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Short Communication

THERMAL DECOMPOSITIONS OF SCANDIUM(III) M-NITROBENZOATE, M-CHLOROBENZOATE, M-HYDROXYBENZOATE AND M-AMINOBENZOATE IN AIR ATMOSPHERE

W. Brzyska and *R. Kurpiel-Gorgol*

DEPARTMENT OF INORGANIC AND GENERAL CHEMISTRY, INSTITUTE
OF CHEMISTRY, MARIE CURIE-SKŁODOWSKA UNIVERSITY,
20–031 LUBLIN, POLAND

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The conditions of thermal decomposition of scandium(III) m-nitrobenzoate, m-chlorobenzoate, m-hydroxybenzoate and m-aminobenzoate were studied. On heating, most of these carboxylates decompose in two steps; only scandium(III) 3-aminobenzoate decomposes in one step. The hydrated complexes first lose crystallization water and are then transformed to Sc_2O_3. The hydration of the complexes is accompanied by an endothermic effect, and the decomposition of the anhydrous complexes by a strong exothermic effect. Scandium(III) 3-nitrobenzoate decomposes explosively.

Rare earth element complexes with m-benzoic acids are little known. m-Hydroxybenzoates of Y, La and lanthanides have been prepared as hydrated salts with a metal to ligand ratio of 1 : 3 [1–4], their IR and X-ray spectra have been recorded and their thermal decompositions in air and nitrogen atmospheres have been studied. Pirkes et al. [5] isolated La, Ce(III), Pr(III), Nd and Sm(III) m-nitrobenzoates with general formula $Ln(NO_2C_6H_4COO)_3 \cdot 2H_2O$. During heating to 300°, these complexes are decomposed. m-Chlorobenzoates and m-aminobenzoates of rare earth elements have not been prepared.

Scandium(III) complexes with m-benzoic acids have not been studied so far.

The aim of our work was to obtain the m-nitrobenzoate, m-chlorobenzoate, m-hydroxybenzoate and m-aminobenzoate of scandium(III) and to examine their thermal decompositions in air atmosphere.

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Experimental

The m-nitrobenzoate and m-chlorobenzoate of scandium(III) were prepared in double decomposition reactions, by adding equivalent amounts of ammonium m-nitrobenzoate (pH 4.7) or m-chlorobenzoate (pH 6.6) to a hot solution of scandium(III) nitrate (pH 4.0). The precipitates formed were heated in the mather liquor for 1 h, filtered off, washed with water to remove NH_4^+ ions and dried at 30° to constant weight.

The m-hydroxybenzoate of scandium(III) was prepared by dissolving freshly precipitated $Sc(OH)_3$ in the equivalent amount of hot m-hydroxybenzoic acid solution. The resulting solution was evaporated on a water bath to reduce the volume to one-quarter, and the product was crystallized. The solid formed was filtered off, washed with water and dried at 30° to constant weight.

The m-aminobenzoate of scandium(III) was prepared by adding a triple excess of m-aminobenzoic acid solution (pH 3.8) to a hot solution of $Sc(NO_3)_3$ (pH 3.7) and crystallizing on a water bath. The solid formed was filtered off, washed with ethanol and dried at 30° to constant weight.

The contents of carbon, hydrogen and nitrogen were determined by elemental analysis, using V_2O_5 as oxidizing agent. The content of chlorine was determined by the Schöniger method. The contents of scandium(III) were determined by ignition of the products to Sc_2O_3 at 900°. The elemental analysis data are given in Table 1.

The data obtained indicated that the scandium(III) m-nitrobenzoate prepared was the hemihydrated salt with a metal to ligand ratio of 1 : 3; the m-chlorobenzoate was the monohydrated basic salt with a metal to ligand ratio of 1 : 1; the m-hydroxybenzoate was the trihydrated salt with a metal to ligand ratio of 1 : 2; and the m-aminobenzoate was the anhydrous salt with a metal to ligand ratio of 1 : 3.

