

THE EFFECT OF EXPERIMENTAL METHODS AND MEASUREMENT CONDITIONS ON VALUES OF THE KINETIC PARAMETERS OF $[\text{Co}(\text{NH}_3)_6]_2(\text{C}_2\text{O}_4)_3 \cdot 4\text{H}_2\text{O}$

Thermal decomposition

E. Ingier-Stocka

INSTITUTE OF INORGANIC CHEMISTRY AND METALLURGY OF RARE ELEMENTS
TECHNICAL UNIVERSITY OF WROCLAW, WYBRZEZE WYSPIANSKIEGO 27, 50-370
WROCLAW, POLAND

Using the thermal decomposition of $[\text{Co}(\text{NH}_3)_6]_2(\text{C}_2\text{O}_4)_3 \cdot 4\text{H}_2\text{O}$ as a basis, the paper presents results which show how computed values of kinetic parameters are influenced by experimental conditions (ambient atmosphere, sample mass, linear heating rate) when using the non-isothermal methods and the Coats-Redfern (CR) modified equation. It also illustrates the influence of the experimental methods i.e. non-isothermal and isothermal (conventional) methods and also a quasi-isothermal-isobaric one which can be recognised as equivalent to Constant Rate Thermal Analysis (CRTA). The results obtained have confirmed the significant influence of the experimental parameters as well as that of the experimental method used on the estimated values of kinetic parameters. The correlation between activation energy (E) and sample mass (m) or heating rate (β) is generally of a linear nature: $E = a + bx$

Keywords: $[\text{Co}(\text{NH}_3)_6]_2(\text{C}_2\text{O}_4)_3 \cdot 4\text{H}_2\text{O}$, experimental conditions, kinetic parameters

Introduction

A survey of the literature dealing with solid-state thermal decomposition reactions shows the influence of measurement conditions on the course of the thermal dissociation of many species under investigation and on the computed values of kinetic parameters (E , A) obtained [1-15]. Therefore there are many objections to the values of kinetic parameters determined from experimental decomposition curves obtained when using non-isothermal and/or isothermal methods [4, 13, 16-22].

The Constant Rate Thermal Analysis (CRTA) method has recently been suggested as a new way to forward the kinetics of heterogeneous solid-state decomposition reactions [16, 23]. The nature and number of possibilities of the CRTA method were reviewed recently by Rouquerol [23]. During the last few years only

a few papers illustrating the suitability of the CRTA method for kinetic studies have been published [4, 24–26].

The aim of this paper is to demonstrate, using the thermal decomposition of $[\text{Co}(\text{NH}_3)_6]_2(\text{C}_2\text{O}_4)_3 \cdot 4\text{H}_2\text{O}$, how the computed values of kinetic parameters are influenced by experimental conditions such as ambient atmosphere, sample mass and linear heating rates when using:

- the non-isothermal method
- the Coats-Redfern modified equation
- a type of experimental method i.e. non-isothermal and isothermal (conventional methods) and a quasi-isothermal-isobaric one, which can be recognised as equivalent to the CRTA method [16, 27].

Experimental

The complex $[\text{Co}(\text{NH}_3)_6]_2(\text{C}_2\text{O}_4)_3 \cdot 4\text{H}_2\text{O}$ was prepared as suggested in the literature [28]. Analytical data are given in reference [29]. Measurements of the thermal decomposition of this amine complex under non-isothermal, isothermal and quasi-isothermal-isobaric conditions were carried out using a Derivatograph C (MOM, Budapest) in flowing air or argon atmospheres ($\sim 4 \text{ dm}^3 \text{ h}^{-1}$) between 293 and 873 K.

A sample mass of 40 mg was chosen after preliminary measurements [29, 30] showed this to be the best amount of the compound for the main part of the experiments carried out on the Derivatograph and these are presented in this paper.

