-(benzene)dicarboxylato]dihydroxothorium(IV) dihydrate was described in a previous work [14]. Tetra(3-methylbenzoato)thorium(IV) was prepared similarly as tetra(2-methylbenzoato)thorium(IV). Tetra(4-methylbenzoato)thorium(IV) was prepared similarly as tetra(2-methylbenzoato)thorium(IV) [14], but to a suspension of 4-methylbenzoic acid (6.3 g of acid + 500 ml H_2O) some drops of ammonia were added. Dihydroxodi(4-methylbenzoato)thorium(IV) monohydrate was prepared similarly as dibenzoatodihydroxothorium(IV) monohydrate [15], and [1,3-(benzene)dicarboxylato]dihydroxothorium(IV) dihydrate as [1,2-(benzene)dicarboxylato]dihydroxothorium(IV) dihydrate [14]. [1,4-(benzene)dicarboxylato]dihydroxothorium(IV) monohydrate was prepared by adding 0.1 mol/l solution of thorium(IV) nitrate to a hot solution of ammonium 1,4-(benzene)-dicarboxylate ($T=343\text{ K}$, $p\text{H } 5.5$). The precipitate formed was heated in the mother liquor for 15 min at 353 K, then was filtered off, washed with hot water to remove NH_4^+ ions and excess acid. The $p\text{H}$ of the mother liquor after precipitation was 5.5 and 4.6, respectively. The precipitate separated was dried to a constant mass at 303 K.

The content of carbon and hydrogen was determined by elemental analysis by combustion of the samples in aluminium capsule with V_2O_5 as oxydation catalyst. The content of thorium(IV) was determined by ignition of 0.2 g samples at 1173 K to ThO_2 and weighing, and from the TG curve. The content of H_2O was determined from the TG curves and by isothermal heating of samples at a definite temperature. On the basis of elemental analysis data the formulae of the complexes were established (Table 1).

The IR spectra of methylbenzoic acids, benzenedicarboxylic acids and their thorium(IV) complexes over the range $4000\text{--}400\text{ cm}^{-1}$ were recorded. The

Table 1 Analytical data

Thorium(IV) complex	% Th		% C		% H	
	calcd.	found	calcd.	found	calcd.	found
Th(2-CH ₃ C ₆ H ₄ COO) ₄ tetra(2-methylbenzoato)thorium(IV)	30.03	29.53	49.75	49.48	3.65	3.81
Th(3-CH ₃ C ₆ H ₄ COO) ₄ tetra(3-methylbenzoato)thorium(IV)	30.03	29.88	49.75	49.93	3.65	3.92
Th(4-CH ₃ C ₆ H ₄ COO) ₄ tetra(4-methylbenzoato)thorium(IV)	30.03	29.88	49.75	50.02	3.65	3.48
Th(OH) ₂ (2-CH ₃ C ₆ H ₄ COO)·H ₂ O dihydroxo(4-methylbenzoato)thorium(IV) monohydrate	41.86	42.28	34.67	35.03	3.27	3.30
Th(OH) ₂ (2-CHOOCC ₆ H ₄ COO)·2H ₂ O 1,2-(benzene)dicarboxylatodihydroxothorium(IV) dihydrate	49.77	48.98	20.61	21.08	2.16	2.66
Th(OH) ₂ (3-CHOOCC ₆ H ₄ COO)·2H ₂ O 1,3-(benzene)dicarboxylatodihydroxothorium(IV) dihydrate	49.77	49.06	20.61	20.48	2.16	2.42
Th(OH) ₂ (4-CHOOCC ₆ H ₄ COO)·H ₂ O 1,4-(benzene)dicarboxylatodihydroxothorium(IV) monohydrate	51.77	51.32	21.44	21.03	1.80	2.29

