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KINETICS OF THE THERMAL DECOMPOSITION OF $[Co(NH_3)_6]_2(C_2O_4)_3{\cdot}4H_2O$

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Abstract

The thermal decomposition of $[Co(NH_3)_6]_2(C_2O_4)_3{\cdot}4H_2O$ was studied under isothermal conditions in flowing air and argon. Dissociation of the above complex occurs in three stages. The kinetics of the particular stages thermal decomposition have been evaluated. The R_N and/or A_M models were selected as those best fitting the experimental TG curves. The activation energies, E, and ln$A$ were calculated with a conventional procedure and by a new method suggested by Koga *et al.* [10, 11]. Comparison of the results have showed that the Arrhenius parameters values estimated by the use of both methods are very close. The calculated activation energies were in air: 96 kJ mol^{-1} ($R_{1.575}$, stage I); 101 kJ mol^{-1} ($A_{1.725}$, stage II); 185 kJ mol^{-1} ($A_{2.9}$, stage III) and in argon: 66 kJ mol^{-1} ($A_{1.25}$, stage I); 87 kJ mol^{-1} ($A_{1.825}$, stage II); 133 kJ mol^{-1} ($A_{2.525}$, stage III).

Keywords: $[Co(NH_3)_6]_2(C_2O_4)_3{\cdot}4H_2O$, kinetic parameters, thermal decomposition

Introduction

Investigations of the thermal decomposition kinetics of solids including complex compounds have been carried out for many years and their usefulness has not been questioned. However reality of the determined kinetic parameters is doubtful. As it is well known the thermal decomposition of solids can be investigated by isothermal or rising temperature techniques or by so-called CRTA methods (Controlled Transformation Rate Thermal Analysis) which have recently met with considerable approval [1–6]. But their spread is delayed by lack of commercial equipment. This being so the isothermal method is still widely used to evaluate kinetic parameters of dissociation of solids.

Up to now two procedures based on testing several conventional model functions $f(\alpha)$, published in reviews [1, 2, 4], derived from the physicogeometric assumption of the reaction interface movement have mostly been used for the identification of the equation of a function that gives the best fit to experimental data. One of the methods of selection the best $g(\alpha)$ (an integral form of model α func-

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tions) consists in checking rectilinearity in the coordinates $g(\alpha)$ *vs.* time according to the equations:

$$g(\alpha) = kt \tag{1}$$

or

$$g(\alpha) = kt + b \tag{2}$$

where α is the degree of conversion, k is the rate constant and t is the isothermal time. The other, i.e. the method of reduced time plots α *vs.* t_{red} (t_{red}=the reduced time, which is the ratio $t/t_{0.5}$ where $t_{0.5}$ is the time required for the reaction to reach half completion). In this method a comparison is made of the shapes of the experimental run curves plotted in coordinates $\alpha - t_{red}$ with the theoretical model curves obtained for particular $g(\alpha)$ [4, 7, 8]. Both the methods arouse some reasonable objections [8, 9]. Now there is agreement in views that the real process of thermal decomposition of solids is far away from any ideal assumed model $g(\alpha)$.

Recently Koga, Šesták, Malek and Tanaka [10, 11] have introduced an idea of an 'accomodation function' which 'was applied to the conventional kinetic model functions $f(\alpha)$ (a differential form of model α functions), in an attempt to reduce the disagreement between the actual process and the idealized one assumed in formulating $f(\alpha)$' [11]. Some non-integer values of n and/or m (instead of integer ones) in the kinetic model function $f(\alpha)$, denoted later as N and M respectively, result from the 'accommodation function' based on the idea of fractal nature of powders [12]. The significance of the non-integer values of N and/or M in the kinetic model function equations is discussed in [11] with its physicochemical meanings.

The aim of this work is to determine the kinetic parameters of the three consecutive stages of thermal decomposition of $[Co(NH_3)_6]_2(C_2O_4)_3 \cdot 4H_2O$ at isothermal conditions. The decomposition sequences, intermediates and final products were determined previously [13, 14]. One conventional procedure (the first one described above) and the method suggested by Koga, Šesták, Malek and Tanaka [10, 11] were used and the values of the kinetic parameters obtained by both methods are compared and discussed.

