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THERMAL DECOMPOSITION OF [Co(NH_3)$_5$Cl]Cl_2
II. Kinetics of thermal decomposition

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The thermal decomposition of [Co(NH_3)$_5$Cl]Cl_2 was studied under non-isothermal conditions, in dynamic air and argon atmospheres. The kinetics of the particular stages of [Co(NH_3)$_5$Cl]Cl_2 thermal decomposition were evaluated from the dynamic weight loss data by means of the modified Coats-Redfern method. The D_n and R_n models were selected as the models best fitting the experimental TG curves. These models suggest that the kinetics and macromechanism of [Co(NH_3)$_5$Cl]Cl_2 decomposition can be governed by diffusive and/or phase boundary processes. The values of the activation energy, E_a, and the pre-exponencial factor, A, of the particular stages of the thermal decomposition were calculated.

Numerous authors [1–20] have discussed the usefulness of the different methods of thermal analysis which are employed in kinetic research on the dissociation of solids. Dynamic methods seem to be the most controversial if one uses them to determine the reaction mechanisms and kinetic parameters.

A review of the literature reveals that, for the past two decades, kinetic analysis of dynamic TG curves has been the most popular method for estimation of the kinetic parameters. The differential and/or integral kinetic equations connected with the "mechanism" of the thermal decomposition of solids presented in numerous publications, e.g. [3, 19, 20], have been used for this estimation. The fact that often more than one functional form $f(\alpha)$ or $g(\alpha)$ fit the experimental results is a general disadvantage of all suggested methods. The selection of a proper model is then practically impossible, and this involves the inability to estimate the real kinetic parameters (E, A). Another disadvantage is the problem pointed out by Arnold *et al.* [21–24] that the mathematical method of treatment of the experimental results influences the choice of the best-fitting model.

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On the other hand, many published papers, e.g. [25–30], contain lists of kinetic parameter values (E, A, n) calculated on the basis of different methods. These values are often the same or very close to each other.

In spite of all objections presented in the literature, the non-isothermal methods continue, as hitherto, to be widely used in thermal analysis and are more often used than the isothermal methods. Kinetic studies of the thermal decomposition of solids comprise about 15% of all research on thermal dissociation [18]. This may be a consequence of the practical importance of dynamic methods, as some authors, e.g. [2, 10, 17], have pointed out. The rapidity of obtaining the experimental results and the apparent ease of the determination of the kinetic parameters could be another reason.

The kinetic analysis data publised on the thermal decomposition of $[Co(NH_3)_5Cl]Cl_2$ in the accessible literature are incomplete. The apparent activation energy has been determined only for the first stage of dissociation of the ammine complex [31–33]. The E_a value of 54.06 $kcal \cdot mol^{-1}$ (226.34 $kJ \cdot mol^{-1}$) calculated by Mori and Tsuchiya [33] from isothermal measurements is about twice as high as the 28 $kcal \cdot mol^{-1}$) (117 $kJ \cdot mol^{-1}$) estimated by Wendlandt and Smith [31, 32] via a non–isothermal method.

In the present work, kinetic analysis of experimental TG curves registered under non-isothermal conditions was performed for the particular stages of thermal decomposition of $[Co(NH_3)_5Cl]Cl_2$ by means of the modified Coats–Redfern (CR) method [34,35]. The results of kinetic analysis by means of the Phadnis–Deshpande (PD) method were published earlier [36].

Experimental

Pentaamminecobalt(III) chloride was prepared by the method described in [37]. The complete analytical data on this compound were given in part I [38].

The experimental procedure was the same as that described previously [39].

Results and discussion

The author is aware of the fact that all methods of kinetic investigations relating to the decomposition of solids (particularly powders) provide data of a relative character. They are correct only for the conditions under which the measurement is performed. It has been taken into consideration that the results of the reaction kinetics studies by thermal analysis may contain considerable errors due to the non-isothermal conditions of the measurement.

Kinetic analysis of the thermal decomposition of $[Co(NH_3)_5Cl]Cl_2$ may be performed, because the particular stages of the dissociation were clearly defined in part I of the present work on the basis of the experimental data (thermal and chemical analyses, X-ray diffraction, reflectance spectroscopy, scanning electron microscopy). It was revealed that dissociation of the above complex occurs in three stages in argon and in four stages in air. In the fourth stage, Co_3O_4 is transformed to CoO; kinetic analysis of this stage was not done.

