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THERMAL DECOMPOSITION OF SCANDIUM(III) BENZENE-TRICARBOXYLATES IN AIR AND NITROGEN ATMOSPHERES

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The conditions of thermal decomposition of scandium(III) hemimellitate, trimellitate and trimezinate in air and nitrogen atmospheres have been studied. On heating, the benzenetricarboxylates of Sc(III) decompose in two stages. First, the hydrated complexes lose crystallization water; heating in air finally yields Sc_2O_3, and heating in a nitrogen atmosphere Sc_2O_3 and C. The dehydration of the complexes is associated with strong endothermic effects. The decomposition of benzenetricarboxylates in air is accompanied by an exothermic effect and in nitrogen by an endothermic effect.

The activation energies of the dehydration and decomposition reactions have been calculated for the Sc(III) benzenetricarboxylates.

The salts of benzenetricarboxylic acids are little known. In recent years hemimellitates [1], trimellitates [2] and trimezinates [3] of Y, La and lanthanides were obtained as hydrated salts, and their isothermal dehydration was studied. Kasalova and Petru [4] prepared the trimezinate of Sc as the dihydrate, and those of Y and La as the hexahydrates, and studied their thermal decompositions. Sc(III) trimezinate [4] is dehydrated at 190–270°. Decomposition of the complex begins at 620°. A search of the available literature show that the hemimellitate and trimellitate of Sc(III) have not been studied so far. As a continuation of our work on the thermal decomposition of scandium(III) carboxylates [5–7], we now report the thermal decomposition of scandium(III) benzenetricarboxylates in air and nitrogen atmospheres.

Experimental

Scandium(III) benzenetricarboxylates were prepared in double decomposition reactions by adding ammonium hemimellitate (pH 5.8), trimellitate (pH 4.6) or trimezinate (pH 5.6) to a hot solution containing Sc(III) nitrate (0.1 M). The precipitate formed was heated in the mother liquor for 1 h, then filtered off, washed with water to remove NH_4^+ ions and dried at 30° to constant mass.

The content of carbon and hydrogen were determined by elementary analysis, using V_2O_5 as oxidizing agent. The content of scandium was determined by ignition of the products to Sc_2O_3 at 900°. The analysis data are given in Table 1.

Table 1 Analytical data

Scandium(III) complexes		%, Sc		%, C		%, H	
Name	Formula	Calcd.	Found	Calcd.	Found	Calcd.	Found
Hemimellitate	$C_6H_3(COO)_3Sc \cdot 6\,H_2O$	12.48	12.97	30.01	30.61	4.20	4.58
Trimellitate	$C_6H_3(COO)_3Sc \cdot 4\,H_2O$	13.87	13.84	33.35	32.63	3.42	3.20
Trimezinate	$C_6H_3(COO)_3Sc \cdot 8\,H_2O$	11.35	12.64	27.28	27.43	4.83	5.19

The results showed that the scandium(III) benzenetricarboxylates were isolated as hydrates with various degrees of hydration. The hemimellitate of Sc(III) was obtained as the hexahydrate, the trimellitate as the tetrahydrate, and the trimezinate as the octahydrate. Kasalova and Petru [4] prepared Sc(III) trimezinate as the dihydrate.

The IR spectra of the benzenetricarboxylic acids and their complexes were recorded over the range 4000–400 cm^{-1}. Analysis of the IR spectra confirmed the results of elementary analysis. Scandium(III) benzenetricarboxylates are white solids, not very soluble in water. The hemimellitate and trimezinate of Sc(III) were prepared as crystalline compounds and the trimellitate as an amorphous one.