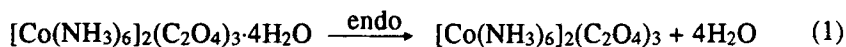
Results and discussion

Effect of the ambient atmosphere and the measurement method

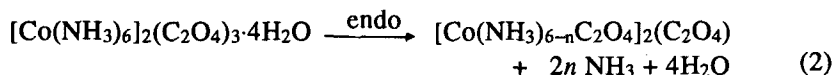
The thermal decomposition of $[\text{Co}(\text{NH}_3)_6]_2(\text{C}_2\text{O}_4)_3 \cdot 4\text{H}_2\text{O}$ proceeds in three stages in both air and argon atmospheres as was proved earlier [29, 35]. On the basis of the physicochemical measurements the probable decomposition sequences are as follows:

Stage I (air, argon)

Non-isothermal and isothermal conditions



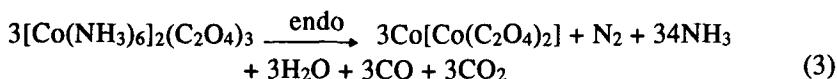
Quasi-isothermal-isobaric conditions



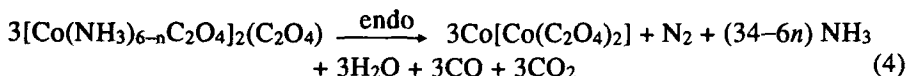
where $n = 1$ or 2

Stage II (air, argon)

Non-isothermal and isothermal conditions

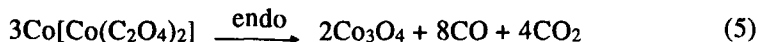


Quasi-isothermal-isobaric conditions

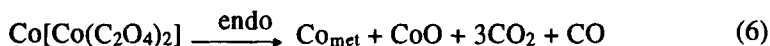


Stage III (air)

Non-isothermal and isothermal conditions



Quasi-isothermal-isobaric conditions

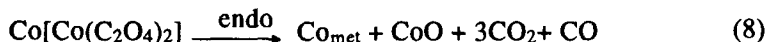


Stage III (argon)

Non-isothermal, quasi-isothermal-isobaric conditions



Isothermal conditions



It should be pointed out that the courses of the first and second stages of decomposition are the same in both atmospheres, but the ambient atmosphere and experimental conditions influence the third stage of the decomposition as well as its final products. This influence is probably connected with the type of gaseous atmosphere within the crucible and bed of the compound during decomposition. The thermal decomposition in quasi-isothermal-isobaric conditions (labyrinth Pt crucible) takes place in an atmosphere of the gaseous products of the dissociation. Thus the ambient atmosphere does not have an influence here, as it does in the non-isothermal or isothermal conditions.

Non-isothermal experiments

Kinetic analysis of the experimental TG curves obtained under non-isothermal conditions and with various heating rates and sample mass was carried out using the Coats-Redfern (CR) method [32, 33] according to the equation:

$$\ln \left(\frac{g(\alpha)}{T^2} \right) = \ln \frac{AR}{\beta E} \left(1 - \frac{2RT}{E} \right) - \frac{E}{RT} \quad (9)$$

where α is the degree of conversion, A – the pre-exponential factor, R – the gas constant, β – the linear heating rate, T – the temperature, E – the activation energy, $g(\alpha)$ – integral functions for the common mechanism solid-state decompositions [19, 34, 35].

The procedure used for estimating E values, together with values obtained, are given in references [30, 34]. The equations determined which describe the dependence of E on m and E on β for the selected best models are listed in Tables 1 and 2. The values of activation energy calculated assuming these dependences for $\beta = 1 \text{ deg}\cdot\text{min}^{-1}$ and $m = 40 \text{ mg}$ are shown in Table 3. For comparison, the values of E estimated by Kissinger's method [31, 36] and by the Arnold-Somogyvári-Paulik-Paulik method [31, 37] (using the software of the Derivatograph) are also given in Table 3.

Table 1 Dependence of activation energy on sample mass (air)

Model	Dependence: $E = a + bm$					
	Stage I			Stage II		
	a	b	r	a	b	r
F_1	128.0	-0.22	0.9899	193.1	+0.28	0.9942
A_2	60.7	-0.11	0.9905	92.7	+0.14	0.9937
A_3	38.3	-0.07	0.9912	59.3	+0.09	0.9915

From Tables 1 and 2 it can be seen that the present results confirm the significant influence of the experimental parameters, i.e. sample mass and heating rate, on the estimated values of the activation energy. The E values calculated from the equation $E = f(\beta)$ for stage III (Tables 1 and 2) are more or less over-estimated compared with those determined by the isothermal method ($E = 184 \text{ kJ}\cdot\text{mol}^{-1}$) or from a single rising temperature non-isothermal experiment ($E(F_1) = 195 \text{ kJ}\cdot\text{mol}^{-1}$; $E(A_2) = 93 \text{ kJ}\cdot\text{mol}^{-1}$) with $m = 40 \text{ mg}$ and β (set value) = $1 \text{ deg}\cdot\text{min}^{-1}$.