Experimental

Materials

The complex $[Co(NH_3)_6]_2(C_2O_4)_3 \cdot 4H_2O$ was prepared as suggested in the literature [15]. The quantitative analysis data were in good agreement with the chemical formula of the complex under study [13]. The sample used was a powder with the specific surface area 4.94 $m^2 g^{-1}$ (the sieve mesh≤0.056 mm).

Methods

Measurements of the thermal decomposition of this ammine complex were carried out under isothermal conditions using a Derivatograph C (MOM, Budapest) in flowing argon (research grade, additionally purified) or air atmospheres ($\sim$4 dm^3 h^{-1}). A preheating step at the constant heating rate β=20 K min^{-1} was followed by an isothermal stage. The isothermal measurements were performed in the temperature ranges of 376–400 K for the first stage reaction, 427–448 K for the second stage and 516–598 K for the third stage. The temperature control of the sample was accurate to ±0.1 K. The thermoanalytical data were collected and stored on a microcomputer. TG data analysis was performed on an IBM PC compatible computer using Statgraphics software. Correlation coefficients together with F-ratio and standard error of estimation were used as a criterion to compare quantitatively the fit of data to various kinetic models.

Results and discussion

The thermal decomposition of $[Co(NH_3)_6]_2(C_2O_4)_3\cdot 4H_2O$ proceeds between 372 and 564 K in air and within the range 372–659 K in argon as it was shown earlier [13]. It was revealed that the courses of the first and second stages of decomposition are the same in both atmospheres. The ambient atmosphere and experimental conditions influence the third stage of the decomposition as well as its final products [13, 14].

On the basis of the physicochemical measurements the probable decomposition sequences under isothermal conditions are as follows:
Stage I (air, argon)

$$[Co(NH_3)_6]_2(C_2O_4)_3\cdot 4H_2O \xrightarrow{\text{endo}} [Co(NH_3)_6]_2(C_2O_4)_3 + 4H_2O \qquad (3)$$

Stage II (air, argon)

$$\begin{aligned} 3[Co(NH_3)_6]_2(C_2O_4)_3 &\xrightarrow{\text{endo}} 3Co[Co(C_2O_4)_2] + N_2 + \\ &+ 34NH_3 + 3H_2O + 3CO + 3CO_2 \end{aligned} \qquad (4)$$

Stage III (air)

$$3Co[Co(C_2O_4)_2] + 4O_2 \xrightarrow{\text{exo}} 2Co_3O_4 + 12CO_2 \qquad (5)$$

Stage III (argon)

$$Co[Co(C_2O_4)_2] \xrightarrow{\text{endo}} Co_{met} + CoO + 3CO_2 + CO \qquad (6)$$

However, it is considered that in the second and third stages of decomposition the secondary reactions can occur so that Eq. (5) is a summary reaction of the two processes:

$$3Co[Co(C_2O_4)_2] \xrightarrow{\text{endo}} 2Co_3O_4 + 8CO + 4CO_2 \tag{7}$$

$$8CO + 4O_2 \xrightarrow{\text{exo}} 8CO_2 \tag{8}$$

Figures 1a–c and 2a–c show the α *vs.* t curves obtained for the particular stages of the sample dissociation in air and argon, respectively. The form of the curves in Fig. 1a (stage I) suggests deceleratory rate equations based on geometric models (R_n) or diffusion mechanisms (D_n) or 'order equations' [4]. The rather sigmoidal shape (with no induction period) of the curves in Fig. 1b (stage II) suggests Avrami-Erofe'ev (A_n) and/or Prout-Tompkins (B_1) sigmoid rate equations but does not exclude the deceleratory rate equations especially at the highest temperature. The α – time curves for the stage III (Fig. 1c) are clearly a sigmoid type and suggest A_n or B_1 model equations. The shape of the curves in Fig. 2a–b (stage I and II in argon) is nearly identical as those given in Fig. 1a–b, respectively. It is in agreement with the probable decomposition sequences determined earlier (Eqs (3) and (4)). They are the same for the first and second stages of decomposition of the compound under investigation in both the gaseous atmospheres.

