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THERMAL DECOMPOSITION OF SCANDIUM(III) o-NITROBENZOATE, o-CHLOROBENZOATE, o-METHYLBENZOATE, o-HYDROXYBENZOATE AND o-AMINOBENZOATE IN AIR ATMOSPHERE

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The conditions of thermal decomposition of scandium o-nitrobenzoate, o-chlorobenzoate, o-methylbenzoate, o-hydroxybenzoate and o-aminobenzoate were studied. On heating, the carboxylates decompose in two steps, only scandium anthranilate decomposes in one step. The hydrated complexes first lose water of crystallization and then are transformed to Sc_2O_3. The dehydration of the complexes is an endothermic process and the decomposition of anhydrous complexes is strongly exothermic. Scandium o-nitrobenzoate decomposes explosively.

Scandium(III) complexes with o-benzoic acids are little known. Crookes [1] has obtained basic scandium(III) o-methylbenzoate $(CH_3C_6H_4COO)_2Sc(OH)\cdot 3H_2O$ in the reaction of ammonium o-methylbenzoate and scandium(III) nitrate solutions. This compound loses water of crystallization at 150°. Crookes has prepared also scandium(III) o-methylbenzoate $2(CH_3C_6H_4COO)ScO\cdot Sc(OH)_3$ by adding o-methylbenzoic acid to a suspension of scandium(III) hydroxide. The prepared complex is sparingly soluble in water and ethanol, and soluble in dilute acids.

Prozorovskaya et al. [2, 3] have prepared scandium(III) salycilate $Sc_2(OHC_6H_4COO)_5OH\cdot H_2O$, recorded its IR spectra, studied the thermal decomposition and determined its density and solubility in water.

Scandium(III) anthranilate was prepared as an anhydrous neutral salt $Sc(NH_2C_6H_4COO)_3$ [2, 4, 5] and its IR spectra and thermal decomposition were recorded.

The compounds of scandium(III) with o-nitro- and o-chlorobenzoic acids are unknown.

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The aim of our work was to obtain o-nitrobenzoate, o-chlorobenzoate, o-methylbenzoate (o-toluate), o-hydroxybenzoate (salicylate), and o-aminobenzoate (anthranilate) of scandium(III) and study their thermal decomposition in air.

Experimental

The o-nitro-, o-chloro-, o-methyl-, o-hydroxy- and o-aminobenzoate of scandium(III) were prepared in double decomposition reaction by adding equivalent amounts of 0.1 *M* solutions of ammonium o-nitrobenzoate (*pH* 3.5), o-chlorobenzoate (*pH* 4.5), o-toluate (*pH* 5.1), salicylate (*pH* 4.8) or anthranilic acid (*pH* 3.6) to a hot solution containing $Sc(NO_3)_3$ (*pH* 4.0). The precipitates formed were heated in the mother liquor for 1 h, filtered off, washed with water to remove NH_4^+ ions and dried at 30° to constant weight.

The carbon, hydrogen and nitrogen content of the prepared complexes was determined by elemental analysis using V_2O_5 as an oxidizing agent. The chlorine content was determined by the Schöniger method. The scandium(III) content was determined from the TG curves by converting the complexes to Sc_2O_3 at 900°. The water content was determined from the TG curves. The elemental analysis data are given in Table 1.

The obtained data indicate that the scandium(III) o-nitrobenzoate is a hemihydrated oxosalt with a metal to ligand ratio of 1:2, o-chloro- and o-methylbenzoate are hemihydrated salts with a metal to ligand ratio of 1:3, salicylate of scandium 3,5 hydrated salt with a metal to ligand ratio of 2:5 and anthranilate is an anhydrous salt with a metal to ligand ratio of 1:3.

The IR spectra recorded for prepared complexes over the range 4000–400 cm^{-1} confirmed the elemental analysis results. The prepared scandium o-benzoates are white solids, with the exception of scandium(III) o-nitrobenzoate which is cream coloured and o-aminobenzoate, which is brown coloured. The complexes are crystalline solids, sparingly soluble in water.

The thermal stability of the prepared complexes was studied. The TG, DTG and DTA curves were recorded. The measurements were made on a derivatograph at a heating rate of 9 deg · min^{-1} and sensitivity TG–100 mg. The samples were heated in air atmosphere in ceramic crucibles. The obtained results are given in Tables 2 and 3, and typical curves are illustrated in Fig. 1.

The studied scandium o-benzoates (with the exception of scandium o-aminobenzoate) on heating in air decompose in two steps. In the first step they are dehydrated endothermically in the temperature range 40–350°, yielding anhydrous salts. This is followed by ignition of organic anions, what is connected with exothermic effects. Sc_2O_3, which is formed at 480–690° is the final product of decomposition.