Table 2 Dependence of activation energy on heating rate (air)

Stage	Dependence	Range of β	Model					
			F_1		A_2		A_3	
			a	b	a	b	a	b
I	$E = a - b\beta$	1-10	117.0	2.48	57.5	1.54	36.2	1.04
II	$E = a - b\beta$	1-20	208.8	3.06	100.6	1.55	64.5	1.05
III	$E = a - b\beta$	3.7-23.6*	761.1	23.49	375.4	11.64	248.6	7.86
III	$E = \exp(a - b\beta)$	3.7-23.6*	6.8	0.06	6.1	0.06	5.7	0.06

*the β values observed in stage III were obtained at a strong exothermic effect of the reaction; the range of β set values was 2-20 deg min⁻¹

Isothermal experiments

The kinetic model functions in integral form $g(\alpha)$ were examined for the particular stages of the thermal decomposition of $[\text{Co}(\text{NH}_3)_6]_2(\text{C}_2\text{O}_4)_3 \cdot 4\text{H}_2\text{O}$ using conventional isothermal analysis, using the following equation:

$$g(\alpha) = kt \quad (13)$$

where k is the rate constant and t the isothermal run time. The E values calculated using the best models for stages I–III are listed in Table 3. Because the activation energy values determined by the isothermal method are nearly the same for various well-fitting models, average values are shown. All the original data has been reported previously [38].

Table 3 Activation energy values determined by various experimental methods (air)

Model	$E / \text{kJ} \cdot \text{mol}^{-1}$			Method of estimation	Experim. method
	I stage	II stage	III stage		
F_1	115 ^a	206 ^a	719 ^d	CR	ni(TG)
A_2	56 ^a	99 ^a	357 ^d	CR	ni(TG)
A_3	35 ^a	63 ^a	239 ^d	CR	ni(TG)
–	103	136	135	K	ni(DTG)
–	107	131	131	K	ni(DSC)
–	126	132	–	ASPP	ni(TG-DTG)
–	98	103	184		i
–	68 ^b	108	173	FS	qii
	94 ^c				

CR – Coats-Redfern method; K – Kissinger method; ASPP – Arnold-Somogyvári-Paulik-Paulik method; FS – Fatu-Segal method; ^a – E values calculated from a linear dependence $E = a + b\beta$ for $\beta = 1$; ^b – $\alpha < 0.6$; ^c – $\alpha \geq 0.6$; ^d – E values calculated from exponential dependence $E = \exp(a + b\beta)$ for $\beta = 3.7$; ni – non-isothermal; i – isothermal; qii – quasi-isothermal-isobaric method

Quasi-isothermal-isobaric experiments

Determination of the activation energy from QTG experiments was based on the method described in Ref. [26] using Eq. (14).

$$\ln A - \frac{E}{RT} + \ln f(\alpha) = \ln c_i \quad (14)$$

where $c_i = \frac{d\alpha}{dt}$ – a constant rate; $f(\alpha)$ is a differential function for the common mechanisms operating in solid-state reactions; A , E , R , T and α have their usual meanings.

A series of experiments was carried out at different but constant decomposition rates (c_1, c_2, \dots). For a series of a given value of α in each experiment (for example $\alpha = 0.5$) the activation energy E was determined using Eq. (15).

$$E = -R \frac{\Delta \ln c}{\Delta (1/T)} \quad (15)$$

The characteristics of all the isokinetic T - α curves and the calculated E values, together with a discussion, have been given previously [39]. The mean values of E for the particular stages of the decomposition are presented in Table 3. For stages II and III the calculated activation energy values were constant over the whole range of α which fulfilled the isokinetic conditions ($0.2 < \alpha < 0.8$ for stage II and $0.45 < \alpha < 0.8$ for stage III). For stage I the condition $d\alpha/dt = c$ was only fulfilled over a narrow interval of conversion ($0.45 < \alpha < 0.65$) making the determined values of E rather doubtful.