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

The studied complexes of scandium(III) are white solids, with the exception of scandium(III) m-aminobenzoate, which is brown; the complexes are crystalline, sparingly soluble in water.

The thermal stabilities of the prepared complexes were studied. The TG, DTG and DTA curves were recorded. The measurements were made on an OD–102 derivatograph at a heating rate of 9 deg/min, at a TG sensitiviuy of 100 mg. The samples were heated in air atmosphere in ceramic crucibles. Alumina was used as reference material. The results obtained are presented in Figs 1–4 and Tables 2 and 3.

During heating, the prepared scandium(III) carboxylates decompose in two steps, with the exception of scandium(III) m-aminobenzoate, which decomposes in

Table 1 Analytical data

Scandium(III) Complexes		Sc, %		C, %		H, %		N, %		Cl, %	
name	formula	calcd.	found	calcd.	found	calcd.	found	calcd.	found	calcd.	found
m-nitrobenzoate	$Sc(NO_2C_6H_4COO)_3 \cdot 0.5H_2O$	8.14	9.20	45.67	45.76	2.37	2.54	7.61	7.57	—	—
m-chlorobenzoate	$Sc_2O(ClC_6H_4COO)_2(OH)_2 \cdot H_2O$	19.17	19.48	35.85	35.39	2.58	2.51	—	—	15.12	14.47
m-hydroxybenzoate	$Sc_2O(OHC_6H_4COO)_4 \cdot 3H_2O$	12.69	12.39	47.47	47.40	3.70	3.69	—	—	—	—
m-aminobenzoate	$Sc(NH_2C_6H_4COO)_3$	9.92	9.94	55.64	55.26	4.00	4.17	9.27	9.11	—	—

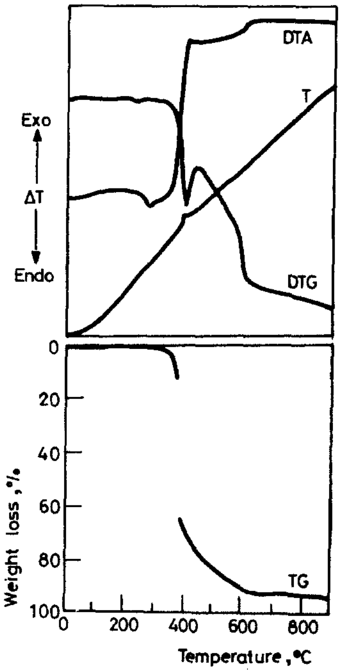

Fig. 1 TG, DTG and DTA curves of Sc(III) m-nitrobenzoate

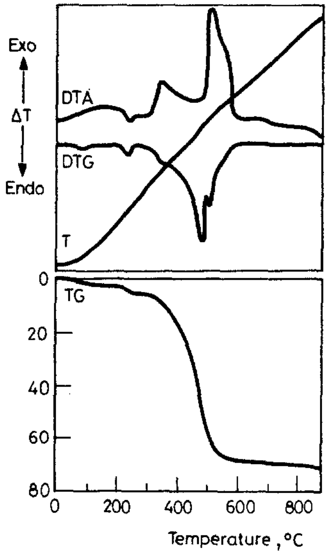

Fig. 2 TG, DTG and DTA curves of Sc(III) m-chlorobenzoate

Table 2 Temperature data of dehydration of scandium(III) m-nitrobenzoate, m-chlorobenzoate, m-hydroxybenzoate and m-aminobenzoate in air atmosphere

