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THERMAL DECOMPOSITION OF THORIUM(IV) SALTS OF BENZENE CARBOXYLIC ACIDS IN AIR ATMOSPHERE

II. Thorium(IV) salts of hydroxy- and aminobenzoic acids

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The thermal stabilities of thorium(IV) salts of ortho-, meta- and para-hydroxy- and aminobenzoic acids were studied. The salts were prepared as hydrated compounds with general formula $Th(OH)_2(R\text{-}C_6H_4COO)_2\cdot nH_2O$, were R = OH or NH_2, and n = 2, 3 or 4, while the salt of 3-aminobenzoic acid was anhydrous. On heating, the salts undergo dehydration in two or three steps and di(R-benzoato)dihydroxothorium(IV) or di(2-hyroxybenzoato)oxothorium(IV) is then transformed directly to ThO_2.

The temperatures of beginning of decomposition and ThO_2 formation decrease with decreasing values of the Hammett constant δ and von Bakkum constant δ^n.

Keywords: complexes

Introduction

Of the compounds of thorium(IV) with aminobenzoic acids, only the salts of 2-aminobenzoic acid have been well studied [1–6]. The thorium(IV) salts of 4-aminobenzoic acid are little known [2, 7] and that of 3-aminobenzoic acid is described in only one paper [8]. Wendlandt presented TG curves of di(2-aminobenzoato)dihydroxothorium(IV) [6] and (4-aminobenzoato)trihydroxothorium(IV) [7].

Wendlandt [6], Deshmukh [9–10] and Kovalenko [11] prepared di(3-hydroxybenzoato)dihydroxothorium(IV) and di(4-hydroxybenzoato)dihydroxothorium(IV) and studied their thermal stability [6, 11]. Some salts of thorium(IV) with 2-hydroxybenzoic acid have been prepared as solids [12–19], but their

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properties have not been studied exactly. Of these different salts only the thermal decompositions of di(2-hydroxybenzoato)oxothorium(IV) trihydrate [15, 17] and $Th(OC_6H_4COO)_2{\cdot}4H_2O$ [18] have been studied.

This paper reports on the thermal decomposition of thorium(IV) salts with general formula $Th(OH)_2(R\text{-}C_6H_4COO)_2{\cdot}nH_2O$, where R = OH or NH_2 in the ortho-, meta- or para-position.

Experimental

Di(2-aminobenzoato)dihydroxothorium(IV) tetrahydrate, di(3-aminobenzoato)dihydroxothorium(IV), di(3-hydroxybenzoato)dihydroxothorium(IV) trihydrate and di(4-hydroxybenzoato)dihydroxothorium(IV) tetrahydrate were prepared by adding 200 ml of a 0.05 *M* aqueous solution of thorium(IV) nitrate to a boiling solution of the appropriate acid (5.6 g of acid in 300 ml of water). Next, an aqueous solution of ammonia was added to form the precipitate, which was then heated at the boiling temperature for 15 minutes, left to stand overnight, filtered off and washed with hot water to remove NH_4^+ ions and free acid. The *pH* of the mother liquor after precipitation was 4.4, 3.5, 2.2 and 2.5, respectively.

Di(4-aminobenzoato)dihydroxothorium(IV) tetrahydrate was prepared by adding a 0.1 *M* aqueous solution of ammonium 4-aminobenzoate (*pH* 5.6) to a boiling 0.05 *M* solution of thorium(IV) nitrate. The subsequent preparation was the same as for the preceding salts. Di(2-hydroxybenzoato)dihydroxothorium(IV) tetrahydrate was prepared by dissolving thorium (IV) hydroxide in a boiling solution of a stoichiometric quantity of 2-hydroxybenzoic acid (5.6 g of acid and 300 ml of H_2O). Next, the solution was neutralized to *pH* 5 to obtain a precipitate. The *pH* of the mother liquor after filtration was 3.6 and 4.1, respectively.

The separated precipitates were dried to constant mass at 303 K. X-ray study by the Debye-Scherrer method revealed that the prepared compounds are crystalline with large unit cells and low symmetry.

The contents of carbon, hydrogen and nitrogen were determined by standard analysis. The content of thorium(IV) was determined by heating the sample (0.2 g) at 1173 K to ThO_2 and weighing, and from the TG curves.

The content of crystallization water was determined from the TG curves and by isothermal heating of the samples at a definite temperature.

