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THERMAL ANALYSIS OF β-$Co_2(OH)_3Cl$ AND $Zn_5(OH)_8Cl_2 \cdot H_2O$

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ABSTRACT

Samples of β-$Co_2(OH)_3Cl$ and $Zn_5(OH)_8Cl_2 \cdot H_2O$ have been prepared and their thermal decomposition studied in air and N_2 by DTA and TG up to 1000°C. X-Ray diffraction analysis of the thermal treatment products in air at various temperatures from 100 to 1000°C was also carried out. The results obtained made it possible to establish the steps through which the pyrolysis of both compounds proceeds.

INTRODUCTION

The hydroxychlorides β-$Co_2(OH)_3Cl$ and $Zn_5(OH)_8Cl_2 \cdot H_2O$, described earlier by Feitknecht and Oswald [1,2], were characterized using X-ray diffraction by de Wolff [3], Nowacki and Silverman [4], and Allman [5].

The first study of the thermal decomposition of α-$Co_2(OH)_3Cl$ was that of García Martínez and Cano Ruíz [6], who attributed the endothermic peak at 450°C in the DTA curve of this compound to the simultaneous loss of water and hydrogen chloride.

The thermal stability of $CoCl_2 \cdot 6\,H_2O$ has been extensively studied by Lumme and Junkkarinen [7,8], Pribylov and Baranova [9], Simmons and Wendlandt [10], and Grindstaff and Fogel [11], among others. The last three papers are concerned with the dehydration of this compound, which takes place at relatively low temperatures.

The thermal decomposition of $CoCl_2 \cdot 6\,H_2O$ at temperatures up to 950°C was studied by TG by Lumme and Junkkarinen [7,8], who found that the anhydrous salt is formed in air at 208°C and decomposes to Co_3O_4 between 300 and 738°C.

$$CoCl_2 + 2/3\ O_2 \rightarrow 1/3\ Co_3O_4 + Cl_2$$

In nitrogen, the dehydration takes place at about the same temperature, but the anhydrous salt does not dissociate until 500°C.

$$CoCl_2 \rightarrow Co + Cl_2$$

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Finally, they reported that between 550 and 921°C, $CoCl_2$ also sublimes with a mass loss of 87.6%.

For $Zn_5(OH)_8Cl_2 \cdot H_2O$, García Martínez and Cano Ruíz [6] suggested that the endothermic effects they observed at 170, 240 and 540°C in the DTA curve of this compound were due to loss of water of hydration and crystallization together with hydrogen chloride. Mata Arjona, Aycart Andrés, García Martínez and Cano Ruíz [12] also suggested that the pyrolysis of this compound takes place according to the equation

$$Zn_5(OH)_8Cl_2 \cdot H_2O \rightarrow 5\ ZnO + 2\ HCl + 5\ H_2O$$

Simultaneously, Srivastava and Secco [13] established by DTA and TG that, at a heating rate of 20°C min^{-1} in air, the same compound dehydrates in two stages, viz.

$$Zn_5(OH)_8Cl_2 \cdot H_2O \xrightarrow{110^\circ-147^\circ C} Zn_5(OH)_8Cl_2 + H_2O$$

$$Zn_5(OH)_8Cl_2 \xrightarrow{167^\circ-266^\circ C} 4\ ZnO + ZnCl_2 + H_2O$$

and that, above 266°C, it continues to lose weight, initially at a slow rate and then, above 400°C, more quickly. This weight loss is due to the volatilization of $ZnCl_2$, which is complete at 350°C. To account for the difference between the calculated and the observed loss of weight, they suggested that partial hydrolysis of $ZnCl_2$ occurred.

$$ZnCl_2 + H_2O \rightarrow ZnO + 2\ HCl$$

The endothermic peaks observed at 187, 200, 262 and 708°C were assigned to the two dehydrations mentioned above and to the melting and volatilization of $ZnCl_2$. The different temperatures, 535 and 708°C, observed for the complete vaporization of $ZnCl_2$ in the TG and DTA curves, respectively, were attributed to different experimental conditions.

Finally, Hoffman and Lauder [14], through mass spectrometric measurements, confirmed that the dehydration of zinc hydroxychloride proceeds according to the equation

$$Zn_5(OH)_8Cl_2 \rightarrow ZnCl_2 + 4\ ZnO + 4\ H_2O$$

and that partial hydrolysis of $ZnCl_2$ takes place at 250°C.