Kinetic analysis of the experimental TG curves recorded under non-isothermal conditions was performed by means of Eq. (1) ((CR) method [34, 35]):

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\frac{AR}{\beta E_a}\left[1-\frac{2RT}{E_a}\right] - \frac{E_a}{RT} \qquad (1)$$

where:

α = conversion degree

A = pre-exponential factor

R = gas constant

β = linear heating rate (deg·min^{-1})

T = temperature (K)

E_a = activation energy

The values of conversion degree, α, were determined for each stage of decomposition of the complex compound. The activation energies, E_a, for the particular stages of decomposition in both argon and air atmospheres were determined from Eq. (1) in the coordinate system ln $[g(\alpha)/T^2]$ *vs.* $10^3/T$. It was primarily assumed that linearity of the plot of the above dependence suggested the "mechanism" connected with a particular functional form of α.

The algebraic expressions of integral $g(\alpha)$ functions for the most common mechanism operating in solid-state decompositions, published e.g. in [3,19,20] and tested in the present work, are listed in Table 1.

The linear regression parameters were estimated by means of the least square method. The regression analysis was performed for each of the tested expressions. Snedecor's test, Eq. (2), was used as a measure of the significance of the particular function $g(\alpha)$:

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

where:

r = linear regression coefficient

N = the number of measuring points

Table 1 Kinetic models investigated

Symbol	$g(\alpha)$	Macromechanism
D_1	α	one–dimensional diffusion (power law)
D_2	$(1-\alpha)\ln(1-\alpha)+\alpha$	two–dimensional diffusion; cylindrical symmetry
D_3	$3/2[1-[1-\alpha)^{1/3}]^2$	three–dimensional diffusion; spherical symmetry, Jander eq.
D_4	$3/2[[1-2/3\alpha-(1-\alpha)^{2/3}]$	three–dimensional diffusion; spherical symmetry, Ginstling–Brounshtein eq.
F_1	$[-\ln(1-\alpha)]$	random nucleation; only one nucleus on each partcle
A_2	$[-\ln(1-\alpha)]^{1/2}$	random nucleation; Avrami I eq.
A_3	$[-\ln(1-\alpha)]^{1/3}$	random nucleation; Avrami II eq.
R_1	α	phase boundary reaction (zero order); Polanyi–Wigner eq.
R_2	$2[1-[1-\alpha)^{1/2}]$	phase boundary reaction; cylindrical symmetry
R_3	$3[1-[1-\alpha)^{1/3}]$	phase boundary reaction; spherical symmetry

If $F \geq F_{cr}$, it was assumed that the functional form $f(\alpha)$ was essential and therefore the "mechanism" of the decomposition stage was assigned as probable. F_{cr} is the critical value of Snedecor's random variable F fitting the condition $P(F \geq F_{cr}) = 0.01$.

Values of the apparent activation energy, E_a, pre–exponential factor A, linear regression coefficient r, Snedecor's variable F, and the standard error of estimation S, obtained from analysis of the dynamic TG curves on the basis of Eq. (1), are listed in Table 2. The values in Table 2 were obtained from those tested equations which best fit the experimental TG curves. From Table 2, it can be seen that the best-fitting expressions for the first stage of $[Co(NH_3)_5Cl]Cl_2$ decomposition in air and argon are the same. These are the D_1, D_2 and R_1 functions. The activation energy values calculated for a particular model (e.g. D_1) in both gaseous atmospheres are very close to each other. This is in agreement with the sequences of thermal decomposition of $[Co(NH_3)_5Cl]Cl_2$ for stage I presented in [38]. The E_a values evaluated for the D_1 model is close to the E_a value of 117.2 $kJ \cdot mol^{-1}$ calculated by the Freeman–Carroll method and reported by Wendlandt and Smith [31, 32].

The best-fitting models selected for the second stage of dissociation in air (D_1, D_2) and argon (F_1, D_3) atmospheres are different, but the sequences of the decomposition are the same [38]. The secondary reaction suggested in

[38] can probably influence the course of this stage in argon (e.g. the main and secondary reactions proceed in parallel). On the other hand, the results obtained with the PD method [40] under strictly the same experimental conditions and reported in [36] are in agreement with the sequences of decomposition not only for the first stage, but also for the second.

Table 2 Kinetic parameters values from dynamic TG experiments in air and argon atmospheres; m = 200 mg, $\beta = 1.25$ deg·min^{-1}