Comparison of the results

The data listed in Table 3 show quite good agreement between the E values obtained using isothermal (i) and quasi-isothermal-isobaric (qii) methods for stages I and II. When using non-isothermal (ni) methods for stage I, the nearest E values to $E(i)$ or $E(qii)$ are those determined using the Kissinger equation (DTG and DSC curves). For the second stage the $E(ni)$ values calculated for the A_2 model using linear dependence given in Table 1 and 2 are quite close to $E_{av}(i)$ or $E_{av}(qii)$.

For stage III the results cannot be compared because of the different residues obtained by the different experimental methods. Additionally, a sudden periodic jump in temperature was observed in the course of non-isothermal and isothermal experiments, which resulted in some perturbation of the linear rise of temperature or its stability [30, 38]. Details of the way to determine E values in this case have already been presented [30, 38]. Only E values for isothermal and non-isothermal conditions can be compared, and they are relatively close to each other.

The values calculated by the Kissinger method are clearly lower ($E = 130 \text{ kJ}\cdot\text{mol}^{-1}$) and the nearest to $E = 110 \text{ kJ}\cdot\text{mol}^{-1}$ the value estimated by Deb *et al.* [40] using non-isothermal TG curves for the decomposition of $\text{Co}[\text{Co}(\text{C}_2\text{O}_4)_2]$ in air.

The activation energy value of $E(qii) = 173 \text{ kJ}\cdot\text{mol}^{-1}$ is somewhat lower than that calculated by Deb ($E = 191 \text{ kJ}\cdot\text{mol}^{-1}$) for the decomposition of $\text{Co}[\text{Co}(\text{C}_2\text{O}_4)_2]$ in nitrogen. The dissociation sequences determined by Deb, as well as those presented in this paper for stage III in air and qii conditions (Eq. 6), are the same.

Conclusions

1. The thermal decomposition of $[\text{Co}(\text{NH}_3)_6]_2(\text{C}_2\text{O}_4)_3 \cdot 4\text{H}_2\text{O}$ occurs in three stages in argon or air atmospheres.
2. The courses of the first and second stages of decomposition are the same in both atmospheres.
3. The ambient atmosphere and the experimental methods influence the third stage of decomposition as well as its final products.
4. The values of activation energy are influenced by experimental conditions. It can be described as a linear correlation for stages I and II and as an exponential one for stage III.
5. In general, the E values decrease with increase in sample mass and heating rate.
6. The E values obtained from isothermal and quasi-isothermal-isobaric methods are in good agreement for stages I and II.
7. The E values for stage III determined in isothermal and non-isothermal conditions can be compared (the same final residues) and they are relatively close to each other.

References

- 1 W. W. Wendlandt, *Thermal Analysis*, J. Wiley and Sons, 3rd ed., New York 1986.
- 2 J. Paulik and F. Paulik, *Simultaneous Thermoanalytical Examinations by Means of the Derivatograph* p8 in *Thermal Analysis*, Vol. XII, Part A, W. W. Wendlandt (Ed.), Elsevier, Amsterdam 1981.
- 3 G. Widmann and R. Riesen, *Thermal Analysis, Terms, Methods, Applications*, A. Hüthig, Verlag Heidelberg 1987.
- 4 M. Reading, D. Dollimore, J. Rouquerol and F. Rouquerol, *J. Thermal Anal.*, 29 (1984) 775.
- 5 J. Pysiak, *Thermochim. Acta*, 148 (1989) 165.
- 6 D. Dollimore and T. A. Evans, *Thermochim. Acta*, 178 (1991) 263.
- 7 D. Dollimore and T. A. Evans, *Thermochim. Acta*, 179 (1991) 49.
- 8 P. D. Garn, *Thermochim. Acta*, 135 (1988) 71.
- 9 K. N. Ninan and C. G. R. Nair, *Thermochim. Acta*, 30 (1979) 25.
- 10 J. Simon, *J. Thermal Analysis*, 5 (1973) 271.
- 11 D. T. Y. Chen, *J. Thermal Analysis*, 7 (1975) 61.
- 12 P. K. Gallagher and D. W. Johnson, *Thermochim. Acta*, 6 (1973) 67.
- 13 M. Arnold, G. E. Veress, J. Paulik and F. Paulik, *J. Thermal Anal.*, 17 (1979) 507; *Anal. Chim. Acta*, 124 (1981) 341.
- 14 D. Blecic and Z. D. Zivkovic, *Thermochim. Acta*, 60 (1983) 69.
- 15 M. E. M. Emam, *J. Thermal. Anal.*, 35 (1989) 775.
- 16 M. Reading, *Thermochim. Acta*, 135 (1988) 37.
- 17 J. H. Flynn, *J. Thermal Anal.*, 34 (1988) 367.
- 18 J. Šesták, *Thermophysical Properties of Solids, Their Measurements and Theoretical Thermal Analysis*, Academia Prague 1984, Chapt. 8 and 9.
- 19 W. E. Brown, D. Dollimore and A. K. Galwey, *Comprehensive Chemical Kinetics*, vol. 22, Ed. C. H. Bamford and C. F. H. Tipper, Elsevier, Amsterdam 1980.
- 20 P. D. Garn, *J. Thermal Anal.*, 13 (1978) 581.