The formulae of the prepared salts were established from the elemental analysis (Table 1).

The IR spectra were recorded in the range 4000–400 cm^{-1}. Analysis of the IR spectra confirmed the compositions of the salts. The absorption bands of the deformation vibrations β(OH) of –OH groups at 1483 cm^{-1} (2–OH) and

Table 1 Analytical data

Thorium(IV) complex	% Th		% C		% H		% N	
	calcd.	found	calcd.	found	calcd.	found	calcd.	found
$Th(OH)_2(2\text{–}OHC_6H_4COO)_2 \cdot 4H_2O$ (grey)* di(2–hydroxybenzoato)dihydroxothorium(IV) tetrahydrate	37.95	38.44	27.50	28.02	3.29	2.91	—	—
$Th(OH)_2(3\text{–}OHC_6H_4COO)_2 \cdot 3H_2O$ (flesh-brown) di(3–hydroxybenzoato)dihydroxothorium(IV) tetrahydrate	39.04	39.37	28.29	28.55	3.05	3.00	—	—
$Th(OH)_2(4\text{–}OHC_6H_4COO)_2 \cdot 4H_2O$ (white) di(4–hydroxybenzoato)dihydroxothorium(IV) tetrahydrate	37.95	37.44	27.50	27.74	3.29	2.98	—	—
$Th(OH)_2(2\text{–}NH_2C_6H_4COO)_2 \cdot 4H_2O$ (cream) di(2–aminobenzoato)dihydroxothorium(IV) tetrahydrate	38.02	38.32	27.55	28.01	3.63	3.59	4.59	4.77
$Th(OH)_2(3\text{–}NH_2C_6H_4COO)_2$ (ligh brown) di(3–aminobenzoato)dihydroxothorium(IV)	43.10	42.89	31.24	30.78	2.62	3.13	5.20	5.41
$Th(OH)_2(4\text{–}NH_2C_6H_4COO)_2 \cdot 2H_2O$ (cream) di(4–aminobenzoato)dihydroxothorium(IV) dihydrate	40.40	40.07	29.28	29.64	3.16	3.58	4.88	4.67

()* — the colour of complex

1240–1160 cm^{-1} (2-, 3- and 4–OH), of γ(OH) at 940 cm^{-1} (3–OH) and of the valency bond ν(OH) at 3220 cm^{-1} (2–OH) show that the –OH group of the hydroxybenzoic acids does not take part in metal-ligand bond formation, independently of the OH group position. The position of the absorption band maximum of the asymmetric (ν_{as} NH_2) and symmetric (ν_s NH_2) valency bond shows that the free electron pair of the nitrogen situated in the ortho- or para-position does not take part in the formation of a Th–N bond [3, 4].

The thermal stabilities of the prepared thorium(IV) carboxylates were studied in the range 293–1273 K; the TG, DTG and DTA curves were recorded on a Q 1500 D derivatograph (Paulik-Paulik-Erdey). Samples of 100 mg were heated in air atmosphere at a heating rate of 10 deg·min^{-1} with a sensitivity for TG of 100 mg, DTG 500 μV and DTA 500 μV. The results obtained are presented in Fig. 1–6 and Tables 2 and 3. The activation energy of dehydration (E_a) was calculated by the Pletneyev and Fotiyev method [20]. The temperature of beginning of decomposition (TBD) was determined by a method described previously [21]. The nature of the solid decomposition products was calculated from the weight loss in the TG curves and confirmed by recording the IR spectra.