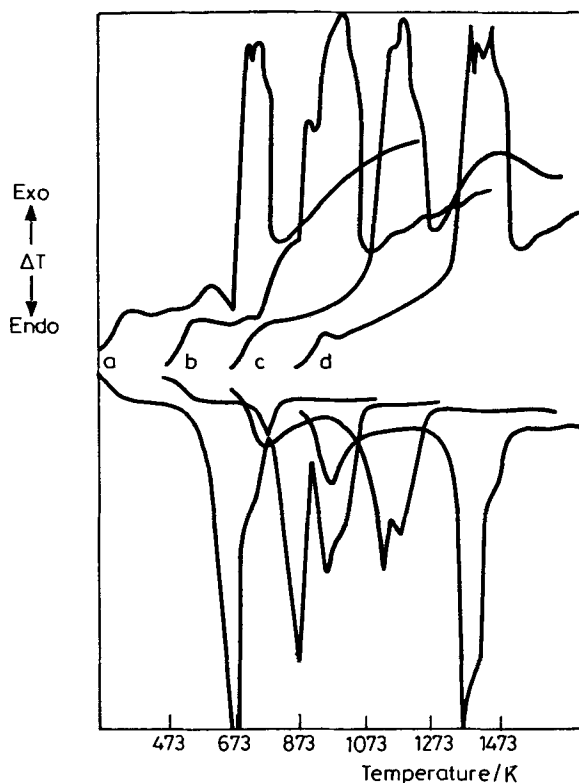


Fig. 1 DTA and DTG curves of: a) $\text{Th}(\text{2-CH}_3\text{C}_6\text{H}_4\text{COO})_4$; b) $\text{Th}(\text{4-CH}_3\text{C}_6\text{H}_4\text{COO})_4$; c) $\text{Th}(\text{OH})_2(\text{2-COOC}_6\text{H}_4\text{COO})\cdot\text{2H}_2\text{O}$; d) $\text{Th}(\text{OH})_2(\text{3-COOC}_6\text{H}_4\text{COO})\cdot\text{2H}_2\text{O}$

analysis of the IR spectra confirms the results obtained on the basis of elemental analysis and permits to define the way of thorium(IV) cation coordination by methylbenzoate and benzenedicarboxylate anions. It was established that the position of the substituent in thorium(IV) methylbenzoates does not influence the way of coordination of thorium(IV). Analysis of the position change of the absorption bands of asymmetric ($\nu_{\text{as}}\text{COO}$) and symmetric ($\nu_{\text{s}}\text{COO}$) vibrations of the methylbenzoate group in thorium(IV) complexes compared to the position in the IR spectra of the sodium salts suggests that the methylbenzoate anion is a bidentate chelating ligand.

The thermal stability of thorium(IV) methylbenzoates and basic benzenedicarboxylates was studied over the range 293–1273 K. The TG, DTG, DTA curves were recorded on a Q 1500 derivatograph (Paulik-Paulik-Erdey) at a heating rate of $10 \text{ deg}\cdot\text{min}^{-1}$. 100 mg samples were heated in ceramic crucibles in air atmosphere. The DTA and DTG curves are presented in Fig. 1, and the TG curves in Fig. 2. The thermal data of the dehydration process are presented

in Table 2 and those of the decomposition in Table 3. The values of the activation energy of the dehydration reaction (E_a) were calculated on the basis of the method of Pletnyev and Fotiyev [16]. The intermediates of decomposition were determined from the TG curve and confirmed by using IR spectra. The onset temperature of the decomposition (TBD) was determined from the TG curve by the method described in our previous work [15].

Results and discussion

Thorium(IV) complexes with methylbenzoic acids are crystalline solids of low symmetry and big unit cells. The basic thorium(IV) salts with benzenedicarboxylic acids are amorphous. All the complexes prepared are white, with the exception of [1,4-(benzene)dicarboxylato]-dihydroxothorium(IV) monohydrate which is pale brown.

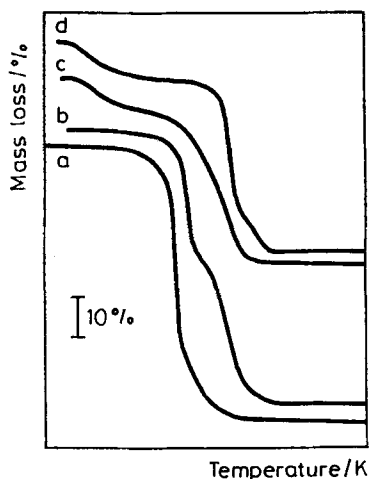


Fig. 2 TG curves of: a) $\text{Th}(2\text{-CH}_3\text{C}_6\text{H}_4\text{COO})_4$; b) $\text{Th}(4\text{-CH}_3\text{C}_6\text{H}_4\text{COO})_4$; c) $\text{Th}(\text{OH})_2(2\text{-COOC}_6\text{H}_4\text{COO})\cdot 2\text{H}_2\text{O}$; d) $\text{Th}(\text{OH})_2(3\text{-COOC}_6\text{H}_4\text{COO})\cdot 2\text{H}_2\text{O}$

On the basis of DTG, DTA and TG curves (Figs 1 and 2) and thermal data of dehydration (Table 2) and decomposition (Table 3) it was found that the complexes prepared decompose in many steps but the intermediates are very unstable and their determination is impossible.