- 21 F. Paulik and J. Paulik, *Thermochim. Acta*, 4 (1972) 189.
- 22 G. Liptay, *Thermochim. Acta*, 150 (1989) 93.
- 23 J. Rouquerol, *Thermochim. Acta*, 144 (1989) 209.
- 24 A. Ortega, S. Akhauayri, F. Rouquerol and J. Rouquerol, *Thermochim. Acta*, 163 (1990) 25.
- 25 J. M. Criado, F. Rouquerol and J. Rouquerol, *Thermochim. Acta*, 38 (1980) 109.
- 26 D. Fatu and E. Segal, *Thermochim. Acta*, 61 (1983) 215.
- 27 F. Paulik and J. Paulik, *J. Thermal Anal.*, 5 (1973) 253.
- 28 *Inorg. Synt.*, 2 (1946) 220.
- 29 E. Ingier-Stocka, *Thermochim. Acta* (in press).
- 30 E. Ingier-Stocka, *Thermochim. Acta* (in press).
- 31 E. Ingier-Stocka, *J. Thermal Anal.*, 36 (1990) 2139.
- 32 A. V. Coats and J. P. Redfern, *Nature (London)*, 201 (1964) 68.
- 33 J. Zsako, *J. Thermal Anal.*, 5 (1973) 239.
- 34 E. Ingier-Stocka, *Thermochim. Acta*, 170 (1990) 107.
- 35 J. M. Criado, J. Morales and V. Rives, *J. Thermal Anal.*, 14 (1978) 221.
- 36 H. E. Kissinger, *Anal. Chem.*, 29 (1957) 1702.
- 37 M. Arnold, P. Somogyvári, J. Paulik and F. Paulik, *J. Thermal Anal.*, 32 (1987) 679.
- 38 E. Ingier-Stocka, in preparation.
- 39 E. Ingier-Stocka, in preparation.
- 40 N. Deb, P. K. Gogoi and N. N. Dass, *J. Thermal Anal.*, 35 (1989) 27.

Zusammenfassung — Vor dem Hintergrund der thermischen Zersetzung von $[\text{Co}(\text{NH}_3)_6]_2(\text{C}_2\text{O}_4) \cdot 34\text{H}_2\text{O}$ werden Resultate dargelegt, wie berechnete kinetische Parameter bei Anwendung der nichtisothermen Methode und der modifizierten Coats-Redfern (CR) Gleichung durch Versuchsbedingungen (Atmosphäre, Probenmasse, lineare Aufheizgeschwindigkeit) beeinflusst werden. Außerdem wird der Einfluß der experimentellen Methoden, d.h. der nichtisothermen und isothermen (konventionellen) Methoden sowie eine quasi-isotherme-isobare Methode dargelegt, die als äquivalent zur Constant Rate Thermal Analysis (CRTA) anerkannt werden kann. Die Resultate bestätigen einen bedeutenden Einfluß sowohl der Versuchsbedingungen als auch der Versuchsmethode zur Schätzung der kinetischen Parameter. Die Korrelation zwischen der Aktivierungsenergie (E) und der Probenmasse (m) oder Aufheizgeschwindigkeit (β) ist im allgemeinen linear: $E = a + bx$.