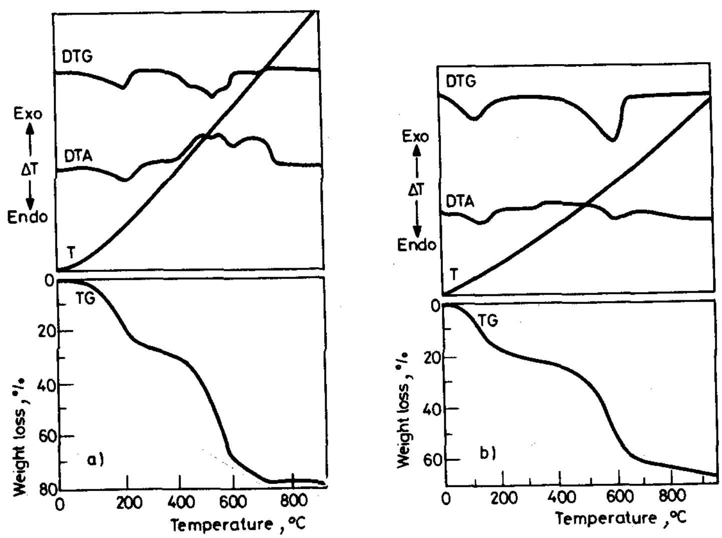

Fig. 1 TG, DTG and DTA curves of Sc(III) hemimellitate a) in air, b) in N_2

The thermal stabilities of Sc(III) hemimellitate, trimellitate and trimezinate were studied by the use of TG, DTG and DTA techniques. The measurements were made with an OD-102 derivatograph at a heating rate of 9 degree/min^{-1}. The samples were heated in air or nitrogen atmosphere. The recorded TG, DTG and DTA curves are given in Figs 1–3. From the thermal curves of the benzenetricarboxylates, the temperatures of thermal decomposition were evaluated and are presented in Tables 2 and 3.

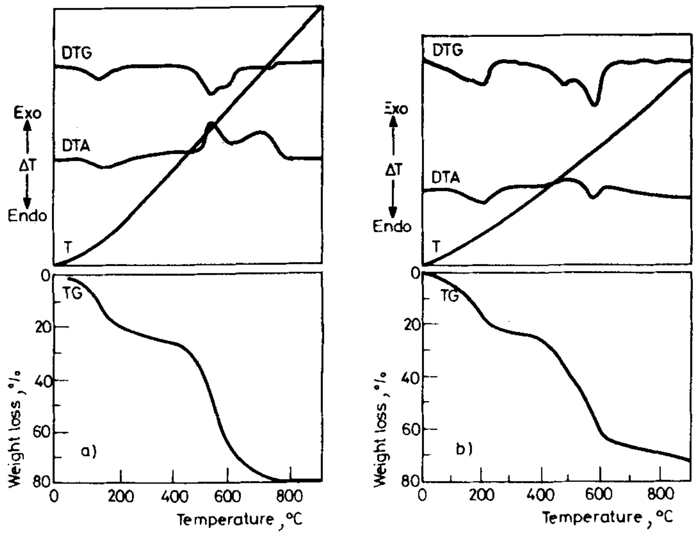

Fig. 2 TG, DTG and DTA curves of Sc(III) trimellitate a) in air, b) in N_2

The benzenetricarboxylates of scandium(III) decompose in two stages. On heating in air, the trimellitate and trimezinate are dehydrated in the temperature range 35–280° to the accompaniment of a strong endothermic effect, and anhydrous complexes subsequently decompose to Sc_2O_3. The burning of the organic anion is accompanied by a strong exothermic effect. Heating of the hexahydrate of Sc(III) hemimellitate leads to the endothermic loss of 5 molecules of crystallization water, the resulting monohydrate then decomposing directly to the oxide. The decomposition and burning of the monohydrate are associated with two exothermic effects, at 560 and 680°.