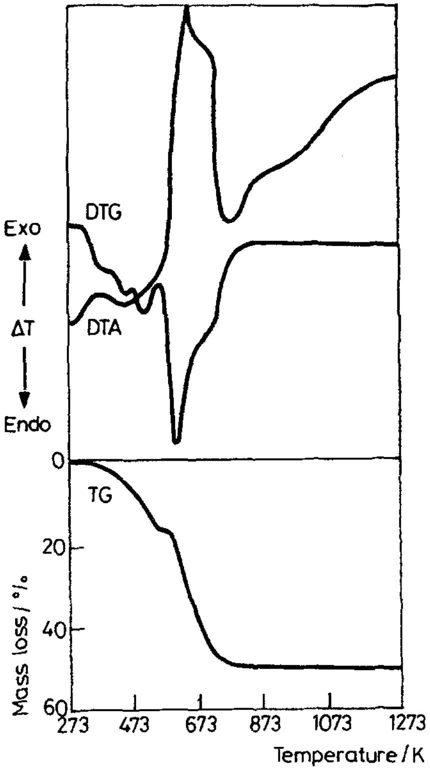

Fig. 1 Thermoanalytical curves of $Th(OH)_2(2\text{–}OHC_6H_4COO)_2\cdot 4H_2O$

Table 2 Thermal data of dehydration reaction

Thorium(IV) complex	Temperature range of dehydration / K	Peak temperature / K		Loss of weight / %		Number of H_2O molecules		E_a / kJ·mol^{-1}
		DTG	DTA	calcd.	found			
$Th(OH)_2(2\text{–}OHC_6H_4COO)_2\cdot 4H_2O$	338 – 393	378	—	2.95	3.20	1		59
	393 – 473	443	453	5.89	5.60	2	5!	
	473 – 543	503	503	5.89	6.40	2		
$Th(OH)_2(3\text{–}OHC_6H_4COO)_2\cdot 3H_2O$	348 – 453	383	393	6.06	5.60	2	3	30
	463 – 548	513	513	3.03	3.20	1		
$Th(OH)_2(4\text{–}OHC_6H_4COO)_2\cdot 4H_2O$	353 – 453	398	408	11.89	12.00	4		29
$Th(OH)_2(2\text{–}NH_2C_6H_4COO)_2\cdot 4H_2O$	333 – 413	373	383	2.95	3.20	1	4	23
	413 – 483	473	473	8.85	8.40	3		
$Th(OH)_2(4\text{–}NH_2C_6H_4COO)_2\cdot 2H_2O$	353 – 493	383	383	3.14	3.20	1	2	X
	493 – 533	523	523	3.14	3.20	1		

The value of E_a were determined only for first step of dehydration

! 4 molecules of crystallization water and one water molecule of decomposition of $2OH^-$ groups.

X E_a cannot be determined because the weight loss is very small in large range of temperature

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

Complex	Temperature range / K		Peak temperature / K		Loss of weight / %		T_k /
	dehydration	decomposition*	DTG	DTA	calcd.	found	K
$Th(OH)_2(2\text{–}OHC_6H_4COO)_2{\cdot}4H_2O$	338 – 543	{?} 543 – 738	603	640 713	56.81	56.00	738
$Th(OH)_2(3\text{–}OHC_6H_4COO)_2{\cdot}3H_2O$	348 – 548	578 – 798 (603) – 798	628	653	55.57	54.80	798
$Th(OH)_2(4\text{–}OHC_6H_4COO)_2{\cdot}4H_2O$	353 – 453	(?) 523 – 793 (?) (533) – 793	548 593 683	588 708	56.81	56.40	793
$Th(OH)_2(2\text{–}NH_2C_6H_4COO)_2{\cdot}4H_2O$	333 – 483	523 – 773 (543) – 773	623 633	678 693	56.74	56.40	773
$Th(OH)_2(3\text{–}NH_2C_6H_4COO)_2$	—	593 – 873 (618) – 873	653 733	808	50.95	51.20	873
$Th(OH)_2(4\text{–}NH_2C_6H_4COO)_2{\cdot}2H_2O$	353 – 533	(?) 533 – 863 (?) (543) – 863	613 738	803	54.03	53.60	863

(?) temperature of decomposition beginning (TBD) cannot be determined exactly because dehydration products are very unstable

* temperature of decomposition beginning is determined by using point decomposition' method and value in bracket — by using '0.8' method. T_k temperature of ThO_2 formation

