

STUDIES ON THERMAL DECOMPOSITION OF 3-CHLOROBENZOATES OF RARE EARTH ELEMENTS IN AIR ATMOSPHERE

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The conditions of thermal decomposition of the 3-chlorobenzoates of Y, La and the lanthanides from Ce(III) to Lu have been studied. The complexes of La, Pr(III), Sm, Eu, Gd, Tb(III) and Dy were prepared as heptahydrates, those of Ce(III) and Y as pentahydrates, that of Nd as the tetrahydrate, that of Ho as the dihydrate and those of Er, Tm, Yb and Lu as anhydrous salts. On heating, these complexes decompose in three or two stages. They first lose some water molecules and then decompose to oxides through the intermediate formation of LnOCl. Cerium(III) 3-chlorobenzoate loses its crystallization water in two stages and yields the anhydrous salt, which is then transformed directly into CeO₂. All these complexes melt before decomposition in the temperature range 441–513 K.

Much work is currently being done on the thermal decomposition of rare earth complexes with organic compounds [1–4], to elucidate the mechanisms of decomposition and the natures of the decomposition products. The rare earth salts of 3-chlorobenzoic acid are known. Kedrovskaya et al. [5] determined the stability constants of La, Nd and Yb 3-chlorobenzoates. Biryuline and Chikunova [6] prepared Tb and Eu(III) 3-chlorobenzoates as trihydrated salts and determined their solubilities in water. Scandium(III) 3-chlorobenzoate has been prepared and its thermal stability determined [7]. The salts of the remaining rare earths with 3-chlorobenzoic acid have not been prepared and studied.

As a continuation of our work on the thermal decomposition of rare earth salts of aromatic acids [8–10], we now report the thermal decomposition of the 3-chlorobenzoates of Y, La and lanthanides.

Experimental

The 3-chlorobenzoates of Y, La and the lanthanides from Ce(III) to Lu were prepared by adding equivalent quantities of a 0.5 M solution of ammonium 3-chlorobenzoate (pH 4.5–5.0) to a hot 0.1 M solution of Y, La or lanthanide chloride (cerium(III) was used as nitrate), followed by crystallization on a water-bath at 333 K. The precipitate formed was filtered off, washed with methanol to remove NH_4^+ ions dried at 303 K to constant weight. The 3-chlorobenzoates of Y, La and the lanthanides were prepared as crystalline solids sparingly soluble in water. The salts of Y, La, Ce(III), Sm, Eu(III), Gd, Tb(III), Dy, Tm and Lu were white, that of Pr green, those of Nd and Er pink, that of Ho cream, and that of Yb slightly pink.

The carbon and hydrogen contents of the complexes were determined by elemental analysis with V_2O_5 as oxidizing agent. The chlorine contents were determined by the Schöniger method [9]. The rare earth contents were determined by using oxalic acid, and from the TG curves. The water contents were determined from the TG curves and by isothermal heating at a definite temperature. The results obtained are given in Table 1.

The results show that the 3-chlorobenzoates of Y, La and the lanthanides were prepared as compounds with a metal to ligand ratio of 1 : 3. The 3-chlorobenzoates of La, Pr, Sm, Eu(III), Gd, Tb(III) and Dy were prepared as heptahydrates, those of

