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THERMAL DECOMPOSITIONS OF SCANDIUM(III) 2,4-DINITROBENZOATE, 3,5-DINITROBENZOATE, 2,4-DICHLOROBENZOATE AND 3,4-DIAMINOBENZOATE IN AIR ATMOSPHERE

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The thermal decompositions of scandium 2,4-dinitrobenzoate, 3,5-dinitrobenzoate, 2,4-dichlorobenzoate and 3,4-diaminobenzoate were studied. On heating, the carboxylates decompose in two steps. The hydrated complexes first lose crystallization water and are transformed to Sc_2O_3. The dehydration of the complexes is accompanied by an endothermic effect and decomposition of the anhydrous or monohydrate complezes by strong exothermic effects. Scandium 2,4-dinitrobenzoate and 3,5-dinitrobenzoate decompose explosively.

Introduction

Rare earth element salts of dibenzoic acids are little known. In the literature we can find only one paper on the 2,4-dinitrobenzoates of Y, La and the lanthanides [1]. These salts were prepared as dihydrates with a metal to anion ratio of 1:3, their IR and X spectra were registered, and their thermal decompositions in air atmosphere were studied. These compounds are crystalline and slightly soluble in water (their solubilities are of the order of 10^{-2} $mole \cdot dm^{-3}$). When heated, the 2,4-dinitrobenzoates of Y, La and the lanthanides lose crystallization water and next decompose explosively. 3,5-Dinitrobenzoates, 2,4-dichlorobenzoates and 3,4-diaminobenzoates of the rare earth elements have not been reported.

Scandium(III) salts of dibenzoic acids have not been studied so far.

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The aim of our work was to obtain the 2,4-dinitrobenzoate, 3,5-dinitrobenzoate, 2,4-dichlorobenzoate and 3,4-diaminobenzoate of scandium(III) and examine their thermal decompositions in air atmosphere.

Experimental

The 3,5-dinitrobenzoate and 2,4-dichlorobenzoate of scandium were prepared in double decomposition reactions by adding an equivalent amount of ammonium 3,5-dinitrobenzoate (*pH* 4,1) or 2,4-dichlorobenzoate (*pH* 7.2) to a hot solution of scandium nitrate (*pH* 4.0).

The 2,4-dinitrobenzoate and 3,4-diaminobenzoate of scandium were prepared by adding an equivalent amount of 2,4-dinitrobenzoic acid (*pH* 1.5) or 3,4-diaminobenzoic acid (*pH* 4.0) to a hot suspension of $Sc(OH)_3$.

The precipitates formed were heated in the mother liquor for 1 h, then filtered off, washed with water and dried at 30 °C to constant weight.

The carbon, hydrogen and nitrogen contents of the resulting salts were determined by elemental analysis, using V_2O_5 as oxidizing agent. The chlorine content was determined by the Schöniger method. The content of scandium was determined by ignition of the salts to Sc_2O_3 at 900°C and from the TG curves. The content of water was determined from the TG curves. The elemental analysis data are given in Table 1.

The data obtained indicated that the prepared scandium 2,4-dinitrobenzoate was a hemihydrated basic salt with a metal to anion ratio of 1:2, the 3,5-dinitrobenzoate was a hemihydrated basic salt with a metal to anion ratio of 1:1, the 2,4-dichlorobenzoate was a tetrahydrated oxo salt with a metal to anion ratio of 5:3, and the 3,4-diaminobenzoate was a tetrahydrated oxo salt with a metal to anion ratio of 2:3.

The IR spectra of the prepared salts were registered over the range 4000–400 cm^{-1}. Analysis of the spectra confirmed the elemental analysis results. The 3,5-dinitrobenzoate and 2,4-dichlorobenzoate of scandium are white solids, the 2,4-dinitrobenzoate of scandium is a cream solid and the 3,4-diaminobenzoate of scandium is a brown solid. With the exception of scandium 2,4-dichlorobenzoate, the prepared salts are cystalline and sparingly soluble in water.