When heated in a nitrogen atmosphere, the benzenetricarboxylates of scandium(III) decompose in two stages. The tetrahydrate of Sc(III) trimellitate is dehydrated in an endothermic process and the anhydrous complex next decomposes to a mixture of Sc_2O_3 and carbon. The hydrates of Sc(III) hemimellitate and trimezinate lose 5 and 7 molecules of water, respectively, yielding the monohydrates, which then are decomposed to Sc_2O_3 and C. The decomposition of the benzenetricarboxylates in nitrogen

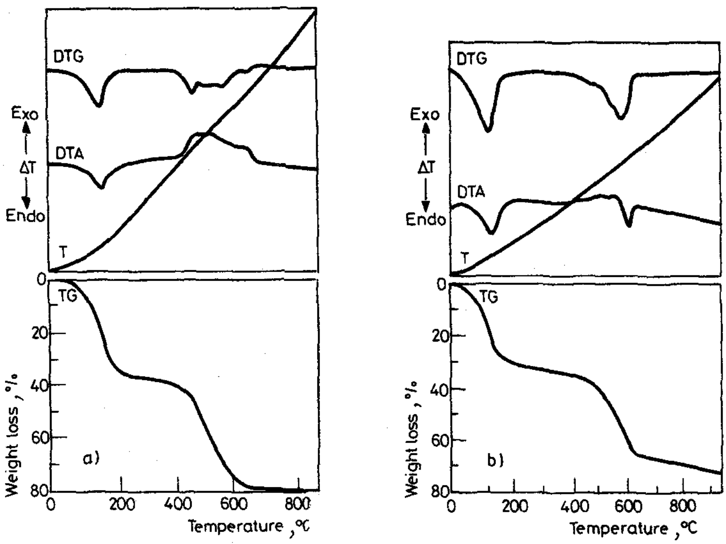

Fig. 3 TG, DTG and DTA curves of Sc(III) trimezinate a) in air, b) in N_2

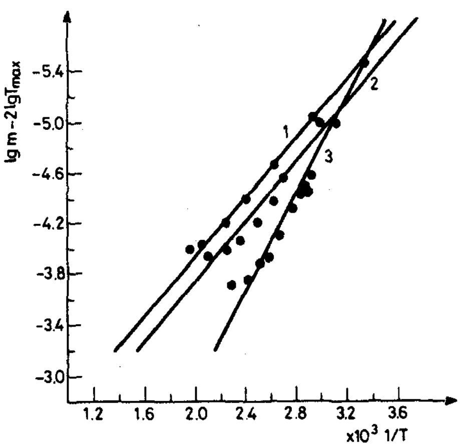

Fig. 4 Graphic presentation of activation energy of dehydration reaction of: 1 — Sc(III) hemimellitate, 2 — Sc(III) trimellitate, 3 — Sc(III) trimezinate

Table 2 Temperature data of dehydration of scandium(III) benzenetricarboxylates in air and nitrogen atmosphere

Complex	Air / N_2	Temperature range of dehydration °C	Peak temperature of DTG, °C	Endothermic peaks, °C	Loss of weight, %		Loss of H_2O molecules, n	Activation energy of dehydration reaction, kJ · mol^{-1}
					Calcd.	Found		
ScL · 6 H_2O [1, 2, 3]	A	40–250	200	210	25.01	25.0	5	5.0
	N	30–370	195	200	25.01	25.0	5	5.0
ScL · 4 H_2O [1, 2, 4]	A	35–280	130	140	22.23	22.2	4	5.0
	N	30–340	125	120	22.23	22.0	4	5.0
ScL · 8 H_2O [1, 2, 5]	A	35–242	120	130	36.38	36.0	8	7.9
	N	25–270	110	120	31.80	32.0	7	7.9

is accompanied by strong endothermic effects at 580–620°. The Sc_2O_3 obtained as final product contains 10.6–13% of carbon.

From the TG and DTA curves the activation energy of dehydration was calculated by a graphical method [8–11] (Fig. 4, Table 2). The activation energies of the hemimellitate and trimellitate are the same, 5 kJ · mol^{-1}, while that of the trimezinate, which is more hydrated, is 7.9 kJ · mol^{-1}.

The activation energies for the decomposition of Sc(III) benzenetricarboxylates in nitrogen were calculated via the Horowitz and Metzger [9] equation as modified by Dharwadkar and Karkhanavala [12] (Fig. 5, Table 3). It was found that the decomposition energies for all the benzenetricarboxylates of scandium are the same.