Table 1 Analytical data

Complex	M, %		C, %		H, %		Cl, %	
	calcd.	found	calcd.	found	calcd.	found	calcd.	found
Y(C ₇ H ₄ O ₂ Cl) ₃ · 5H ₂ O	13.77	14.02	39.07	39.04	3.43	3.40	16.47	16.53
La(C ₇ H ₄ O ₂ Cl) ₃ · 7H ₂ O	18.98	19.18	34.47	34.50	3.58	3.50	14.54	14.54
Ce(C ₇ H ₄ O ₂ Cl) ₃ · 5H ₂ O	20.11	19.21	36.19	36.30	3.18	3.08	15.26	15.76
Pr(C ₇ H ₄ O ₂ Cl) ₃ · 7H ₂ O	19.21	19.37	34.38	34.80	3.57	3.31	14.50	14.48
Nd(C ₇ H ₄ O ₂ Cl) ₃ · 4H ₂ O	21.12	20.58	36.93	37.03	2.95	2.43	15.57	15.67
Sm(C ₇ H ₄ O ₂ Cl) ₃ · 7H ₂ O	20.29	20.42	33.92	34.02	3.52	3.54	14.30	14.35
Eu(C ₇ H ₄ O ₂ Cl) ₃ · 7H ₂ O	20.40	19.86	33.87	33.97	3.52	3.48	14.28	14.27
Gd(C ₇ H ₄ O ₂ Cl) ₃ · 7H ₂ O	20.97	20.65	33.63	33.72	3.49	3.36	14.18	14.33
Tb(C ₇ H ₄ O ₂ Cl) ₃ · 7H ₂ O	21.14	21.20	33.55	33.17	3.49	3.55	14.15	14.36
Dy(C ₇ H ₄ O ₂ Cl) ₃ · 7H ₂ O	21.52	21.26	33.40	33.39	3.47	3.29	14.08	14.14
Ho(C ₇ H ₄ O ₂ Cl) ₃ · 2H ₂ O	24.70	24.27	37.78	37.24	2.41	2.44	15.93	16.10
Er(C ₇ H ₄ O ₂ Cl) ₃	26.38	26.23	39.79	39.50	1.91	2.04	16.78	16.68
Tm(C ₇ H ₄ O ₂ Cl) ₃	26.58	25.64	39.68	39.44	1.90	1.87	16.73	16.46
Yb(C ₇ H ₄ O ₂ Cl) ₃	27.05	26.35	39.43	39.20	1.89	1.79	16.63	16.61
Lu(C ₇ H ₄ O ₂ Cl) ₃	27.27	26.73	39.31	39.26	1.89	1.80	16.58	16.60

Y and Ce(III) as pentahydrates, that of Nd as the tetrahydrate, that of Ho as the dihydrate and those of Er, Tm, Yb and Lu as anhydrous salts.

The IR spectra of the prepared complexes were recorded over the range 4000–400 cm^{-1} . They are similar to one another. Analysis of the IR spectra confirmed the compositions of the complexes. The X-ray spectra revealed that the prepared complexes are crystalline compounds with large unit cells. They are characterized by low symmetry. The thermal stabilities of La and the light lanthanide 3-chlorobenzoates were studied by heating these complexes in air atmosphere to 1773 K, whereas the complexes of Y and the heavy lanthanides (which are less stable) were heated to 1273 K. The measurements were made on a Q-1500 D derivatograph. The TG, DTG and DTA curves were recorded. The samples were heated in platinum crucibles at heating rates of 5 and 15 $\text{deg} \cdot \text{min}^{-1}$ for Y and the heavy lanthanide complexes and at heating rates of 7.5 and 15 $\text{deg} \cdot \text{min}^{-1}$ for La and the light lanthanide complexes. Alumina was used as a reference material. From the thermal curves of La and lanthanide 3-chlorobenzoates, the temperatures of thermal decomposition were evaluated and are presented in Tables 2 and 3. As examples, the TG, DTG and DTA curves of Y, La and Ho 3-chlorobenzoates, recorded at a heating rate of 15 $\text{deg} \cdot \text{min}^{-1}$, are given in Figs 1–3. The natures of the solid decomposition products were calculated from the weight losses in the TG curves and were confirmed by recording IR spectra and on the basis of chemical analysis.

Results and discussion

When heated, the 3-chlorobenzoates of Y, La and the lanthanides decompose in different ways (Tables 2 and 3, Figs 1–3). The hydrated complexes of Y, La, Pr(III), Nd, Sm, Gd, Tb(III) and Dy decompose in three steps. They are stable up to 323–348 K, but then lose some water molecules in the range 343–453 K, this step being accompanied by a strong endothermic effect.