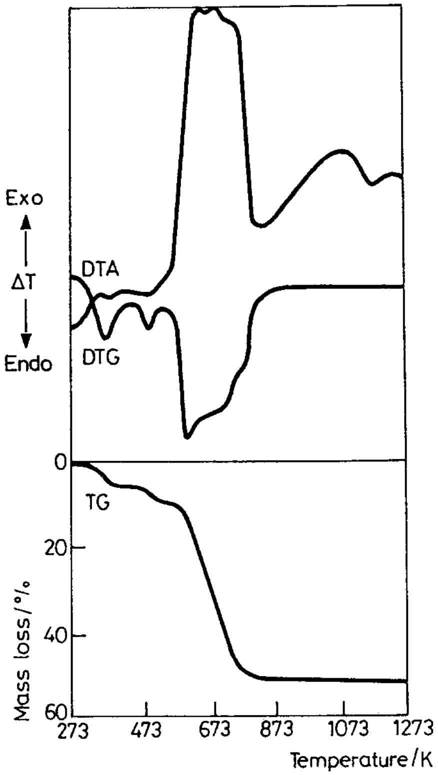

Fig. 2 Thermoanalytical curves of $Th(OH)_2(3\text{-}OHC_6H_4COO)_2 \cdot 3H_2O$

Results and discussion

The thorium(IV) salts with general formula $Th(OH)_2(R\text{-}C_6H_4COO)_2 \cdot nH_2O$ generally contain 2–4 molecules of crystal water. Only the salt of 3-aminobenzoic acid is anhydrous. The hydrated salts undergo dehydration on heating and the anhydrous dihydroxo or oxo compounds next decompose.

The thermal data on the dehydration reactions are presented in Table 2 and Fig. 7. The salts are dehydrated in one, two or three steps in the temperature range 333–548 K. In the first step of dehydration (333–493 K), the salts lose one water molecule. This is indubitably outer sphere water, because the energies of dehydration are small (Table 2). Only the salts of thorium(IV) with the 4-hydroxy- and the 3-hydroxy-acid lose 4 and 2 outer sphere water molecules, respectively. The second step of dehydration (393–548 K) is connected with the loss of 1 to 3 outer sphere water molecules, except for di(4-aminobenzoato)-

dihydroxothorium(IV) hydrate, which loses one water molecule from the inner sphere, which proves the high temperature of dehydration (493 K).

The thorium(IV) salt of 2-hydroxybenzoic acid is dehydrated in three steps. In the third step, it loses the last crystal water molecule, with simultaneous decomposition of the –OH groups to form di(hydroxybenzoato)oxothorium(IV). The water molecule lost in this step is probably inner sphere water.

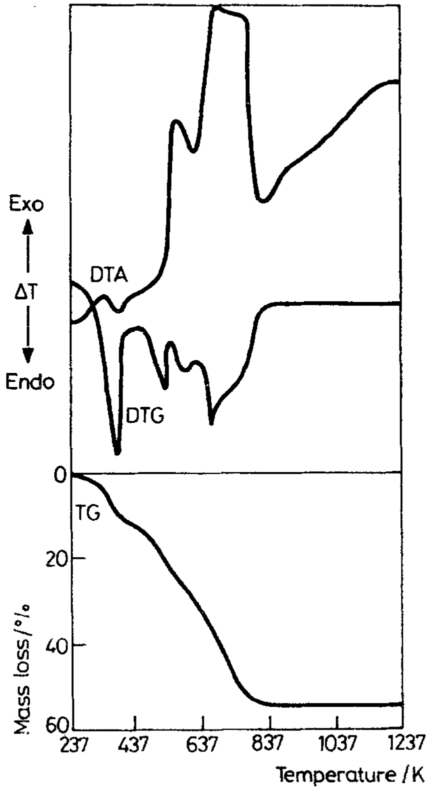

Fig. 3 Thermoanalytical curves of $Th(OH)_2(4\text{–}OHC_6H_4COO)_2\cdot 4H_2O$

The results permit the suggestion that the thorium(IV) salt of 2-hydroxybenzoic acid has the formula $[Th(OH)_2(2\text{–}OHC_6H_4COO)_2\cdot H_2O]\cdot 3H_2O$, while that of 4-aminobenzoic acid is $[Th(OH)_2(4\text{–}NH_2C_6H_4COO)_2\cdot H_2O]\cdot H_2O$. These suppositions can be verified by establishing the full crystallographic and molecular structures of the salts.

In general, it may be said that the prepared salts (with general formula $Th(OH)_2(R\text{–}C_6H_4COO)_2\cdot nH_2O$, where R = 3–OH, 4–OH, 2–NH_2 or 4–HN_2) are dehydrated to di(R-benzoato)dihydroxothorium(IV), whereas that of 2-hydroxybenzoic acid yields di(2-hydroxybenzoato)oxothorium(IV).