The thermal stabilities of the prepared salts were studied. The TG, DTG and DTA curves were registered. The measurements were made on an OD-102 derivatograph at a heating rate of 9 deg·min^{-1} and sensitivities TG - 100 mg, DTA - 1/10, DTG - 1/5. The samples were heated in air atmosphere

Table 1 Analytical data

Scandium(III) complexes Name	Formula	% Sc Calc.	% Sc Found	% C Calc.	% C Found	% H Calc.	% H Found	% N Calc.	% N Found	% Cl Calc.	% Cl Found
2,4-dinitrobenzoate	$Sc[(NO_2)_2C_6H_3COO]_2OH\cdot 0.5H_2O$	9.12	9.37	34.09	35.44	1.64	1.88	11.36	11.38	–	–
3,5-dinitrobenzoate	$Sc[(NO_2)_2C_6H_3COO](OH)_2\cdot 0.5H_2O$	15.03	15.90	28.11	28.94	2.02	2.15	9.36	9.35	–	–
2,4-dichlorobenzoate	$Sc_5O_6[Cl_2C_6H_3COO]_3\cdot 4H_2O$	23.35	23.60	26.19	26.53	1.78	1.95	–	–	22.09	21.97
3,4-diaminobenzoate	$Sc_4O_3[(NH_2)_2C_6H_3COO]_6\cdot 4H_2O$	14.90	14.60	41.80	42.56	4.18	4.61	13.93	14.16	–	–

Table 2 Temperature data of dehydration of scandium 2,4-dinitrobenzoate, 3,5-dinitrobenzoate, 2,4-dichlorobenzoate and 3,4-diaminobenzoate in air atmosphere

Complexes		Temp. range of dehydration reaction / °C	Peak temperature of DTG / °C	Effects exo / °C	Effects endo / °C	Loss of weight / % Calc.	Loss of weight / % Found	Lossof H_2O molecules *n*
$Sc[(NO_2)_2C_6H_3COO]_2OH\cdot 0.5H_2O$	(2.1)	50 – 210	70	80	(–)	1.83	1.75	0.5
$Sc[(NO_2)_2C_6H_3COO](OH)_2\cdot 0.5H_2O$	(3.5)	40 – 240	70	65	(–)	3.01	3.00	0.5
$Sc_5O_6[Cl_2C_6H_3COO]_3\cdot 4H_2O$	(2.4)	45 – 325	80	90	(–)	5.60	5.50	3
$Sc_4O_3[(NH_2)_2C_6H_3COO]_6\cdot 4H_2O$	(3.4)	50 – 175	95	60	115	4.48	4.50	3

(–) The exothermic effect connected with the polymorphic transformation is so strong that the endothermic effects of dehydration are not observed