Table 1 Analytical data

Scandium(III) complexes		Sc, %		C, %		H, %		N, %		Cl, %	
name	formula	calcd.	found.	calcd.	found.	calcd.	found.	calcd.	found.	calcd.	found.
o-nitrobenzoate	$Sc_2O(NO_2C_6H_4COO)_4 \cdot 0.5H_2O$	11.54	10.87	43.15	42.79	2.20	2.44	7.19	7.12	—	—
o-chlorobenzoate	$Sc(ClC_6H_4COO)_3 \cdot 0.5H_2O$	8.64	8.80	48.44	48.53	2.52	2.56	—	—	20.43	19.52
o-methylbenzoate	$Sc(CH_3C_6H_4COO)_3 \cdot 0.5H_2O$	9.79	9.78	62.75	62.67	4.83	4.68	—	—	—	—
o-hydroxybenzoate	$Sc_2(OH)(OHC_6H_4COO)_5 \cdot 3.5H_2O$	10.51	10.43	49.14	49.09	3.89	4.14	—	—	—	—
o-aminobenzoate	$Sc(NH_2C_6H_4COO)_3$	9.92	9.98	55.64	55.86	4.00	4.14	9.27	9.42	—	—

Table 2 Temperature of dehydration of scandium o-nitrobenzoate, o-chlorobenzoate, o- methylbenzoate, o-hydroxybenzoate and o-aminobenzoate in air atmosphere

Complexes	Temperature range of dehydration reaction, °C	Peak temperature of DTG, °C	Effects		Melting point, °C	Loss of weight, %		Loss of H_2O molecules, n
			exothermic, °C	endothermic, °C		calcd.	found.	
$Sc_2O(NO_2C_6H_4COO)_4 \cdot 0.5H_2O$	210–310	—	80	290	—	1.15	1.00	0.5
$Sc(ClC_6H_4COO)_3 \cdot 0.5H_2O$	240–350	275	80	280	—	1.73	1.50	0.5
$Sc(CH_3C_6H_4COO)_3 \cdot 0.5H_2O$	230–280	260	120	265	—	1.96	2.00	0.5
		75		80				
$Sc_2(OH)(OHC_6H_4COO)_5 \cdot 3.5H_2O$	40–220	140	(—)	150	—	7.37	7.50	3.5
		200		210				
$Sc(NH_2C_6H_4COO)_3$	—	—	90	—	340	—	—	—

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

Table 3 Temperature data of decomposition of scandium o-nitrobenzoate, o-chlorobenzoate, o-methylbenzoate, o-hydroxybenzoate and o-aminobenzoate in air atmosphere

Complexes	Temperature range		Temperature of explosion, °C	Peak temperatures of DTG, °C	Loss of weight, %		Exothermic effect, °C	T_k, °C
	of dehydration, °C	of decomposition, °C			calcd.	found.		
$Sc_2O(NO_2C_6H_4COO)_4 \cdot 0.5H_2O$	210–310	310–480	370	(×)	82.05	(83.32)	(×)	480
$Sc(ClC_6H_4COO)_3 \cdot 0.5H_2O$	240–350	350–630	—	520	86.76	86.50	560 605	630
$Sc(CH_3C_6H_4COO)_3 \cdot 0.5H_2O$	230–280	280–625	—	450 [280]	84.99	85.00	420 560	625
$Sc_2(OH)(OHC_6H_4COO)_5 \cdot 3.5H_2O$	40–220	220–560	—	380	83.88	84.00	435 350 460	560
$Sc(NH_2C_6H_4COO)_3$	—	310–690	—	355 430	84.79	85.00	495 580	690

( ) 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

[ ] The decomposition proceeds with accompaniment of endothermic effect (290 °C)

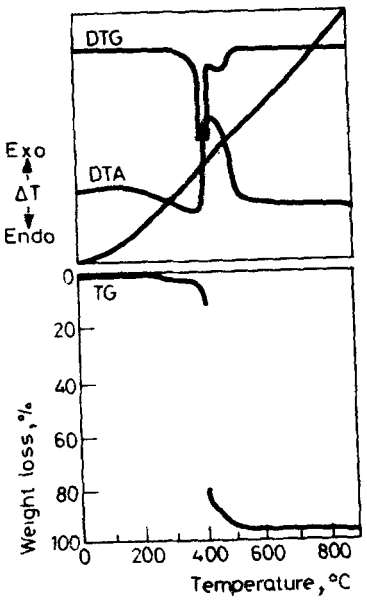

Fig. 1 TG, DTG and DTA curves of Sc(III) o-nitrobenzoate

The high temperatures of dehydration of scandium(III) o-nitrobenzoate (210–310°), o-chlorobenzoate (240–350°) and o-methylbenzoate (230–280°) suggest that the water of crystallization is inner sphere water and molecules of these complexes exist as dimers with formula: $[Sc_4O_2(NO_2C_6H_4COO)_8 \cdot H_2O]$, $[Sc_2(ClC_6H_4COO)_6 \cdot H_2O]$ and $[Sc_2(CH_3C_6H_4COO)_6 \cdot H_2O]$, respectively.