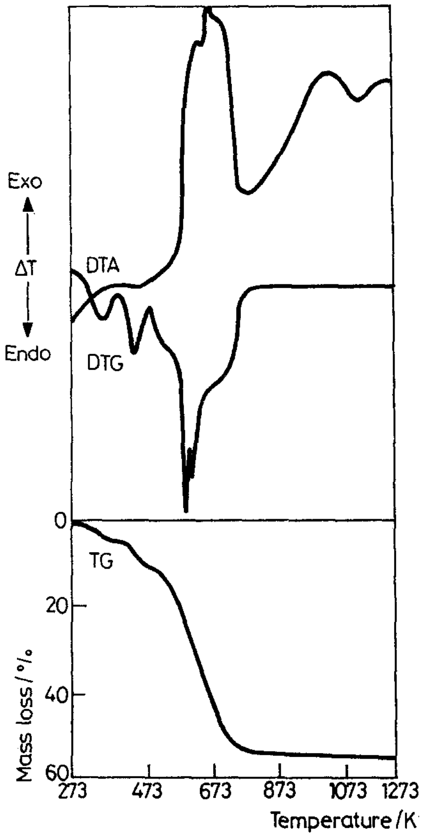

Fig. 4 Thermoanalytical curves of $Th(OH)_2(2\text{-}NH_2C_6H_4COO)_2\cdot4H_2O$

It should be stated that the intermediates in the dehydration are very unstable and their separation is probably impossible.

On heating, the dehydrated thorium(IV) salts of 2-hydroxy- and 4-hydroxybenzoic acid decompose directly to ThO_2. Di–(4-hydroxybenzoato)dihydroxothorium(IV) decomposes in two steps. In the first step, the –OH groups decompose to form H_2O, and the –OH groups on the benzene ring are eliminated to form dibenzoatooxothorium(IV). This compound decomposes directly to ThO_2.

Anhydrous di(3-aminobenzoato)dihydroxothorium(IV) decomposes directly to ThO_2 on heating.

Di(2-aminobenzoato)dihydroxothorium(IV) and di(4-aminobenzoato)dihydroxothorium(IV) decompose to ThO_2 with the intermediate formation of dibenzoatooxothorium(IV).

The results indicate the following thermal decomposition scheme.

1. R = 3–NH$_2$:

$$\mathrm{Th(OH)_2(R{-}C_6H_4COO)_2} \xrightarrow{T>873\,\mathrm{K}} \mathrm{ThO_2}$$

2. R = 3–OH:

$$\mathrm{Th(OH)_2(R{-}C_6H_4COO)_2{\cdot}3H_2O} \xrightarrow{T>453\,\mathrm{K}} \mathrm{Th(OH)_2(R{-}C_6H_4COO)_2{\cdot}H_2O}$$

$$\xrightarrow{T>548\,\mathrm{K}} \mathrm{Th(OH)_2(R{-}C_6H_4COO)_2} \xrightarrow{T>798\,\mathrm{K}} \mathrm{ThO_2}$$

3. R = 2–OH:

$$\mathrm{Th(OH)_2(R{-}C_6H_4COO)_2{\cdot}4H_2O} \xrightarrow[\text{in two steps}]{T>473\,\mathrm{K}} \mathrm{Th(OH)_2(R{-}C_6H_4COO)_2{\cdot}H_2O}$$

$$\xrightarrow{T>543\,\mathrm{K}} \mathrm{ThO(R{-}C_6H_4COO)_2} \xrightarrow{T>738\,\mathrm{K}} \mathrm{ThO_2}$$

4. R = 2–NH$_2$ or 4–NH$_2$:

$$\mathrm{Th(OH)_2(R{-}C_6H_4COO)_2{\cdot}}n\mathrm{H_2O} \xrightarrow[\text{in two steps}]{T>483\,\mathrm{K\ and\ }533\,\mathrm{K}} \mathrm{Th(OH)_2(R{-}}$$

$$\mathrm{C_6H_4COO)_2} \xrightarrow{T>603\,\mathrm{K}} \mathrm{ThO(C_6H_5COO)_2} \xrightarrow{T>733\,\mathrm{K\ and\ }863\,\mathrm{K}} \mathrm{ThO_2}$$

5. R = 4–OH:

$$\mathrm{Th(OH)_2(R{-}C_6H_5COO)_2{\cdot}4H_2O} \xrightarrow{T>453\,\mathrm{K}} \mathrm{Th(OH)_2(R{-}C_6H_4COO)_2}$$

$$\xrightarrow{T>573\,\mathrm{K}} \mathrm{ThO(C_6H_4COO)_2} \xrightarrow{T>793\,\mathrm{K}} \mathrm{ThO_2}$$

TBD for the thorium(IV) salts of the hydroxybenzoic acid increases in the sequence

$$\text{para} \le \text{ortho} < \text{meta}$$

Determination of TBD for the ortho-salt is very difficult because the third step of dehydration is connected with decomposition of the –OH group, and for this reason TBD is the temperature of oxo salt formation. This temperature can be determined exactly.