The hydrates of La and Pr(III) lose three water molecules in the first step, those of Nd and Sm two, those of Eu and Y four, and those of Gd, Tb(III) and Dy five water molecules. The hydrates obtained next melt, this process involving a strong endothermic effect, and then decompose in the temperature range 455–1008 K to the oxychlorides LnOCl , which are converted to the oxides Ln_2O_3 , Pr_6O_{11} and Tb_4O_7 at 863–1663 K. The burning of the organic ligand is accompanied by an exothermic effect at 833–873 K. The pentahydrate of Ce(III) 3-chlorobenzoate is stable up to 343 K, but then loses its crystalline water in two steps to yield the anhydrous salt, which melts at 583 K. This salt is stable up to 583 K and then decomposes directly to CeO_2 in the temperature range 583–948 K. The dihydrate of

Table 2 Temperature data of dehydration of Y, La and lanthanide 3-chlorobenzoates in air atmosphere with heating rate of 7.5 deg·min⁻¹ and 5 deg·min⁻¹

Complexes	Temperature range of dehydration, K	Loss of weight, %		Loss of H ₂ O molecules, n	Endothermic peaks, K	Melting point, K
		calcd.	found			
Y(C ₇ H ₄ O ₂ Cl) ₃ ·5H ₂ O	323-393	11.16	12.0	4	361	465
La(C ₇ H ₄ O ₂ Cl) ₃ ·7H ₂ O	348-453	7.39	7.0	3	403	513
Ce(C ₇ H ₄ O ₂ Cl) ₃ ·5H ₂ O		5.70	5.6	2	433	583
	453-573	12.93	12.0	3		
Pr(C ₇ H ₄ O ₂ Cl) ₃ ·7H ₂ O	343-453	7.37	7.0	3	421	491
Nd(C ₇ H ₄ O ₂ Cl) ₃ ·4H ₂ O	348-445	5.28	5.2	2	418	525
Sm(C ₇ H ₄ O ₂ Cl) ₃ ·7H ₂ O	343-438	4.85	4.8	2	403	508
Eu(C ₇ H ₄ O ₂ Cl) ₃ ·7H ₂ O	348-453	9.60	9.2	4	418	513
Gd(C ₇ H ₄ O ₂ Cl) ₃ ·7H ₂ O	343-453	12.01	12.2	5	433	498
Tb(C ₇ H ₄ O ₂ Cl) ₃ ·7H ₂ O	333-393	11.98	12.0	5	368	469
Dy(C ₇ H ₄ O ₂ Cl) ₃ ·7H ₂ O	338-398	11.93	11.2	5	365	455
Ho(C ₇ H ₄ O ₂ Cl) ₃ ·2H ₂ O	333-393	5.40	6.0	2	363	441
Er(C ₇ H ₄ O ₂ Cl) ₃	—	—	—	—	—	463
Tm(C ₇ H ₄ O ₂ Cl) ₃	—	—	—	—	—	473
Yb(C ₇ H ₄ O ₂ Cl) ₃	—	—	—	—	—	483
Lu(C ₇ H ₄ O ₂ Cl) ₃	—	—	—	—	—	483

Table 3 Temperature data of decomposition of Y, La and lanthanide 3-chlorobenzoates in air atmosphere with heating rate of $7.5 \text{ deg} \cdot \text{min}^{-1}$ and $5 \text{ deg} \cdot \text{min}^{-1}$