Complexes	Temperature	Peak	Effects		Melting point, °C	Loss of weight, %		Loss of H_2O molecules, *n*
	range of dehydration °C	temperature of DTG, °C	exothermic, °C	endothermic, °C		calcd.	found	
$Sc(NO_2C_6H_4COO)_3 \cdot 0.5H_2O$	240–320	—	150	290	—	1.63	1.5	0.5
$Sc_2O(ClC_6H_4COO)_2(OH)_2 \cdot H_2O$	40–280	255	140	265	—	3.84	4.0	1
$Sc_2O(OHC_6H_4COO)_4 \cdot 3H_2O$	30–220	195	90	200	—	7.63	8.0	3
$Sc(NH_2C_6H_4COO)_3$	—	—	150	—	300	—	—	—

Table 3 Temperature data of decomposition of scandium(III) m-nitrobenzoate, m-chlorobenzoate, m-hydoxybenzoate and m-aminobenzoate in air atmosphere

Complexes	Temperature range of		Temperature of explosion, °C	Peak temperature of DTG, °C	Loss of weight, %		Exothermic effect, °C	T_k, °C
	dehydration, °C	decomposition, °C			calcd.	found		
$Sc(NO_2C_6H_4COO)_3 \cdot 0.5H_2O$	240–320	320–630	430	(×)	87.51	(86.0)	(×)	630
$Sc_2O(ClC_6H_4COO)_2(OH)_2 \cdot H_2O$	40–280	280–630	—	400	70.60	70.0	405	630
				535			590	
				545				
				580				
				450				
$Sc_2O(OHC_6H_4COO)_4 \cdot 3H_2O$	30–220	220–770	—	510	80.53	81.0	470	770
				380			405	
$Sc(NH_2C_6H_4COO)_3$	—	320–810	—	420	84.79	84.0	500	810
				490				

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

(×) The peaks on DTG and DTA curves are not observed, because the complex is explosive.

one step. First, the hydrated complexes are dehydrated endothermically in the temperature range 40–320°, yielding anhydrous salts. This is followed by ignition of the organic anions, to the accompaniment of exothermic effects. Sc_2O_3, which is formed at 630–810°, is the final product of decomposition.

The high temperature of dehydration (40–320°) of scandium(III) m-nitrobenzoate suggests that the crystallization water is probably inner sphere water, and that this complex exists as a dimer with the formula $[Sc_2(NO_2C_6H_4COO)_6 \cdot H_2O]$.

The low temperature of dehydration of scandium(III) m-hydroxybenzoate indicates that the crystallization water is outer sphere water.

Scandium(III) m-chlorobenzoate is dehydrated in two steps. In the first step, the complex loses 0.5 molecule of crystallization water up to 220°, and in the second step the hemihydrate is transformed to the anhydrous salt at 280°. The results obtained indicate that the crystallization water molecules are bound in various ways. The water lost at lower temperature is probably outer sphere water, while that lost at higher temperature is inner sphere water. These results suggest that scandium(III) m-chlorobenzoate exists as a dimer $[Sc_4O_2(ClC_6H_4COO)_4(OH)_4 \cdot H_2O] \cdot H_2O$. When heated to 390°, the anhydrous basic m-chlorobenzoate of scandium(III) loses two water molecules from the hydroxy groups and is transformed to $Sc_4O_4(ClC_6H_4COO)_4$, which decomposes to Sc_2O_3.

In the DTA curves of the studied scandium(III) m-benzoates there is an exothermic effect at 40–240°. The thermal data on scandium(III) benzoate [6] show that a polymorphic transformation occurs at this temperature.

For scandium(III) m-chlorobenzoate the exothermic effect connected with the polymorphic transformation is so strong that the endothermic effect of the first step of dehydration is not observed.

When scandium(III) m-aminobenzoate is heated at 40–270°, a polymorphic transformation occurs and at 300° the complex melts. Next, at 320–810° the organic ligand undergoes ignition to the accompaniment of an exothermic effect.

The second step of decomposition of the anhydrous scandium(III) m-benzoates is connected with an exothermic effect. Scandium(III) m-nitrobenzoate decomposes explosively at 430°. The m-nitrobenzoates of light lanthanides [5] decompose at temperatures below 300°. Their decomposition reactions are explosive, too.

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