The thermal stability of the thorium(IV) dihydroxodiaminobenzoates increases in the sequence

$$\text{ortho} \le \text{para} < \text{meta}$$

The temperature of ThO_2 formation increases in the same way (Table 3). In this case in is difficult to determine TBD after dehydration without di(3-aminobenzoato)dihydroxothorium(IV).

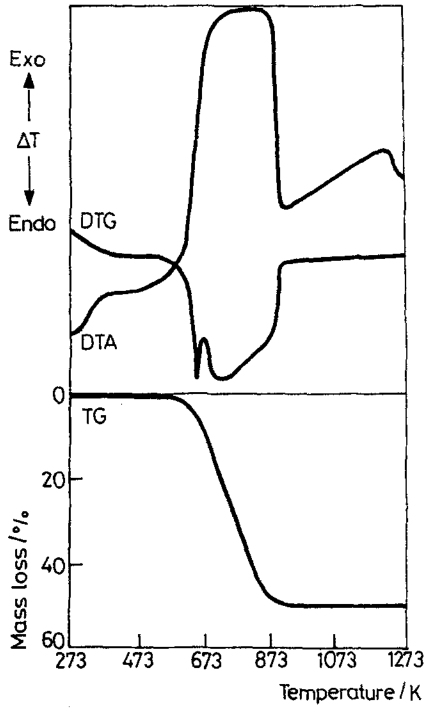

Fig. 5 Thermoanalytical curves of $Th(OH)_2(3\text{-}NH_2C_6H_4COO)_2$

The values of TBD suggest that the thermal stability of salts having on ortho-substituent is comparable to that of para-substituted salts with otherwise the same compositions. The meta-substituted salts have the highest TBD.

To explain this fact, we studied the variation in TBD and simultaneously the change in the Hammett constants of the substituent, δ, which represents the overall influence of the induced and mesomeric moments of the substituents on the electron density at the coordination centre. These data are given in Table 4. The von Bekkum constants δ^n [24], which are more authentic than the Hammett constants, are also given in Table 4.

A comparison of the thermal stabilities of the salts of general formula $Th(OH)_2(R\text{-}C_6H_4COO)_2{\cdot}nH_2O$ (where R = 4–OCH_3 [21], 3–NH_2, 4–NH_2, 3–OH or 4–OH) with TBD for unsubstituted dibenzoatodihydroxythorium(IV) monohydrate [21] suggests that the introduction onto the benzene ring of an electron donor para-substituent with strong +M and -I effects (e.g. –OCH_3, –OH or –NH_2) increases the thermal stability of the compound in comparison with the unsubstituted one.

Table 4 The influence of substituent on the thermal stability of thorium(IV) complexes with general formula $Th(OH)_2(R–C_6H_4COO)_2 \cdot nH_2O$

Substituent	Position of substituent	Value of Hammett's constant of substituent [22, 23]		Value of constant δ^n [24]		TBD /
R		δ_m	δ_p	δ_m^n	δ_p^n	K
–OH	meta (3–)	0.12		0.10		578 (603)
	para (4–)		–0.37		–0.18	523 (533)
–NH_2	meta (3–)	–0.16		–0.04		593 (618)
	para (4–)		–0.66		–0.17	533 (543)

