Journal of Thermal Analysis, Vol. 33 (1988) 487–493

THERMAL DECOMPOSITION REACTIONS OF AMMINECOBALT(III)COMPLEXES

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Simultaneous TG–DTG–DTA studies under non-isothermal conditions on $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5]Cl_2$ and $[Co(NH_3)_6]_2(C_2O_4)_3.4H_2O$ complexes have been carried out in air and argon atmospheres in the temperature range 293–1273 K. All the dissociation processes occur in three main stages. The kinetics of thermal decomposition of the complexes have been evaluated from the dynamic weight loss data, to determine the most probably mechanisms of the stages on the basis of statistical analysis. The decomposition of the compounds was controlled by diffusion and phase boundary reactions except stage III of the oxalate complex in argon (random nucleation). The activation energies E_a of the particular stages of the thermal decomposition were calculated.

The thermal decomposition of amminecobalt(III) complexes has been studied by many investigators. The results obtained have been reported in detail by Wendlandt [1]. Published data concerning the kinetic analysis of the particular stages of thermal decomposition of $[Co(NH_3)_6]Cl_3$ and $[Co(NH_3)_5Cl]Cl_2$ are not complete. In the accessible literature there is no data for decomposition of $[Co(NH_3)_6]_2(C_2O_4)_3 \cdot 4H_2O$. The amminecobalt(III) complexes mentioned above seem to be interesting as intermediate products in the cobalt recovery technology.

In this work the thermal decomposition mechanism of the above compound has been studied in air and argon atmospheres under non-isothermal conditions.

Experimental

All reagents were of AnalaR grade. Hexamminecobalt(III)chloride $[Co(NH_3)_6]Cl_3$, pentamminecobalt(III)chloride $[Co(NH_3)_5Cl]Cl_2$ and hexamminecobalt(III) oxalate tetrahydrate $[Co(NH_3)_6]_2(C_2O_4)_3 \cdot 4H_2O$ were prepared by methods described in [2–4]. The complete analytical data for these complexes is given in the previous paper [5].

Simultaneous TG–DTG–DTA curves were obtained with a Paulik–Paulik–Erdey

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

3427–T derivatograph at 293–1273 K with a heating rate $\beta = 1.25$ deg min^{-1} in flowing air and argon atmospheres. The sample weight was 200 mg, sieve mesh $\leqslant 0.060$ mm.

Results and discussion

The compounds decompose in stepwise manner to yield cobalt(II)chloride, cobalt oxides or metallic cobalt powder as final solid residues.

The thermal decomposition of all complexes studied proceeds in three stages in both gaseous atmospheres. On the basis of the experimental data [5] (weight loss, X-ray diffraction, reflectance spectroscopy, chemical analysis) the probable decomposition sequences of thermal dissociation of complexes studied are presented.

$[Co(NH_3)_6]Cl_3$

I stage (air, argon):

$$6[\mathrm{Co(NH_3)_6}]\mathrm{Cl_3} \xrightarrow{423-553\ \mathrm{K}} 3\mathrm{CoCl_2} + 3(\mathrm{NH_4})_2[\mathrm{CoCl_4}] + \mathrm{N}_{2(g)} + 28\mathrm{NH}_{3(g)} \quad (1)$$

II stage (air, argon):

$$3(\mathrm{NH_4})_2[\mathrm{CoCl_4}] \xrightarrow{553-628\ \mathrm{K}} 6\mathrm{NH_4Cl}_{(g)} + 3\mathrm{CoCl_2} \quad (2)$$

III stage (air):

$$6\mathrm{CoCl_2} + 4\mathrm{O}_{2(g)} \xrightarrow{673-888\ \mathrm{K}} 2\mathrm{Co_3O_4} + 6\mathrm{Cl}_{2(g)} \quad (3)$$

III stage (argon):

$$\mathrm{CoCl}_{2(s)} \xrightarrow{678-1018\ \mathrm{K}} \mathrm{CoCl}_{2(g)} \quad (4)$$

IV stage (only in air):

$$\mathrm{Co_3O_4} \xrightarrow{1213-1228\ \mathrm{K}} 3\mathrm{CoO} + 1/2\ \mathrm{O}_{2(g)} \quad (5)$$

The reaction (1, 2) are compatible with those of Simons and Wendlandt [1].

Table 1 Numerical data, resulting from the analysis of the TG curves obtained for thermal decomposition of $[Co(NH_3)_6]Cl_3$ in air/argon atmospheres, for the most probably mechanisms