EXPERIMENTAL

The samples were prepared by the addition of 25% of the equivalent amount of 1.0 N NaOH to 0.2 M $CoCl_2 \cdot 6\ H_2O$ and $ZnCl_2$ solutions. The products, which were dispersed, were aged in the mother liquor at 70°C for three days with continuous shaking. After filtering and washing with water and ethanol, the samples were dried in vacuo and maintained at 90°C to constant weight.

The chloride content of each sample was determined by Mohr's method and the cobalt and zinc by titration with EDTA employing murexide and

Eriochrome Black T, respectively, as indicators. Samples were also identified by X-ray powder diffraction using a cylindrical camera of 114.6 mm diameter with Fe*Kα* radiation for α-$Co_2(OH)_3Cl$ and Cu*Kα* for the zinc compound.

The thermal decomposition of the samples was studied in air and in a dynamic N_2 atmosphere by DTA and TG up to 1000°C and by X-ray diffraction analysis of the thermal treatment products at various temperatures from 100 to 1000°C.

DTA curves were recorded on an Aminco thermoanalyzer 4-4451A. A sensitivity of 5 mV $in.^{-1}$ for the differential temperature and a heating rate of 8°C min^{-1} were used. Samples of about 50 mg were placed in 1/4 in. long and 1/6 in. i.d. inconel microcups supplied with chromel—alumel thermocouples and located in an inconel block. α-Alumina, previously heated at 1000°C, was employed as inert substance.

TG plots were simultaneously recorded on a DuPont Thermal Analyzer 950. The samples, of about 15—20 mg, were placed in Pt pans. Temperature and mass scales of 100°C $in.^{-1}$ and 4 mg $in.^{-1}$ were used at a heating rate of 12°C min^{-1}. For DTA and TG, a current of dried air or nitrogen was passed through the whole assembly.

The thermal treatments were performed up to 200°C in a Memmert oven and, for higher temperatures, in a Heraeus KS 120 furnace in which the temperatures were determined by means of Pt—Pt/Rh thermocouple with an estimated accuracy of ±10°C. For the X-ray diffraction analysis of the thermal treatment products, the same radiations and camera as indicated for the initial compounds were employed.

RESULTS

The samples had X-ray diffraction patterns identical to those [3—5] of β-$Co_2(OH)_3Cl$ and $Zn_5(OH)_8Cl_2 \cdot H_2O$ and chemical analysis gave the percentages shown in Table 1.

Tables 2—4 present some data from the thermal analysis of the samples. All DTA peaks were endothermic except that indicated in Table 2. In the case of $Co_2(OH)_3Cl$ in nitrogen, a substance was observed on the quartz filament from which the sample holder was suspended.

TABLE 1

Chemical analysis of the samples

		Co (%)	Zn (%)	Cl (%)
β-$Co_2(OH)_3Cl$	Calculated	57.7		17.4
	Found	57.6		17.3
$Zn_5(OH)_8Cl_2 \cdot H_2O_2$	Calculated		59.3	12.9
	Found		59.2	12.9

TABLE 2

DTA peak temperatures and TG mass losses for $Co_2(OH)_3Cl$ in air

Temp. range (°C)	DTA peak temp. (°C)	TG mass loss (%)
270—450	280,440	9.3
450—890	460 [a]	12.1
925—975	960	5.3

[a] Exothermic.

TABLE 3

DTA peak temperatures and TG mass losses for $Co_2(OH)_3Cl$ in nitrogen

Temp. range (°C)	DTA peak temp. (°C)	TG mass loss (%)
300—500	409, 465	13.2
500—1000	720	23.0

TABLE 4

DTA peak temperatures and TG mass losses for $Zn_5(OH)_8Cl_2 \cdot H_2O$ in nitrogen

Temp. range (°C)	DTA peak temp. (°C)	TG mass loss (%)
110—165	146	3.2
165—210	202	9.9
210—300	272	3.2
300—800	678	19.4

Mass losses and identified phases after different thermal treatments of $Co_2(OH)_3Cl$ and $Zn_5(OH)_8Cl_2 \cdot H_2O$ are shown in Tables 5 and 6. The compounds M(OH)Cl (M = Co, Zn) appearing in these tables were identified using the X-ray diffraction data published by Oswald and Feitknecht [15]. The decomposition of $Zn_5(OH)_8Cl_2 \cdot H_2O$ proceeds by the same steps irrespective of whether it is carried out in air or nitrogen. Nevertheless, the data included in Table 4 correspond to the observations under N_2 flow.