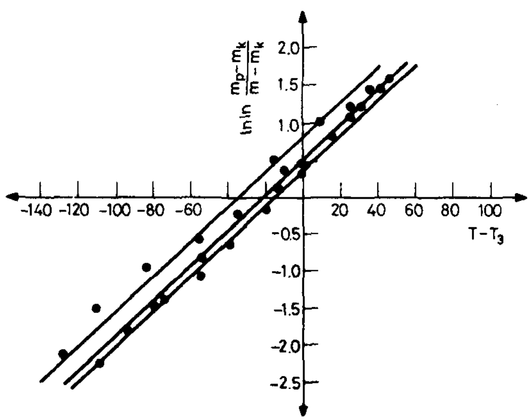

Fig. 5 Graphic presentation of activation energy of decomposition reaction of : 1 – Sc(III) hemimellitate, 2 – Sc(III) trimellitate, 3 – Sc(III) trimezinate

Table 3 Temperature data of decomposition of scandium(III) benzenetricarboxylates in air and nitrogen atmosphere

Complex	Air N$_2$	Temperature range of dehydration °C	Temperature range of decomposition °C	Peak temperature of DTG, °C	Loss of weight % Calcd.	Loss of weight % Found	C, %	Endothermic peaks, °C	Exothermic peaks °C	T_k, °C	k	Activation energy of decomposition reaction, kJ · mol^{-1}
ScL* · 6 H_2O [1, 2, 3]	A	40–250	405–715	555	80.85	80.0	–	–	500 680	715	–	–
	N	30–370	405–715	600	80.85	68.0	12.9	580	–	715	2.3	205
ScL · 4 H_2O [1, 2, 4]	A	35–280	405–715	600	78.73	78.3	–	–	535 680	715	–	–
	N	30–370	405–748	600	78.73	67.0	11.7	590	–	748	2.3	205
ScL · 8 H_2O [1, 3, 5]	A	35–242	400–663	470	82.60	82.0	–	–	540	663	–	–
	N	25–450	470–650	605	82.60	72.0	10.6	620	–	650	2.3	205

L* – $C_6H_3(COO)_3^{3-}$ [1, 2, 3], [1, 2, 4], [1, 3, 5] position of COO$^-$ group

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Zusammenfassung — Es wurden die Bedingungen der thermischen Zersetzung von Scandium(III)-hemimelitat, -trimelitat und -trimezinat in Luft und Stickstoffatmosphäre untersucht. Beim Erhitzen zerfallen die Benzoltricarboxylate des Sc(III) in zwei Schritten. Zunächst verlieren die hydratisierten Komplexe Kristallwasser, danach entsteht beim Erhitzen in Luft Sc_2O_3 und in einer Stickstoffatmosphäre Sc_2O_3 und C. Die Dehydratisierung der Komplexe ist ein stark endothermer Prozess. Die Zersetzung der Benzoltricarboxylate ist endotherm in Stickstoff und exotherm in Luft. Die Aktivierungsenergien der Dehydratisierung und der Zersetzungsreaktionen der Sc(III)-benzoltricarboxylate wurden berechnet.

Резюме — Изучены условия термического разложения скандиевых солей гемимеллитовой, тримеллитовой и тримезиновой кислот в атмосфере воздуха и азота. Бензолтрикарбоксилаты скандия при нагревании разлагаются в две стадии. Сначала гидратированные комплексы теряют кристаллизационную воду, а затем разлагаются при нагревании на воздухе с образованием конечного продукта Sc_2O_3, а при нагревании в атмосфере азота — Sc_2O_3 и углерода. Дегидратация комплексов сопровождается сильными эндотермическими эффектами. Разложение бензолтрикарбоксилатов в воздушной атмосфере сопровождается экзотермическим эффектом, а в атмосфере азота — эндотермическим эффектом. Вычислены энергии активации реакции дегидратации и разложения бензолтрикарбоксилатов скандия.