Anhydrous tetra(2-methylbenzoato)thorium(IV) decomposes in two steps. In the first step it decomposes to thorium(IV) oxocarbonate and carbon, and then produces ThO_2 with simultaneous combustion of carbon. Tetra(3-methylbenzoato)thorium(IV) and tetra(4-methylbenzoato)thorium(IV) decompose to yield

Table 2 Thermal data of Th(IV) complex dehydration

Complex	Temperature range of dehydration / K	Loss of H ₂ O / mole	Loss of mass / %		<i>E_a</i> / kJ·mol ⁻¹
			calcd.	found	
Th(OH) ₂ (4-CH ₃ C ₆ H ₄ COO) ₂ ·H ₂ O	413–513	1	3.20	3.25	31
Th(OH) ₂ (2-COO C ₆ H ₄ COO) ₂ ·2H ₂ O	363–553	2	7.73	8.00	26
Th(OH) ₂ (3-COO C ₆ H ₄ COO) ₂ ·2H ₂ O	348–523	2	7.73	7.60	31
Th(OH) ₂ (4-COO C ₆ H ₄ COO) ₂ ·H ₂ O	358–533	1	4.02	4.00	42

Table 3 Thermal data of decomposition of thorium(IV) complexes

Complex	Temperature range / K*		Peak temperature /K		Loss of mass / %		T _k /K
	dehydration	decomposition	DTG	DTA	calcd.	found	
Th(2-CH ₃ C ₆ H ₄ COO) ₄	-	543-803 (563)-803	698	623	65.83	66.40	803
Th(3-CH ₃ C ₆ H ₄ COO) ₄	-	563-848 (583)-848	673 763	673 763	65.83	66.00	848
Th(4-CH ₃ C ₆ H ₄ COO) ₄	-	553-853 (573)-853	673 763	678 753	65.83	66.00	853
Th(OH) ₂ (4-CH ₃ C ₆ H ₄ COO) ₂ ·2H ₂ O	413-513	553-853 (573)-853	623 733	648 813	53.27	52.00	853
Th(OH) ₂ (2-COOC ₆ H ₄ COO) ₂ ·2H ₂ O	363-553	618-863 (643)-863	743 803	753 793	43.36	44.00	863
Th(OH) ₂ (3-COOC ₆ H ₄ COO) ₂ ·2H ₂ O	348-523	698-893 (723)-893	813	803 813 853	43.36	44.00	893
Th(OH) ₂ (4-COOC ₆ H ₄ COO) ₂ ·H ₂ O	358-533	673-903 (708)-903	823	843	41.09	41.60	903

* temperature of decomposition beginning is determined by using "point decomposition" method and values in bracket - by using "0.8" method
T_k temperature of ThO₂ formation

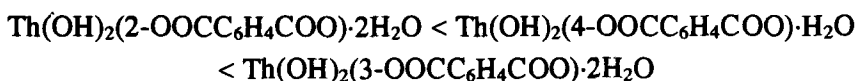
ThO₂ also in two steps but with formation of the intermediate di(methylbenzoato)oxothorium(IV). Dihydroxo(4-methylbenzoato)thorium(IV) monohydrate decomposes in three steps. In the first step it loses water of crystallization forming the anhydrous complex, which then decomposes to ThO₂ with formation of an unidentified intermediate.

The thermal stability of the described complexes (the value of TBD) increases in the order:

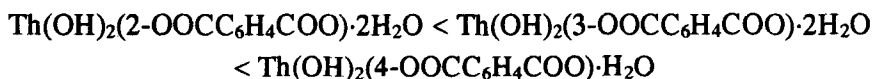


Dihydroxodi(4-methylbenzoato)thorium(IV) monohydrate has similar thermal stability to tetra(4-methylbenzoato)thorium(IV). [1,2-(benzene)dicarboxylato]dihydroxythorium(IV) dihydrate decomposes in two steps. In the first step it loses water of crystallization forming the anhydrous complex which then decomposes directly to ThO₂. [1,3-(benzene)dicarboxylato]dihydroxythorium(IV)-dihydrate and [1,4-(benzene)dicarboxylato]dihydroxythorium(IV)-monohydrate when heated are dehydrated and then the anhydrous complexes decompose to ThO₂ through the intermediate ThOCO₃.