DISCUSSION

Decomposition of $Co_2(OH)_3Cl$

According to the data contained in Tables 2 and 5, the pyrolysis in air of β-$Co_2(OH)_3Cl$ includes three stages Up to 450°C, its decomposition takes

TABLE 5

Mass losses and identified phases after various thermal treatments of $Co_2(OH)_3Cl$ in air

Temperature (°C)	Time (h)	Mass loss (%)	Products [a]
100	1	0.40	H
100	2	0.40	H
100	5	1 09	H
300	1	5.90	S + H + I
300	2	7.15	S + H + I
300	5	8.98	S + H + I
350	10^{-3}	5.86	S + H + I
400	10^{-3}	8 33	S + H + I
450	10^{-3}	8.42	S + H + I
470	10^{-3}	10.87	S + I
470	1	19.43	S
470	5	20.17	S
600	10^{-3}	12.26	S
600	1	20.38	S
600	5	20.91	S
720	10^{-3}	21.44	S
720	1	21.60	S
720	5	21 62	S
900	10^{-3}	23.72	S + C
900	1	25.52	S + C
900	5	25.52	C + S
1000	10^{-3}	24.99	C + S
1000	1	25.36	C + S
1000	5	25.36	C + S

[a] H = $Co_2(OH)_3Cl$, I = $Co(OH)Cl$, S = Co_3O_4, C = CoO.

place according to the reactions

$$Co_2(OH)_3Cl + 1/6\ O_2 \rightarrow Co(OH)Cl + 1/3\ Co_3O_4 + H_2O$$

$$Co(OH)Cl + 1/12\ O_2 \rightarrow 1/6\ Co_3O_4 + 1/2\ CoCl_2 + 1/2\ H_2O$$

to which the two endothermic effects recorded in the DTA curve at 280 and 440°C can be attributed. The observed mass loss, 9.3%, agrees with the calculated value of 9.31%.

The exothermic DTA peak at 460°C corresponds to the reaction

$$3\ CoCl_2 + 2\ O_2 \rightarrow Co_3O_4 + 3\ Cl_2$$

which implies a mass loss of 12.24%, equal to that observed between 450 and 890°C.

The last DTA peak, appearing at 960°C, has to be assigned to the conversion of the spinel Co_3O_4 into the face-centered cubic oxide CoO, viz.

$$2\ Co_3O_4 \rightarrow 6\ CoO + O_2$$

On the other hand, in the thermal decomposition of the same compound, $Co_2(OH)_3Cl$, in nitrogen, two steps can be distinguished as Table 3 shows.

TABLE 6

Mass losses and identified phases after various thermal treatments of $Zn_5(OH)_8Cl_2 \cdot H_2O$ in air

Temperature (°C)	Time (h)	Mass loss (%)	Products [a]
140	2	8.62	II + O + I
140	6	9.45	II + O + I
140	24	9.50	II + O + I
175	2	10.25	II + O + I
175	6	10.56	II + O + I
175	24	11.19	O + II + I
190	2	11.88	O + I
190	6	12.71	O + I
190	24	13.85	O + I + II
215	2	12.60	O + I
215	6	12.91	O + I
215	24	13 75	O + I + II
235	2	12.43	O + I
235	6	13.25	O + I
235	24	14.80	O + I
280	2	13.36	O + I
280	6	13.91	O + I
280	24	16.49	O + I
650	2	34.29	O
650	6	34.29	O
900	10^{-3}	34.29	O
1000	10^{-3}	34.29	O

[a] I = Zn(OH)Cl, II = $Zn_5(OH)_8Cl_2$. O = ZnO.

The two endothermic effects at 409 and 465°C and the mass loss of 13.2% are due to the reactions

$$Co_2(OH)_3Cl - Co(OH)Cl + CoO + H_2O$$

$$2\ Co(OH)Cl \rightarrow CoO + CoCl_2 + H_2O$$

which imply a total calculated loss of mass of 13.23%.