Stage, atm.	Range of α	Model	E_a, kJ mol^{-1}	A, min^{-1}	Statistical parameters		
					r	F*	S
I Air	0.09–0.74	D_2	139.9	$3.28\cdot10^{12}$	0.9998	12428	0.026133
		D_1	128.4	$2.97\cdot10^{11}$	0.9998	12027	0.024383
		R_1	60.0	$1.69\cdot10^{4}$	0.9998	9240	0.012990
II Air	0.16–0.79	D_1	145.6	$2.33\cdot10^{11}$	0.9998	12230	0.019191
		D_2	163.1	$6.14\cdot10^{12}$	0.9989	1809	0.055920
		D_4	170.5	$1.02\cdot10^{13}$	0.9983	1181	0.072362
III Air	0.07–0.84	D_4	156.1	$3.78\cdot10^{7}$	0.9999	37817	0.023001
		R_2	73.0	$3.57\cdot10^{2}$	0.9998	20997	0.014431
I Argon	0.10–0.80	D_1	128.9	$8.76\cdot10^{10}$	0.9985	1303	0.004799
		R_1	57.2	$7.90\cdot10^{3}$	0.9983	1207	0.004987
		D_2	133.7	$7.39\cdot10^{11}$	0.9969	643	0.006820
II Argon	0.07–0.79	F_1	128.9	$2.13\cdot10^{10}$	0.9972	904	0.005175
		D_3	243.3	$5.51\cdot10^{19}$	0.9966	722	0.005789
		A_2	58.6	$2.24\cdot10^{3}$	0.9965	707	0.005848
III Argon	0.08–0.77	D_1	105.5	$7.44\cdot10^{2}$	0.9803	270	0.017990
		D_2	116.2	$2.24\cdot10^{3}$	0.9746	208	0.020385
		R_1	45.3	$9.10\cdot10^{1}$	0.9743	206	0.020480

*F_{cr} values are within the range 9.65–21.2

The courses of the third stage of dissociation in air and argon are different, as was revealed earlier [38], and the funcions $g(\alpha)$ selected for these stages are also different. These are the D_4, R_2 models in air and the D_1, D_2, R_1 models in argon.

A comparison of the best-fitting kinetic models selected by the CR method (Table 2) and the PD method [36] demonstrates their convergence for all stages of the decomposition in air and for stages I and III in argon.

The activation energy values estimated for properly chosen models by the CR of PD method differ more of less, depending on the kinetic model and the decomposition stage. For instance, in air atmosphere for stage I the values of $E_a(R_1)$ – PD and $E_a(R_1)$ – CR are nearest to each other, whereas the $E_a(D_1)$ – PD and $E_a(D_1)$ – CR values are nearest for stage II.

For stage I in argon, the nearest values of E_a are $E_a(D_1)$ – PD and $E_a(D_2)$ – CR, while for stage II they are $E_a(D_1)$ – PD and $E_a(F_1)$ – CR. The highest divergence is shown by the E_a values computed with the CR and PD methods for stage III in argon. This may suggest that the determined activation energy values depend more on the method of mathematical treatment than on the experiment itself.

The $E_a(R_1D_1)$ values computed with the CR method for stage III of $[Co(NH_3)_5Cl]Cl_2$ dissociation in argon are close to the $E_a(R_1D_1)$ values estimated for this stage of $[Co(NH_3)_6]Cl_2$ decomposition with the PD method (very close experimental conditions) [36]. It should be noted that the sequences of stage III of the thermal decomposition of the penta- and hexaammine complexes are the same.

If the assumption is made that the form of $f(\alpha)$ or $g(\alpha)$ is connected with the reaction macromechanism, then it may be considered that the pairs of the D_nR_n mechanism selected for all stages of $[Co(NH_3)_5Cl]Cl_3$ decomposition (in air) are not in conflict with the results of morphological studies presented in part I [38].

The principal conclusion resulting from the data presented above is that the selection of only one kinetic model on the basis of dynamic measurements is practically impossible if the presented method (CR) is used. Of course, it is possible to force a selection of one model with the highest value of Snedecor's variable, F, or the regression coefficient, r, but the differences in their values presented in Table 2 do not entitle the author to do this.

Conclusions

The results presented above show that the particular stages of thermal decomposition of $[Co(NH_3)_5Cl]Cl_2$ in both air and argon atmospheres are governed by diffusive and/or phase boundary reactions (except for stage II in argon). The models D_nR_n are those best fitting the experimental TG curves. This is in agreement with the morphological observations presented previously [38].

The experimental results confirm the probblem, mentioned many times, that it is impossible to choose one kinetic model from dynamic measurements.

The results have confirmed the opinion presented earlier, e.g. by Arnold *et al.* [21–24] and in [41], that the mathematical method of treatment of the experimental results sometimes influences the kinetic parameter values.

It seems to be necessary to study the thermal decomposition of [Co(NH$_3$)$_5$Cl]Cl$_2$ under isothermal conditions, to check if the combination of isothermal and non-isothermal measurements allows easier selection of the models best-fitting the experimental TG curves, followed by the calculation of reliable kinetic parameters.