Stage	Atm.	Mechanism*	E_a, kJ/mol	Statistical parameters			
				r	F	F_{cr}	S
I	argon	D_4	228.3	0.998743	1587	16.3	0.005113
		R_2	120.5	0.998545	1372	($N=7$)	0.010413
			($\alpha=0.06$–0.76)				
II	argon	R_2	119.7	0.995755	351	34.1	0.013385
		D_4	219.9	0.995253	314	($N=5$)	0.007705
			($\alpha=0.10$–0.80)				
III	argon	R_1	50.1	0.996287	1205	10.6	0.020234
		D_1	110.2	0.996282	1204	($N=11$)	0.010125
			($\alpha=0.05$–0.79)				
I	air	R_2	114.6	0.999672	6103	21.2	0.004990
		D_4	214.9	0.999247	2652	($N=6$)	0.004042
			($\alpha=0.05$–0.82)				
II	air	D_4	228.1	0.996523	429	34.1	0.008144
		D_2	200.6	0.995581	337	($N=5$)	0.010442
		R_2	121.1	0.994745	283		0.018877
			($\alpha=0.05$–0.78)				
III	air	D_4	184.0	0.996047	1006	11.3	0.007240
		D_2	164.9	0.995462	876	($N=10$)	0.008657
		R_2	99.2	0.995149	819		0.014884
			($\alpha=0.06$–0.78)				

D_1 — one-dimensionl diffusion (power law)
D_2 — two-dimensional diffusion; cylindrical symmetry
D_3 — three-dimensional diffusion; spherical symmetry; Jander equation
D_4 — three-dimensional diffusion; spherical symmetry
F_1 — random nucleation; only one nucleus on each particle
A_2 — random nucleation; Avrami I equation
A_3 — random nucleation; Avrami II equation
R_1 — zero-order mechanism; Polanyi–Wigner equation
R_2 — phase boundary reaction; cylindrical symmetry
R_3 — phase boundary reaction; spherical symmetry

$[Co(NH_3)_5Cl]Cl_2$

I stage (air, argon):

$$6[Co(NH_3)_5Cl]Cl_2 \xrightarrow{433-543\ K} 3CoCl_2 + 3(NH_4)_2[CoCl_4] + N_{2(g)} + 22NH_{3(g)} \quad (6)$$

The subsequent decomposition stages are the same as for $[Co(NH_3)_6]Cl_3$.

$[Co(NH_3)_6]_2(C_2O_4)_3\cdot 4H_2O$

I stage (air, argon):

$$\begin{aligned}3[Co(NH_3)_6]_2(C_2O_4)_3\cdot 4H_2O \xrightarrow{393\text{–}443\ K} & \ 3[Co(NH_3)_5C_2O_4]_2C_2O_4 + \\ & + 6NH_{3(g)} + 12H_2O_{(g)}\end{aligned} \tag{7}$$

IIa and IIb stages (air, argon, see Table 2):

$$\begin{aligned}3[Co(NH_3)_5C_2O_4]_2C_2O_4 \xrightarrow{443\text{–}553\ K} & \ 6CoC_2O_4 + N_{2(g)} + 28NH_{3(g)} + \\ & + 3H_2O_{(g)} + 6CO_{(g)}\end{aligned} \tag{8}$$

Table 2 Kinetic parameters of the thermal decomposition of $[Co(NH_3)_5Cl]Cl_2$ and $[Co(NH_3)_6]_2(C_2O_4)_3\cdot 4H_2O$ in air/argon atmospheres

Compound	Stage	Argon		Air	
		Mechanism*	E_a, kJ/mol	Mechanism	E_a, kJ/mol
$[Co(NH_3)_5Cl]Cl_2$	I	D_2	190.8	D_1	111.3
		D_1	136.3	R_1	55.6
		R_1	68.3	D_2	149.0
			(α=0.10–0.80)		(α=0.09–0.74)
	II	D_1	142.8	D_2	217.2
		R_1	71.4	D_1	149.7
			(α=0.07–0.79)	R_1	74.8
					(α=0.16–0.79)
	III	D_1	281.3	D_4	181.1
		R_1	140.6	R_2	97.2
			(α=0.08–0.77)		(α=0.07–0.84)
$[Co(NH_3)_6]_2(C_2O_4)_3\cdot 4H_2O$	I	R_2	68.1	D_4	152.3
		D_4	127.3	R_2	81.1
			(α=0.06–0.81)		(α=0.03–0.80)
	IIa	D_2	321.1	D_4	317.8
			(α=0.09–0.92)	D_2	270.6
				R_2	173.0
					(α=0.07–0.92)
	IIb	D_1	17.5	D_1	17.6
		R_1	8.7	R_1	8.8
			(α=0.20–0.90)		(α=0.22–0.93)
	III	F_1	202.8	D_1	18.7
		A_2	101.4	R_1	9.4
		A	67.6		(α=0.07–0.77)
			(α=0.04–0.70)		

* See footnote to Table 1

This is the summary reaction. The detailed sequence has been presented in [5].
III stage (air):

$$6CoC_2O_4 \xrightarrow{553\text{–}568\ K} 2Co_3O_4 + 8CO_{(g)} + 4CO_{2(g)} \tag{9}$$

III stage (argon):

$$CoC_2O_4 \xrightarrow{563\text{–}648\ K} Co + 2CO_{2(g)} \tag{10}$$

$$CoC_2O_4 \xrightarrow{563\text{–}648\ K} CoO + CO_{(g)} + CO_{2(g)} \tag{11}$$

$$3CoC_2O_4 \xrightarrow{563\text{–}648\ K} Co_3O_4 + 4CO_{(g)} + 2CO_{2(g)} \tag{12}$$

IV stage (air argon):

$$Co_3O_4 \xrightarrow{1193\text{–}1213\ K} 3CoO + 1/2\, O_{2(g)} \tag{13}$$

Kinetic analysis of the experimental TG curves was performed by means of the method due to Phadnis and Deshpande [6].