Scandium(III) o-hydroxybenzoate begins to lose water of crystallization at low temperature and the lost water molecules are lost at high temperature. In the temperature range of 40–160° it loses two molecules, the remaining water molecules are lost at 220° and the anhydrous salt is formed. These results indicate that water molecules are bound in different ways. Probably the water of crystallization lost at low temperature is outer sphere water whereas the one lost at high temperature is coordinated in the inner sphere. These results suggest that scandium(III) o-hydroxybenzoate exists as a dimer $[Sc_4(OH)_2(OHC_6H_4COO)_{10} \cdot 3H_2O]H_2O$.

The anhydrous scandium(III) o-hydroxybenzoate heated to 325° is transformed endothermally to $Sc_4O_3(OHC_6H_4COO)_6$, which has probably a chain structure. The composition of this complex is confirmed by elemental analysis and IR spectra

	Sc, %	C, %	H, %
$Sc_4O_3(OHC_6H_4COO)_6$	17.19	48.02	2.88
complex obtained at 325 °C	17.32	48.10	3.12

In the IR spectrum of the complex heated at 325° the positions of absorption bands of asymmetrical and symmetrical vibrations of the COO^- and the OH groups do not change in the comparison with the spectrum of scandium(III) o-hydroxybenzoate. The bands characteristic for basic salt (3570 cm^{-1}) and hydrated salt (3430 and 1640 cm^{-1}) disappear and the band of the Sc–O–Sc bond appears at 600 cm^{-1} [6].

Shestakova et al. [3], on heating scandium(III) o-hydroxybenzoate monohydrate $Sc_2(OH)(OHC_6H_4COO)_3 \cdot H_2O$, obtained at 300° a complex with the formula: $Sc_2O(OHC_6H_4COO)_4$. The intermediate product $Sc_4O_3(OHC_6H_4COO)_6$ obtained by us during heating o-hydroxybenzoate at 325° arises probably as a condensation product of the complex prepared previously [3]. This confirms the suggestion that scandium(III) o-hydroxybenzoate described in our work exists as a dimer.

On the DTA curves of studied scandium(III) o-benzoates in the temperature range 30–210°, an exothermic effect is observed. From the thermal data of scandium(III) benzoate [7] it can be concluded that in this temperaure range polymorphic transformation takes place.

For scandium(III) o-hydroxybenzoate the exothermic effect connected with the polymorphic transformation is particle masked by the strong endothermic effect of the first step of dehydration.

Anhydrous scandium(III) o-aminobenzoate heated at 30–180° undergoes a polymorphic change, at 340° it melts and in the temperature range 310–690° the organic ligand is ignited accompanied by exothermic effect.

Anhydrous scandium(III) benzoates decompose exothermically and scandium(III) o-nitrobenzoate explosively (370°).

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Zusammenfassung — Die Umstände der thermischen Zersetzung des o-Nitrobenzoates, des o-Chlorobenzoates, des o-Methylbenzoates, des o-Hydroxybenzoates und des o-Aminobenzoates von Scandium wurden untersucht. Mit Ausnahme des Scandium-anthranilates, das in einem Schritt zerfällt, zersetzen sich die Karboxylate beim Erhitzen in zwei Schritten. Die hydrierten Komplexe geben zuerst Kristallwasser ab und formen dann Sc_2O_3. Die Dehydrierung der Komplexe ist ein endothermer Prozess, während die Zersetzung der anhydrierten Komplexe stark exotherm abläuft. Scandium-o-nitrobenzoat zersetzt sich explosionsartig.

Резюме — Изучены условия термического разложения о-нитро-, о-хлоро-, о-метил-, о-окси- и о-аминобензоатов скандия. При нагревании все бензоаты разлагаются в две стадии, за исключением антранилата скандия, разлагающегося в одну стадию. Гидраты сначала теряют кристаллическую воду, а затем превращаются до оксида скандия. Процесс дегидратации является эндотермическим, а разложение безводных солей — сильно эксотермическим процессом. Орто-нитробензоат скандия разлагается со взрывом.