

THERMAL DECOMPOSITION REACTIONS OF AMMINECOBALT(III) COMPLEXES

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Simultaneous TG-DTG-DTA studies under non-isothermal conditions on $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, $[\text{Co}(\text{NH}_3)_5]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_6]_2(\text{C}_2\text{O}_4)_3 \cdot 4\text{H}_2\text{O}$ 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 $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ and $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ are not complete. In the accessible literature there is no data for decomposition of $[\text{Co}(\text{NH}_3)_6]_2(\text{C}_2\text{O}_4)_3 \cdot 4\text{H}_2\text{O}$. 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 $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, pentamminecobalt(III)chloride $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ and hexamminecobalt(III) oxalate tetrahydrate $[\text{Co}(\text{NH}_3)_6]_2(\text{C}_2\text{O}_4)_3 \cdot 4\text{H}_2\text{O}$ were prepared by methods described in [2-4]. The complete analytical data for these complexes is given in the previous paper [5].

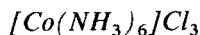
Simultaneous TG-DTG-DTA curves were obtained with a Paulik-Paulik-Erdey

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

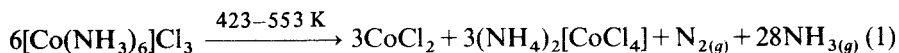
Results and discussion

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.



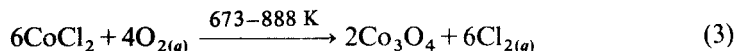
I stage (air, argon):



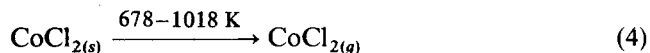
II stage (air, argon):



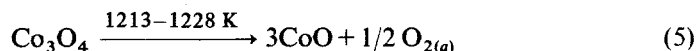
III stage (air):



III stage (argon):



IV stage (only in air):



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 $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ 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	
			($\alpha=0.05-0.78$)					
III	air	R ₂	121.1	0.994745	283		0.018877	
		D ₄	184.0	0.996047	1006	11.3	0.007240	
			($\alpha=0.06-0.78$)					
			D ₂	164.9	0.995462	876	($N=10$)	0.008657
			R ₂	99.2	0.995149	819		0.014884

D₁ — one-dimensional diffusion (power law)

D₂ — two-dimensional diffusion; cylindrical symmetry

D₃ — three-dimensional diffusion; spherical symmetry; Jander equation

D₄ — three-dimensional diffusion; spherical symmetry

F₁ — random nucleation; only one nucleus on each particle

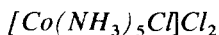
A₂ — random nucleation; Avrami I equation

A₃ — random nucleation; Avrami II equation

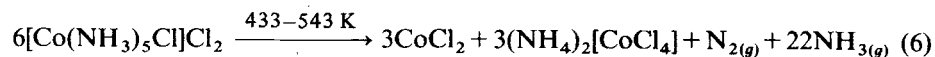
R₁ — zero-order mechanism; Polanyi-Wigner equation

R₂ — phase boundary reaction; cylindrical symmetry

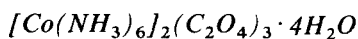
R₃ — phase boundary reaction; spherical symmetry



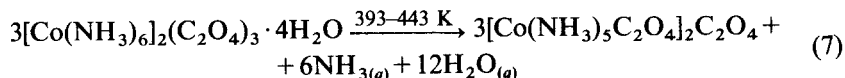
I stage (air, argon):



The subsequent decomposition stages are the same as for $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$.



I stage (air, argon):



Ila and I Ib stages (air, argon, see Table 2):

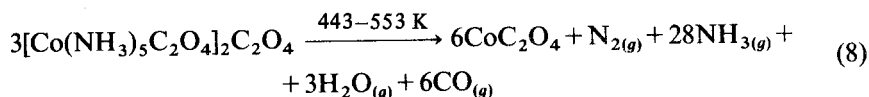
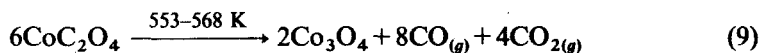


Table 2 Kinetic parameters of the thermal decomposition of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_6]_2(\text{C}_2\text{O}_4)_3 \cdot 4\text{H}_2\text{O}$ in air/argon atmospheres