The form of the curves in Fig. 2c varies with the temperature. At the lowest temperature the shape of the curve is parabolic. At the higher values of temperature it is sigmoid without an induction period. Different kinds of the curves α – time (p=const.) at different temperatures are an example of a typical change of kinetic conditions of a reaction caused by changes of temperature.

At first the kinetic analysis of the experimental TG curves was performed by means of the conventional method. The common used kinetic model functions in integral form $g(\alpha)$ [1, 2, 4, 16] were examined for the particular stages of $[Co(NH_3)_6]_2(C_2O_4)_3 \cdot 4H_2O$ thermal decomposition according to the Eq. (2). Thus, a plot of $g(\alpha)$ *vs.* t should yield a straight line when the appropriate kinetic model is used. The slope provides the apparent rate constant k. The procedure used for the selection of the models which best fit the experimental TG curves was described in detail in [16]. The results obtained this way confirmed the already known fact that more than one functional form, $g(\alpha)$, fits well the experimental data. This is the general disadvantage of the method used above which can lead to an inability to estimate the real kinetic parameters (E, A) [4, 8, 16 –18].

The results obtained for stage III in the example of the dissociation of the sample in argon are presented in Table 1. As can be seen, the sequence of order of the best fitting models based on the statistical parameters values varies with the temperature. All the stages of the decomposition in both gaseous atmospheres generally show the formal obedience of the kinetic curves to the R_n and/or A_m laws (contracting geometry and/or nucleation and growth type reactions) in which the integer values of n and m (or fractional values of N and M – see later) change with temperature.

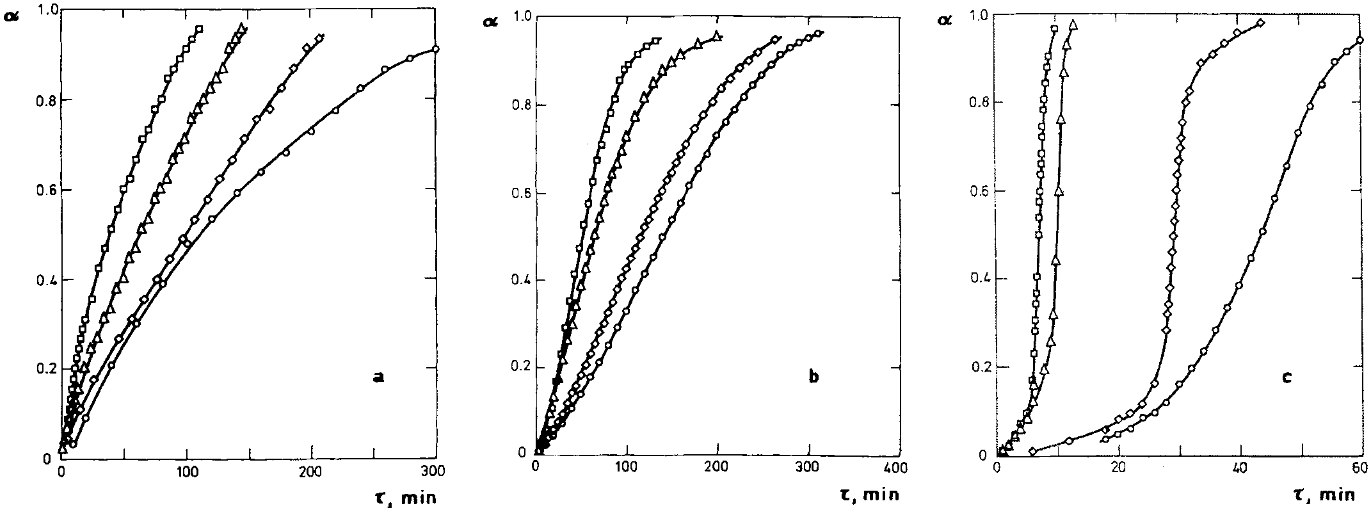

Fig. 1 Isothermal conversion – time curves of $[Co(NH_3)_6]_2(C_2O_4)_3{\cdot}4H_2O$ dissociation in air. a) First stage of dissociation: ○ – 384.7 K; ◇ – 390.0 K; △ – 394.1 K; □ – 399.6 K. b) Second stage of dissociation: ○ – 431.2 K; ◇ – 433.6 K; △ – 439.1 K; □ – 445.1 K. c) Third stage of dissociation: ○ – 516.0 K; ◇ – 528.0 K; △ – 539.1 K; □ – 544.0 K