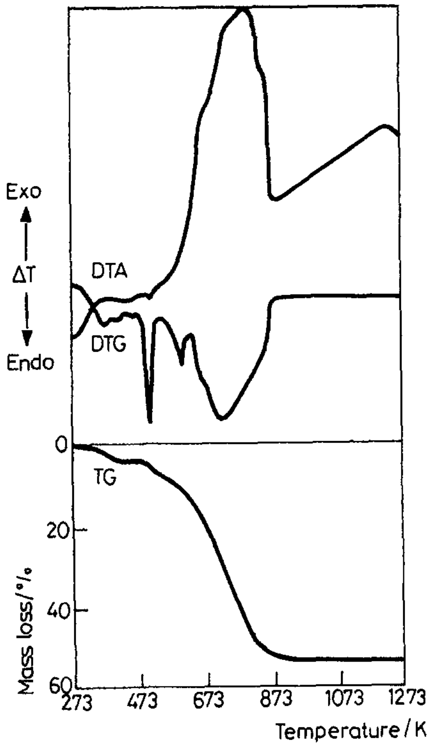

Fig. 6 Thermoanalytical curves of $Th(OH)_2(4–NH_2C_6H_4COO)_2 \cdot 2H_2O$

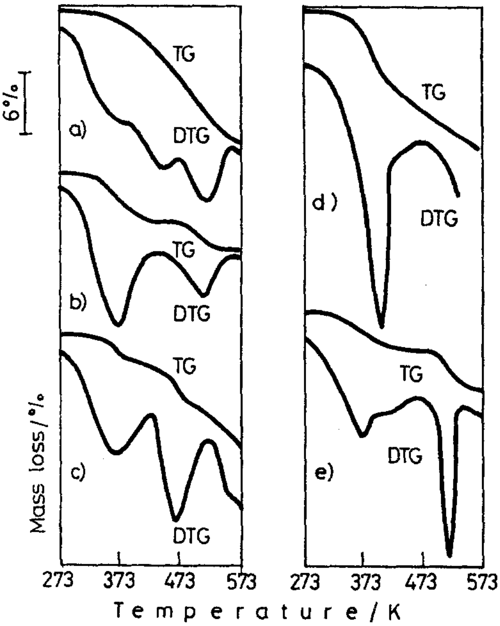

Fig. 7 TG and DTG curves of dehydration reaction of:
a) $Th(OH)_2(2\text{-}OHC_6H_4COO)_2 \cdot 4H_2O$, b) $Th(OH)_2(3\text{-}OHC_6H_4COO)_2 \cdot 3H_2O$,
c) $Th(OH)_2(2\text{-}NH_2C_6H_4COO)_2 \cdot 4H_2O$, d) $Th(OH)_2(4\text{-}OHC_6H_4COO)_2 \cdot 4H_2O$,
e) $Th(OH)_2(4\text{-}NH_2C_6H_4COO)_2 \cdot 2H_2O$

TBD for thorium(IV) salts with the general formula $Th(OH)_2(R\text{-}C_6H_4COO)_2 \cdot nH_2O$, with substituent R in the 3- or 4-position, decreases in the sequence

$$3\text{-}NH_2 > 3\text{-}OH > \text{-}H > 4\text{-}OCH_3 > 4\text{-}NH_2 \approx 4\text{-}OH$$

In the same way (without an NH_2– group in the meta-position on the benzene ring) the Hammett constants δ [22, 23] decrease as follows:

3–OH >	–H >	3–NH2 >	4–OCH3 >	4–OH >	4–NH2
0.12	0.0	–0.16	–0.27	–0.37	–0.66

while the sequence of von Bekkum constants δ^n [24] is

3–OH >	–H >	3–NH2 >	4–OCH3 >	4–NH2 ≈	4–OH
0.10	0.00	–0.04	–0.11	–0.17	–0.18

There is especially good agreement between TBD and δ^n. The numerical value of TBD increases with increasing δ or δ^n.

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Zusammenfassung — Es wurde die Thermostabilität der Thorium(IV)-salze von ortho-, meta- und para-Hydroxy- und Aminobenzoylsäure untersucht.Die Salze wurden als hydratierte Verbindungen der allgemeinen Formel $Th(OH)_2(R\text{-}C_6H_4COO)_2 \cdot nH_2O$ mit R=OH oder NH_2 und n=2,3 oder 4 gefertigt, während das Salz der 3-Aminobenzoylsäure unhydratiert war. Beim Erhitzen zeigen die Salze eine Dehydratation in zwei oder drei Stufen und anschließend werden Di(R-benzoato)dihydroxothorium(IV) oder Di(2-hydroxybenzoato)oxothorium(IV) direkt in ThO_2 umgewandelt.

Die Temperaturen für das Einsetzen der Zersetzung und der ThO_2-Bildung sinken mit abnehmenden Werten für die Hammet-Konstante und die Bakkum-Konstante