At temperatures higher than 500°C, $CoCl_2$ sublimes. One endothermic needle-shaped peak at 720°C corresponds to the melting of this salt.

The measured mass loss, 23.0%, was lower than the calculated value of 31.77%. There are two possible reasons for this difference. First, the fact that the boiling point of $CoCl_2$ was not reached because TG was performed only up to 1000°C; and, secondly, the observation that $CoCl_2$ vapors condensed on the quartz filament from which the thermobalance sample holder was suspended.

It should be mentioned here that the assumption of Lumme and Junkkarinen [8] that $CoCl_2$ dissociates into metallic cobalt and chlorine seems rather unlikely since the residue of TG and DTA is always CoO. On the other hand, they observed a mass loss of 78.6% of $CoCl_2$. This would correspond to a loss of 23.3% for $Co_2(OH)_3Cl$, about the same as we observed in this temperature range.

Pyrolysis of $Zn_5(OH)_8Cl_2 \cdot H_2O$

The data of Tables 4 and 5 make it possible to distinguish the following changes in the thermal decomposition of $Zn_5(OH)_8Cl_2 \cdot H_2O$.

	Mass loss (%)	
	Obs	Calc.
$Zn_5(OH)_8Cl_2 \cdot H_2O \xrightarrow{110-165°C} Zn_5(OH)_8Cl_2 + H_2O$	3.2	3.26
$Zn_5(OH)_8Cl_2 \xrightarrow{165-210°C} 2\ Zn(OH)\ Cl + 3\ ZnO + 3\ H_2O$	9.9	9.78
$2\ Zn(OH)\ Cl \xrightarrow{210-300°C} ZnO + ZnCl_2 + H_2O$	3.2	3.26
$ZnCl_2(l) \xrightarrow{300-800°C} ZnCl_2(g)$	19.4	24.71

These changes imply a total mass loss of 35.7% (observed) and 41.01% (calculated).

The difference between the observed and calculated losses for the vaporization of $ZnCl_2$ is due to the hydrolysis of some of the $ZnCl_2$.

$ZnCl_2 + 2\ H_2O \rightarrow ZnO + 2\ HCl$

In this way, only a fraction of the $ZnCl_2$ would be lost through vaporization, i.e. the fraction which did not undergo hydrolysis. The data for 650, 900 and 1000°C shown in Table 6 support this assumption.

According to Srivastava and Secco [13], the peak appearing at about 200°C is due to the reaction

$Zn_5(OH)_8Cl_2 \rightarrow 4\ ZnO + ZnCl_2 + 4\ H_2O$

and the next one, which they observed at 262°C, corresponds to the melting of $ZnCl_2$. However, they did not carry out the identification of the thermal treatment products and therefore missed the presence of Zn(OH)Cl. This compound has been repeatedly found by us as indicated in Table 6.

On the other hand, we were not able to resolve the peak appearing at 272°C for the decomposition reaction of Zn(OH)Cl and that for the melting of $ZnCl_2$, which is 275°C [16]. It may be that $ZnCl_2$, which can dissolve ZnO thus lowering its melting point, melts at the same temperature as that at which thermal decomposition of Zn(OH)Cl takes place. Much clearer is the peak at 678°C, which corresponds to the boiling point of $ZnCl_2$.

Finally, one comment about some data in Table 6. Among the products of 24 h treatments at 190 and 215°C, the initial compound, $Zn_5(OH)_8Cl_2$, was identified. On the other hand, this compound did not appear when it was heated for two or six hours.

This last observation can be related to that of Hoffman and Lauder [14] who were not able to explain why one sample of Zn(OH)Cl accompanied with traces of $ZnCl_2$ gave an X-ray diffraction pattern identical to that of $Zn_5(OH)_8Cl_2$ when irradiated for 12 h in a Lindeman tube open to the air.

Both observations could be explained by the fact that Zn(OH)Cl is, like $ZnCl_2$, hygroscopic [15]: its prolonged exposure to moist air would lead to its hydrolysis according to the reaction

$$5\ Zn(OH)Cl + 3\ H_2O \rightarrow Zn_5(OH)_8Cl_2 + 3\ HCl$$

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