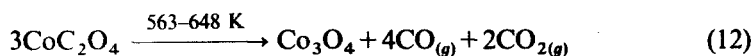
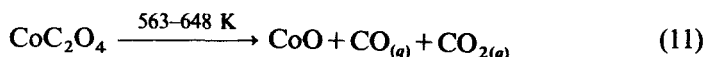
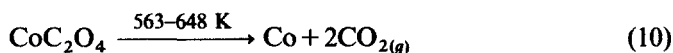
Compound	Stage	Argon		Air	
		Mechanism*	E_a , kJ/mol	Mechanism	E_a , kJ/mol
$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	I	D ₂	190.8	D ₁	111.3
		D ₁	136.3	R ₁	55.6
		R ₁	68.3	D ₂	149.0
			($\alpha=0.10-0.80$)		($\alpha=0.09-0.74$)
	II	D ₁	142.8	D ₂	217.2
		R ₁	71.4	D ₁	149.7
			($\alpha=0.07-0.79$)	R ₁	74.8
				($\alpha=0.16-0.79$)	
	III	D ₁	281.3	D ₄	181.1
R ₁		140.6	R ₂	97.2	
		($\alpha=0.08-0.77$)		($\alpha=0.07-0.84$)	
$[\text{Co}(\text{NH}_3)_6]_2(\text{C}_2\text{O}_4)_3 \cdot 4\text{H}_2\text{O}$	I	R ₂	68.1	D ₄	152.3
		D ₄	127.3	R ₂	81.1
			($\alpha=0.06-0.81$)		($\alpha=0.03-0.80$)
	IIa	D ₂	321.1	D ₄	317.8
			($\alpha=0.09-0.92$)	D ₂	270.6
				R ₂	173.0
				($\alpha=0.07-0.92$)	
	IIb	D ₁	17.5	D ₁	17.6
		R ₁	8.7	R ₁	8.8
			($\alpha=0.20-0.90$)		($\alpha=0.22-0.93$)
	III	F ₁	202.8	D ₁	18.7
		A ₂	101.4	R ₁	9.4
A		67.6		($\alpha=0.07-0.77$)	
		($\alpha=0.04-0.70$)			

* See footnote to Table 1

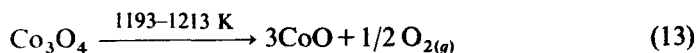
This is the summary reaction. The detailed sequence has been presented in [5].
III stage (air):



III stage (argon):



IV stage (air argon):



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.

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

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 $f(\alpha)$.

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

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

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

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 $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ as an example are listed in Table 1. Kinetic parameters of the thermal decomposition of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_6]_2(\text{C}_2\text{O}_4)_3 \cdot 4\text{H}_2\text{O}$ 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 $[\text{Co}(\text{NH}_3)_6]_2(\text{C}_2\text{O}_4)_3 \cdot 4\text{H}_2\text{O}$ 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: $E_a(\text{D}_1) \approx 2E_a(\text{R}_1)$; $E_a(\text{F}_1) \approx 2E_a(\text{A}_2) \approx 3E_a(\text{A}_3)$, which are analogous to the dependence $E_a(\text{D}_3) \approx 2E_a(\text{R}_3)$ 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

- 1 W. W. Wendlandt and J. P. Smith, *The Thermal Properties of Transition – Metal Ammine Complexes*, Elsevier, Amsterdam 1967, p. 37.
- 2 *Inorg. Synt.*, 2 (1946) 217.
- 3 *Ibid.*, 9 (1977) 160.
- 4 *Ibid.*, 2 (1946) 220.
- 5 E. Ingier-Stocka, in preparation to press.
- 6 A. B. Phadnis and V. V. Deshpande, *Thermochim. Acta*, 62 (1983) 361.
- 7 J. M. Criado, J. Morales and V. Rives, *J. Thermal Anal.*, 14 (1978) 221.

Zusammenfassung — Simultane TG—DTG—DTA-Untersuchungen an den Komplexverbindungen $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ und $[\text{Co}(\text{NH}_3)_6]_2(\text{C}_2\text{O}_4)_3 \cdot 4\text{H}_2\text{O}$ 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 $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ и $[\text{Co}(\text{NH}_3)_6]_2(\text{C}_2\text{O}_4)_3 \cdot 4\text{H}_2\text{O}$. 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.