Equation (14) was used to obtain the activation energy and to determine a probable mechanism of the particular steps of decomposition of the compounds studied.

$$f(\alpha)g(\alpha) = \frac{RT^2}{E}\frac{d\alpha}{dT} \tag{14}$$

where: $f(\alpha)$ and $g(\alpha)$—algebraic expression of differential and integral functions for the most common mechanisms operating in solid-state decompositions [6, 7].

A linearity of the plot of $f(\alpha)g(\alpha)$ vs. $T^2\frac{d\alpha}{dT}$ indicates the mechanism determining the functional form of α. The plot of the above equation often becomes more or less linear. Therefore it could be very difficult to decide the validity of a particular mechanism for a reaction under investigation and also the real kinetic parameters.

The linear regression parameters were estimated by means of the least square method and a regression analysis for each tested mechanism has been performed. Snedecor's test (F) was used as a measure of the significance of the particular function $f(\alpha)$.

$$F = \frac{r^2(N-2)}{1-r^2} \tag{15}$$

where: r — linear agression coefficient
N — the number of measured points

If $F \geqslant F_{cr}$ we assumed that the functional form $f(\alpha)$ had been essential and therefore we assigned the probably mechanism of the deconposition stage. (F_{cr}-critical value of Snedecor's random variable F fitting the condition $P(F \geqslant F_{cr}) = 0.01$).

The values of activation energies (E_a), linear regression coefficients (r) and standard errors of estimation (S), obtained from analysis of the TG curves for $[Co(NH_3)_6]Cl_3$ as an example are listed in Table 1. Kinetic parameters of the thermal decomposition of $[Co(NH_3)_5Cl]Cl_2$ and $[Co(NH_3)_6]_2(C_2O_4)_3 \cdot 4H_2O$ are given in Table 2.

Generally, we suppose that the particular decomposition stages of the complexes studied consist of few chemical reactions. The most complicated one is the stage IIa of $[Co(NH_3)_6]_2(C_2O_4)_3 \cdot 4H_2O$ decomposition. The decomposition of the compounds under investigations was controlled by diffusion and phase boundary reaction except stage III in the case of oxalate complex in argon (random nucleation, Table 2).

The following relations of the activation energy values of the existing mechanisms were noticed: $E_a(D_1) \approx 2E_a(R_1)$; $E_a(F_1) \approx 2E_a(A_2) \approx 3E_a(A_3)$, which are analogous to the dependence $E_a(D_3) \approx 2E_a(R_3)$ published by Criado [7].

The kind of the gaseous atmosphere effects only a mechanism of the III stage of decomposition of all compounds studied. It is confirmed by the probably decomposition sequences presented above (3, 4, 9–12).

The mechanism of stage III depends on the complex anion. Simple salts of cobalt(II) i.e. $CoCl_2$ and CoC_2O_4 are the intermediate products at the beginning of the stage III decomposition. At the earlier stages of the decomposition the reduction Co(III) to Co(II) has been observed.

The statistical analysis appears to be more useful for the selection of the probably mechanisms of the thermal decomposition on the basis of the equation (14) than the graphical method suggested by Phadnis and Deshpande [6].

References

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Zusammenfassung — Simultane TG—DTG—DTA-Untersuchungen an den Komplexverbindungen $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$ und $[Co(NH_3)_6]_2(C_2O_4)_3 \cdot 4H_2O$ unter nichtisothermen Bedingungen wurden in Luft und Argonatmosphäre bei 293–1273 K durchgeführt. Die Zersetzung läuft in jeweils drei Stufen ab. Für die kinetische Auswertung der thermischen Zersetzung der Komplexverbindungen aus den dynamischen Gewichtsabnahmekurven wurde der wahrscheinlichste Mechanismus der einzelnen Stufen mit Hilfe von statistischen Analysen ermittelt. Die Zersetzung der Komplexverbindungen wird meist durch Diffusions- und Phasengrenzreaktionen kontrolliert, nur bei der 3. Stufe des Oxalatkomplexes in Argon herrscht statistische Keimbildung. Die Aktivierungsenergien E_a der einzelnen Zersetzungsstufen werden berechnet.

Резюме — В атмосфере воздуха и аргона проведены в интервале температур 293—1273 К неизотермические совмещенные ТГ—ДТГ и ДТА исследования комплексов $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$ и $[Co(NH_3)_6]_2(C_2O_4)_3 \cdot 4H_2O$. Все процессы диссоциации протекают в три стадии. Исходя из данных динамической потери веса, проведена оценка кинетика термического разложения и на основании статистического анализа определен наиболее возможный механизм реакционных стадий. Разложение определяется диффузионным механизмом и механизмом поверхности раздела фаз, за исключением стадии III реакции разложения оксалатного комплекса в аргоне, подчиняющейся механизму произвольного образования центров кристаллизации. Вычислены энергии активации E_a отдельных стадий разложения.