References

1 J. H. Flynn, J. Thermal Anal., 34 (1988) 367.
2 W. W. Wendlandt, Thermal Methods of Analysis, J. Wiley and Sons, New York, 2nd edn., 1973, p. 43.
3 W. E. Brown, D. Dollimore and A. K. Galwey, Comprehensive Chemical Kinetics, C. H. Bamford and C. F. H. Tipper (Eds.), vol. 22, Elsevier, Amsterdam 1980.
4 J. M. Criado, M. Gonzalez, A. Ortega and C. Real, J. Thermal Anal., 34 (1988) 1387.
5 N. Z. Lyakhov, M. Maciejewski and A. Reller, J. Solid State Chem., 58 (1985) 398.
6 A. Reller and H. R. Oswald, J. Solid State Chem., 62 (1986) 306.
7 Z. G. Szabo, Thermochim. Acta, 135 (1988) 59
8 M. Reading, Thermochim. Acta, 135 (1988) 32.
9 P. D. Garn, Thermochim. Acta, 135 (1988) 71.
10 H. Tanaka, Proc. 10th Int. Conf. on the Reactivity of Solids, Materials Science Monographs 28B, Elsevier, Amsterdam 1985, p. 643.
11 M. Maciejewski, J. Thermal Anal., 33 (1988) 243.
12 C. Rózycki and M. Maciejewski, Thermochim. Acta, 96 (1985) 91.
13 H. Anderson, J. Thermal Anal., 33 (1988) 133.
14 J. Šestàk, J. Thermal Anal., 16 (1979) 503.
15 L. Reich and S. S. Stivala, Thermochim. Acta, 60 (1983) 251.
16 R. Gomez-Villacieros, L. Hernan, J. Morales, A. Ortega and J. L. Tirado, Thermochim. Acta, 85 (1985) 283.
17 E. Urbanovici and E. Segal, J. Thermal Anal., 33 (1988) 265.
18 G. Liptay, Thermochim. Acta, 150 (1989) 93.
19 L. Reich and S. S. Stivala, Thermochim. Acta, 73 (1984) 165.
20 J. M. Criado, J. Morales and V. Rives, J. Thermal Anal., 14 (1978) 221.
21 M. Arnold, G. E. Veress, J. Paulik and F. Paulik, J. Thermal Anal., 17 (1979) 507
22 M. Arnold, G. E. Veress, J. Paulik and F. Paulik, 6th ICTA Proc., 1 (1980) 69.
23 M. Arnold, G. E. Veress, J. Paulik and F. Paulik, Anal. Chim., Acta, 124 (1981) 341.
24 M. Arnold, G. E. Veress, J. Paulik and F. Paulik, Thermochim. Acta, 52 (1982) 67.
25 M. Badea and D. Marinescu, Thermochim. Acta, 149 (1989) 189.
26 M. Badea and E. Segal, Thermochim. Acta, 149 (1989) 251.
27 M. E. M. Emam, J. Thermal Anal., 34 (1988) 1241.
28 J. E. House, Jr. and G. L. Jeyaray, J. Thermal Anal., 29 (1984) 41.
29 H. Langfelderova, M. Linkesová, P. Ambrovic and Riedlmajerova, J. Thermal Anal., 35 (1989) 857.
30 M. E. M. Emam, J. Thermal Anal., 35 (1989) 775.
31 W. W. Wendlandt and J. P. Smith, Thermal Properties of Transition Metal Ammine Complexes, Elsevier, Amsterdam 1967, Chapt. 4.
32 W. W. Wendlandt and J. P. Smith, J. Inorg. Nucl. Chem., 25 (1963) 843.
33 M. Mori and R. Tsuchiya, Bull. Chem. Soc. Jpn., 32 (1958) 467.

34 A. W. Coats and J. P. Redfern, Nature, 201 (1964) 68.
35 J. Zsakó, J. Thermal Anal., 5 (1973) 239.
36 E. Ingier-Stocka, J. Thermal Anal., 33 (1988) 487.
37 Inorg. Synth., 9 (1977) 160.
38 E. Ingier-Stocka, J. Thermal Anal., in press

Zusammenfassung — In dynamischer Luft- bzw. Argonatmosphäre wurde die thermische Zersetzung von $[Co(NH_3)_5Cl]Cl_2$ unter nichtisothermen Bedingungen untersucht. Die Kinetik für die Einzelschritte der thermischen Zersetzung von $[Co(NH_3)_5Cl]Cl_2$ wurde mit Hilfe der modifizierten Coats-Redfern-Methode anhand der dynamischen Masseverlustangaben entwickelt. Dabei standen die Modelle D_n und R_n am besten mit den experimentellen TG-Kurven in Übereinstimmung. Diese Modelle lassen darauf schließen, daß die Kinetik und der Makromechanismus der Zersetzung von $[Co(NH_3)_5Cl]Cl_2$ durch Diffusions- und/oder durch Phasen-grenzprozesse kontrolliert werden. Für die einzelnen Teilschritte der thermischen Zersetzung wurden auch die Aktivierungsenergie E_a und der präexponentielle Faktor A berechnet.