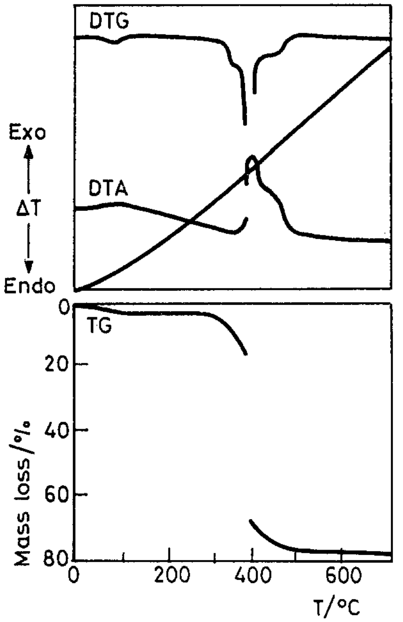

Fig. 1 TG, DTG and DTA curves of Sc(III) 2,4-dinitrobenzoate

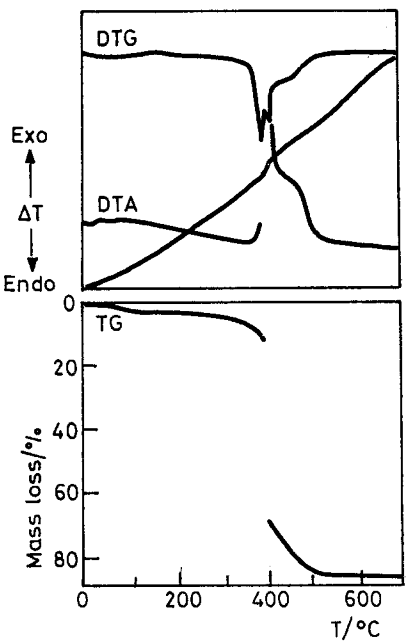

Fig. 2 TG, DTG and DTA curves of Sc(III) 3,5-dinitrobenzoate

in ceramic crucibles. Alumina was used as reference material. The obtained results are given in Figs 1–4 and Tables 2 and 3.

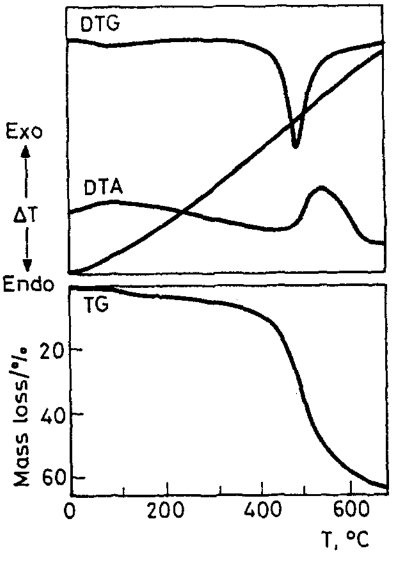

Fig. 3 TG, DTG and DTA curves of Sc(III) 2,4-dichlorobenzoate

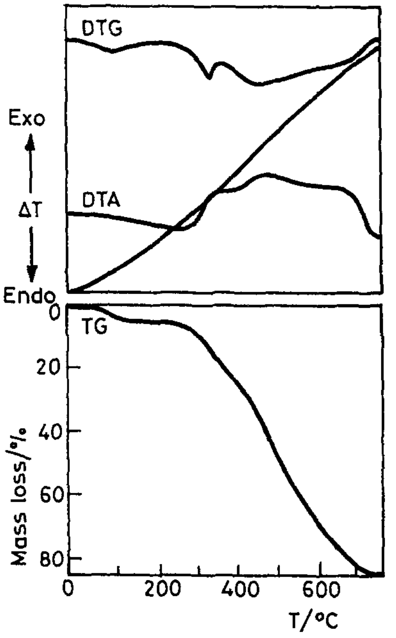

Fig. 4 TG, DTG and DTA curves of Sc(III) 3,4-diaminobenzoate

Table 3 Temperature data of decomposition of scandium 2,4-dinitrobenzoate, 3,5-dinitrobenzoate, 2,4-dichlorobenzoate and 3,4-diaminobenzoate in air atmosphere

Complexes		Temperature range of dehydration / °C	Temperature range of decomposition / °C	Temp. of explosion / °C	Peak temp. of DTG / °C	Loss of weight / % Calc.	Loss of weight / % Found	Exothermic effect / °C
$Sc[(NO_2)_2C_6H_3COO]_2OH\cdot 0.5H_2O$	(2.4)	50 – 210	210 – 480	380	350 (x)	86.02	(85.63)	(x) 405
$Sc[(NO_2)_2C_6H_3COO](OH)_2\cdot 0.5H_2O$	(3.5)	40 – 240	240 – 500	395	(x)	76.94	(75.97)	(x)
$Sc_5O_6[Cl_2C_6H_3COO]_3\cdot 4H_2O$	(2.4)	45 – 325	325 – 695	–	490	64.19	63.76	540
$Sc_4O_3[(NH_2)_2C_6H_3COO]_6\cdot 4H_2O$	(3.4)	50 – 175	175 – 695	–	320 450	77.14	77.60	345 465

( ) Loss of weight was calculated on the basis of results obtained by slowly ignition of complexes on the burner and next in the furnace at 900°C

(x) The peaks on DTG and DTA curves are not observed, because the complexes are explosive

When heated in air atmosphere, the studied carboxylates of scandium decomposed in two steps. In the first step they were dehydrated endothermically in the temperature range 40°–325°C, yielding anhydrous salts (with the exceptions of scandium 2,4-dichlorobenzoate and 3,4-diaminobenzoate, which formed monohydrates). This was followed by ignition of the organic anions, to the acompaniment of exothermic effects. Sc_2O_3, formed at 480°–695°C, was the final product of decomposition.