Complexes	Temperature range of dehydration, K		Temperature range of decomposition to LnOCl, K		Loss of weight, %		Exothermic peaks, K	Temperature range of decomposition to Ln ₂ O ₃ , K	Loss of weight, %		Temperature of oxide formation, T _p , K
	calcd.	found	calcd.	found	calcd.	found			calcd.	found	
Y(C ₇ H ₄ O ₂ Cl) ₃ · 5H ₂ O	323-393	—	465-863	—	78.25	78.2	833	863-1143	82.51	82.2	1143
La(C ₇ H ₄ O ₂ Cl) ₃ · 7H ₂ O	348-453	—	513-943	—	73.98	73.5	853	943-1663	77.74	77.5	1663
Ce(C ₇ H ₄ O ₂ Cl) ₃ · 5H ₂ O	343-453	—	—	—	—	—	853	583-948	75.30	76.4	948
Pr(C ₇ H ₄ O ₂ Cl) ₃ · 7H ₂ O	453-573	—	—	—	—	—	—	—	—	—	—
Nd(C ₇ H ₄ O ₂ Cl) ₃ · 4H ₂ O	343-453	—	491-943	—	73.78	72.8	853	943-1551*	75.40	75.6	1551
Sm(C ₇ H ₄ O ₂ Cl) ₃ · 7H ₂ O	348-445	—	525-943	—	71.35	71.8	853	943-1485	75.37	76.0	1485
Eu(C ₇ H ₄ O ₂ Cl) ₃ · 7H ₂ O	343-438	—	508-1005	—	72.80	71.6	863	1005-1401	76.55	76.4	1401
Gd(C ₇ H ₄ O ₂ Cl) ₃ · 7H ₂ O	348-453	—	513-1008	—	72.60	72.5	853	1008-1353	76.37	77.0	1353
Tb(C ₇ H ₄ O ₂ Cl) ₃ · 7H ₂ O	343-453	—	498-1008	—	72.18	72.4	853	1008-1308	75.83	76.4	1308
Dy(C ₇ H ₄ O ₂ Cl) ₃ · 7H ₂ O	333-393	—	469-863	—	72.40	72.0	848	863-1193**	75.67	76.0	1193
Ho(C ₇ H ₄ O ₂ Cl) ₃ · 2H ₂ O	338-398	—	455-873	—	71.67	71.2	853	873-1193	75.31	75.2	1193
Er(C ₇ H ₄ O ₂ Cl) ₃	333-393	—	441-873	—	67.59	69.0	853	873-1161	73.70	73.2	1161
Tm(C ₇ H ₄ O ₂ Cl) ₃	—	—	460-885	—	65.51	66.0	853	885-1118	69.83	70.0	1118
Yb(C ₇ H ₄ O ₂ Cl) ₃	—	—	473-890	—	65.33	65.8	838	890-1093	69.65	70.4	1093
Lu(C ₇ H ₄ O ₂ Cl) ₃	—	—	483-913	—	64.96	66.0	863	913-1088	69.20	69.6	1088
Lu(C ₇ H ₄ O ₂ Cl) ₃	—	—	483-933	—	64.71	64.8	873	933-1093	69.00	69.6	1093