The thermal stability of these compounds (TBD) increases in the order:



whereas the temperature of ThO₂ formation increases in the order:

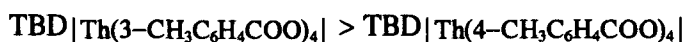


The dehydration process for all hydrated complexes proceeds in one step at 348–553 K. According to the values of dehydration energy (Table 2) the water of crystallization is coordinated in the outer sphere. The thermal stability defined by TBD for two ranges of complexes with the same composition has higher values for the meta then for the para isomers. For the benzenedicarboxylic acids the substituent is simultaneously the second centre of coordination and it is why the interpretation of experimental data is complicated. In contrast, for the salts of methylbenzoic acids the increase in the thermal stability connected with the change of substituent position in the benzene ring from para to meta can be caused by mesomeric and induction effects of the substituent on the centre of reaction (carboxylate group). The combined effects of the substituents compared to the unsubstituted compound was described numerically by Hammett's substituent constants δ . From an analysis of the values of Hammett's con-

stants for $-\text{CH}_3$, $-\text{OH}$ and $-\text{NH}_2$ groups and thermal stabilities of thorium(IV) benzenecarboxylates with these substituents [17] it is clear that the complex with higher thermal stability contains the substituent in such position relative to the reaction centre for which the Hammett's constant of the substituent has a higher value (e.g. 3- CH_3 $\delta = -0.07$ [18], 4- CH_3 $\delta = -0.17$ [18]). The same dependence is observed for the complexes prepared:

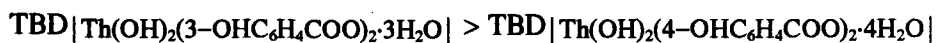
$$\delta_{(3-\text{CH}_3)} > \delta_{(4-\text{CH}_3)}$$

and



$$\delta_{(3-\text{OH})} > \delta_{(4-\text{OH})}$$

and [17]



$$\delta_{(3-\text{NH}_2)} > \delta_{(4-\text{NH}_2)}$$

and [17]



The interaction of the substituent in para position on the reaction centre is due to simultaneous induction and mesomeric effects. The substituent in the meta position influences the electron density by an induction effect, because the transformation of mesomeric effect is weakened ($\delta_m = \delta_i + 0.3\delta_M$) [19, 20]. It is possible to suggest that the substituent with positive value of δ_i causes a change of the electron density of the reaction centre which increases the degree of the ionic bond Th-O and in consequence gives rise to an increase in the thermal stability of the thorium(IV) complex. The mesomeric effect of a substituent characterized by a negative value of δ_M evokes the adverse action and causes a decrease in the thermal stability. The weakness of the δ_M effect (in meta position) causes an increase in the thermal stability of the meta isomer compared to the para isomer.

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Zusammenfassung — Es wurden die Bedingungen und die Produkte der thermischen Zersetzung von Thorium(IV)komplexen der allgemeinen Formel $\text{Th}(\text{R}-\text{C}_6\text{H}_4\text{COO})_4$ (mit $R=2\text{-CH}_3$, 3-CH_3 , 4-CH_3), $\text{Th}(\text{OH})_2(4\text{-CH}_3\text{C}_6\text{H}_4\text{COO})_2\cdot\text{H}_2\text{O}$ und $\text{Th}(\text{OH})_2(\text{R}-\text{C}_6\text{H}_4\text{COO})_2\cdot n\text{H}_2\text{O}$ (mit $R=2\text{-COO}$, 3-COO , $n=2$; $R=4\text{-COO}$, $n=1$) untersucht. Wasserfreie Thoriumkomplexe zersetzen sich in zwei Schritten. Beim Erhitzen zersetzt sich Tetra(2-methylbenzoato)thorium(IV) über das Zwischenprodukt ThOCO_3 in ThO_2 , während sich Tetra(3-methylbenzoato)thorium(IV) und Tetra(4-methylbenzoato)thorium(IV) über Oxokomplexe in ThO_2 zersetzen. Hydratisierte Thorium(IV)komplexe werden in einem Schritt dehydratisiert, die wasserfreien Komplexe zersetzen sich dann anschließend in zwei Schritten zu ThO_2 . Di[1,2-(benzol)dicarboxylato]dihydroxythorium(IV) zersetzt sich unmittelbar in ThO_2 , die 1,3- und 1,4-Isomere dagegen über intermediäre Thorium(IV)oxocarbonate.