The low temperatures of dehydration of scandium 2,4-dinitrobenzoate and 3,5-dinitrobenzoate suggest that the crystallization water is probably outer sphere water, and that the molecules of these complexes exist as the dimers $Sc[(NO_2)_2C_6H_3COO]_2OH\}_2 \cdot H_2O$ and $\{Sc[(NO_2)_2C_6H_3COO](OH)_2\}_2 \cdot H_2O$, respectively.

Scandium 2,4-dichlorobenzoate begins to lose crystallization water at low temperature and the loss is completed only at high temperature. In the first step, the salt loses 2 molecules of crystallization water up to 150°C (over the temperature range 45°–100°C it loses the first water molecule), and in the second step the dihydrate is transformed to the monohydrate at 325°C. The results indicate that the crystallization water molecules are bonded in various ways. The water lost at lower temperature is probably outer sphere water, and the remaining 2 water molecules are inner sphere water. These results suggest that scandium 2,4-dichlorobenzoate exists as $[Sc_5O_6(Cl_2C_6H_3COO)_3 \cdot 2H_2O] \cdot 2H_2O$.

Scandium 3,4-diaminobenzoate loses 3 molecules of crystallization water over the temperature range 50°–175°C (the first 2 molecules of water are lost up to 100°C), to yield the monohydrate. Three molecules of water are probably outer sphere water, while the last water molecule, which is lost during decomposition, is inner sphere water. These results suggest that scandium 3,4-diaminobenzoate exists as $\{Sc_4O_3[(NH_2)_2C_6H_3COO]_6 \cdot H_2O\} \cdot 3H_2O$.

Examination of the IR spectra and elemental analyses of the salts ignited at suitable temperatures confirm the compositions of the hydrated salts.

The DTA curves of the studied scandium dibenzoates reveal an exothermic effect in the temperature range 30°–180°C. The thermal data on scandium benzoate [2] indicate that a polymorphic transformation takes place in this temperature range. For scandium 2,4-dinitrobenzoate, 3,5-dinitrobenzoate, 2,4-dichlorobenzoate and 3,4-diaminobenzoate (first step of dehydration), the exothermic effect connected with the polymorphic transformation is so strong that the endothermic effect of dehydration is not observed.

The second step of decomposition of anhydrous scandium 2,4-dinitrobenzoate and 3,5-dinitrobenzoate and monohydrated 2,4-dichlorobenzoate and 3,4-diaminobenzoate is associated with exothermic effects. Scandium 2,4-dinitrobenzoate (380°C) and scandium 3,5-dinitrobenzoate (395°C) decompose explosively.

References

1 W. Ferenc, Monatsch. Chem., in press.
2 W. Brzyska, R. Kurpiel-Gorgol and M. Dabkowska, J. Thermal Anal., 29 (1984) 1299.

Zusammenfassung — Es wurde die thermische Zersetzung von Skandium-2,4-dinitrobenzoat, 3,5-dinitrobenzoat, 2,4-dichlorbenzoat und 3,4-diaminobenzoat untersucht. Beim Erhitzen zersetzen sich die Carboxylate in zwei Schritten. Zuerst verlieren die hydratierten Komplexe Kristallwasser und werden dann zu Sc_2O_3 umgebildet. Die Dehydratation der Komplexe wird von einem endothermen Effekt begleitet, die Zersetzung von unhydrierten oder Monohydratkomplexen von einem starken exothermen Effekt. Skandium-2,4-dinitrobenzoat und 3,5-dinitrobenzoat zersetzen sich explosiv.