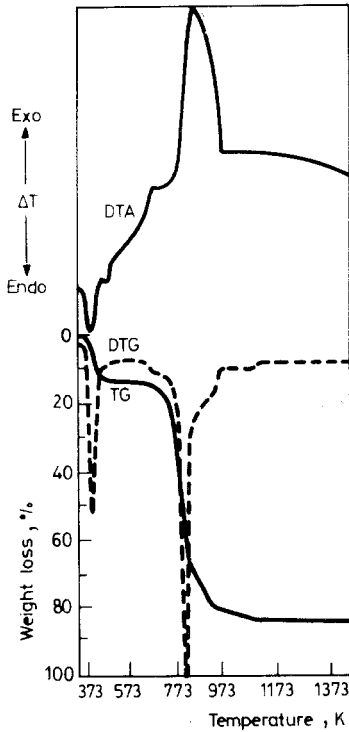


Fig. 1 TG, DTG and DTA curves of $Y(C_7H_4O_2Cl)_3 \cdot 5H_2O$

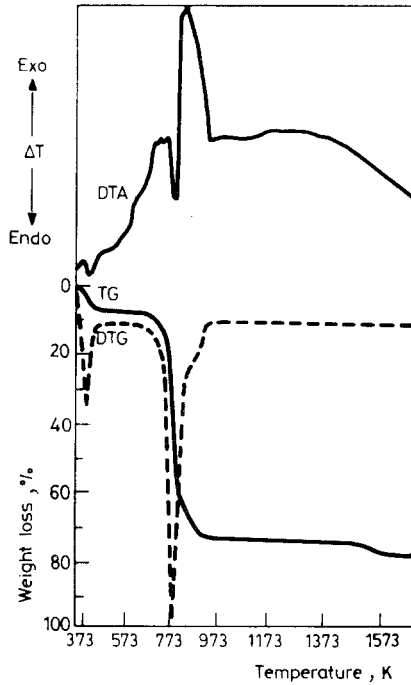


Fig. 2 TG, DTG and DTA curves of $La(C_7H_4O_2Cl)_3 \cdot 7H_2O$

Table 4 Temperature of rare earth oxide formation

V	T_k , K	La	Ce	Pr	Nd	Sm	Eu	Gd	
7.5 deg/min		1663	948	1551	1485	1401	1353	1308	
15 deg/min		1603	883	1538	1456	1381	1293	1273	
ΔT_k		60	65	13	29	20	60	35	
V	T_k , K	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
5 deg/min		1193	1193	1161	1118	1093	1088	1093	1143
15 deg/min		1223	1173	1173	1138	1133	1138	1118	1158
ΔT_k		30	20	12	20	60	50	25	15

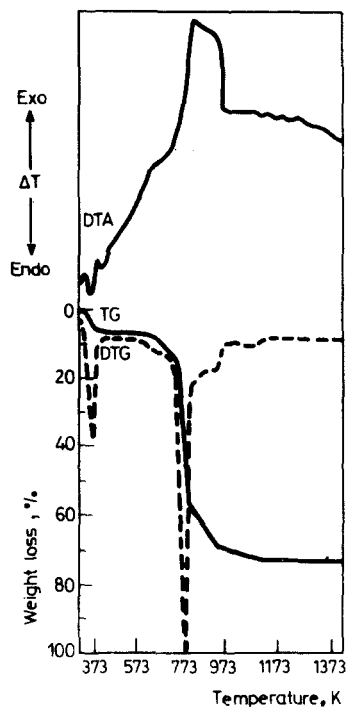


Fig. 3 TG, DTG and DTA curves of $\text{Ho}(\text{C}_7\text{H}_4\text{O}_2\text{Cl})_3 \cdot 2\text{H}_2\text{O}$

of the Ho complex decomposes in two steps. In the first step it loses two water molecules and then decomposes in the temperature range 441–873 K to HoOCl , which is converted to the oxide Ho_2O_3 at 873–1161 K. The anhydrous complexes of Er, Tm, Yb and Lu decompose in two steps when heated. In the temperature range 460–933 K they decompose to LnOCl , which are converted to the oxides Ln_2O_3 at 885–1118 K. The melting temperatures of the prepared complexes were determined at heating rates of 15, 7.5 and 5 $\text{deg} \cdot \text{min}^{-1}$ (Table 5). The obtained results are consistent. Anhydrous Ce(III) 3-chlorobenzoate has the highest melting point, and the holmium salt the lowest one. The complexes of the heavy lanthanides melt at lower temperatures than the complexes of the light lanthanides. The melting temperatures of the 3-chlorobenzoates vary periodically with increasing atomic number of the metal in the lanthanide series.

The temperatures of oxide formation depend on the rate of heating of the sample. At a heating rate of 15 $\text{deg} \cdot \text{min}^{-1}$ the temperatures of oxide formation are lower than those at heating rates 7.5 or 5 $\text{deg} \cdot \text{min}^{-1}$ (Table 4). The temperatures of rare earth oxide formation decrease with increasing atomic number and ionic potential in the lanthanide series (Table 4) and for the heavy lanthanides are markedly lower

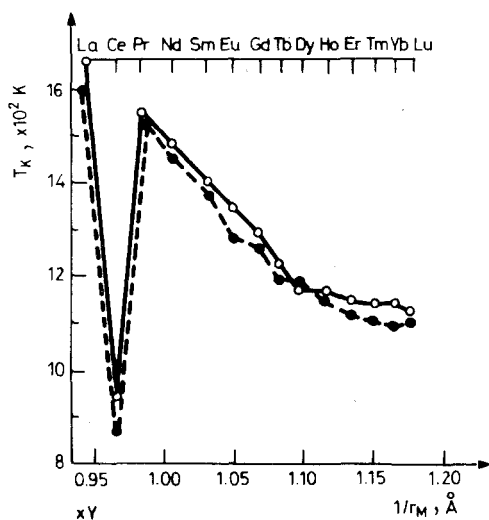


Fig. 4 Relationship between T_k and $1/r_M$ (Goldschidt's value)

Table 5 Melting points of Y, La and lanthanide 3-chlorobenzoates

V	Melting point T_i , K							
	La	Ce	Pr	Nd	Sm	Eu	Gd	
7.5 deg/min	513	583	491	525	508	513	498	
15 deg/min	513	580	488	525	505	510	496	
ΔT_i	0	3	3	0	3	3	2	

V	Melting point T_i , K							
	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
5 deg/min	469	455	441	463	473	483	483	465
15 deg/min	471	458	444	465	475	483	485	468
ΔT_i	2	3	3	2	2	0	2	3

than for the light lanthanides, except cerium (Fig. 4). CeO_2 has the lowest temperature of formation and the anhydrous complex decomposes directly to the oxide. Analogous findings are very often observed during studies of complexes in the lanthanide series.

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Zusammenfassung — Die Bedingungen der thermischen Zersetzung der 3-Chlorbenzoate von Y und La sowie die der Lanthanide von Ce(III) bis Lu wurden untersucht. Die Komplexe von La, Pr(III), Sm, Eu, Gd, Tb(III) und Dy wurden als Heptahydrate, die von Ce(III) und Y als Pentahydrate, der von Nd als Tetrahydrat, der von Ho als Dihydrat und die von Er, Tm, Yb und Lu als wasserfreie Salze dargestellt. Beim Erhitzen zersetzen sich diese Komplexe in drei oder zwei Schritten. Sie verlieren zunächst einige Wassermoleküle und zersetzen sich dann zu den Oxiden, wobei intermediär LnOCl gebildet wird. Cer(III)-3-chlorbenzoat gibt das Kristallwasser in zwei Schritten unter Bildung des wasserfreien Salzes ab, welches sich dann direkt in CeO₂ umwandelt. Alle diese Komplexe schmelzen vor der Zersetzung im Temperaturbereich von 441–513 K.

Резюме — Изучены условия термического разложения 3-хлорбензоатов иттрия, лантана и лантаноидов. Комплексы лантана, празеодима, самария, европия, гадолиния, тербия и диспрозия были получены в виде гептагидратов, серия и иттрия — в виде пентагидратов, неодимия — тетрагидрата, гольмия — дигидрата, а комплексы эрбия, тулия, иттербия и лютеция — в виде безводных солей. Все указанные комплексы при нагревании разлагаются в две или три стадии. Сначала они теряют несколько молекул воды, а затем разлагаются до окислов через промежуточную стадию образования LnOCl. 3-хлорбензоат трехвалентного церия теряет кристаллизационную воду в две стадии, давая безводную соль, которая затем разлагается прямо до двуокиси церия. Перед разложением все комплексы плавятся в интервале температур 441–513 K.