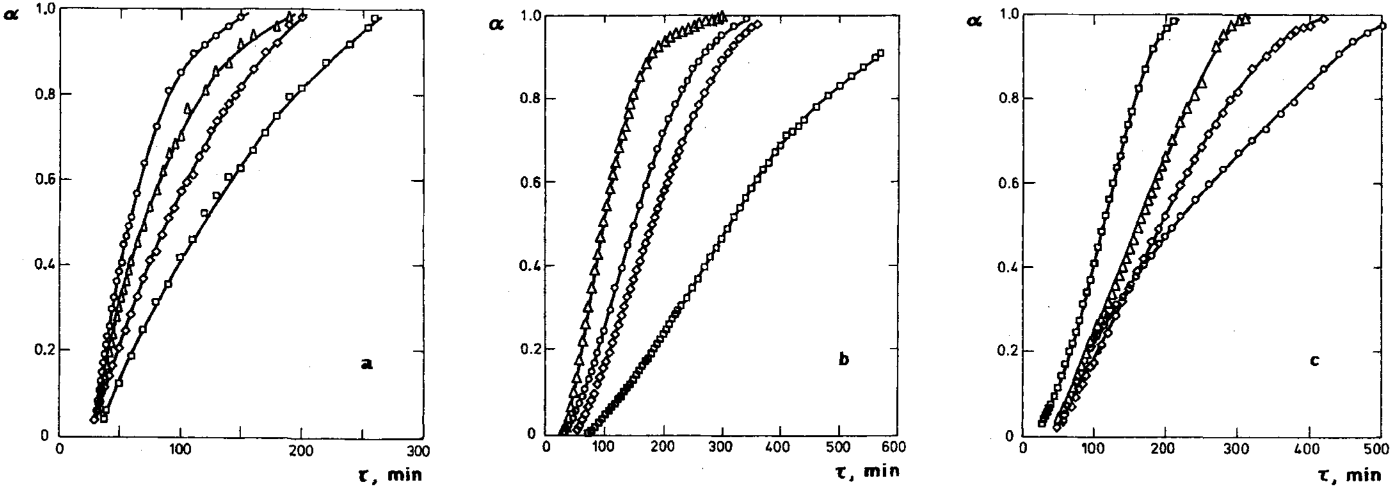

Fig. 2 Isothermal conversion – time curves of $[Co(NH_3)_6]_2(C_2O_4)_3 \cdot 4H_2O$ dissociation in argon. a) First stage of dissociation: □ – 376.0 K; ◇ – 381.5; Δ – 386.1 K; o – 391.9 K. b) Second stage of dissociation: □ – 427.1 K; ◇ – 437.3 K; o – 439.9 K; Δ – 447.7 K. c) Third stage of dissociation: o – 573.9 K; ◇ – 584.1 K; Δ – 588.3 K; □ – 597.2 K

Table 1 Comparison of the best fitting models together with the corresponding apparent rate constant values selected by means of integer values of *n* and/or *m* and non-integer values of *N* and/or *M* in the model functions determined for the third stage of $[Co(NH_3)_6]_2(C_2O_4)_3\cdot 4H_2O$ decomposition in argon; $0.05\leq\alpha\leq 0.95$

T/K	Model	Rate const.	Statistical parameters		
		$k\times10^3$/min^{-1}	r	F^a	S
573.9	R_2	3.313±0.043	0.9971	5879	0.0328
	D_1	2.153±0.038	0.9947	3175	0.0290
	R_3	3.945±0.085	0.9922	2141	0.0648
	A_2	3.063±0.067	0.9920	2086	0.0510
	R_1	2.084±0.049	0.9906	1790	0.0374
	(A_3)	2.145±0.062	0.9859	1185	0.0474
584.1	A_2	4.519±0.049	0.9982	8525	0.0262
	R_2	4.780±0.063	0.9973	5708	0.0338
	A_3	3.229±0.047	0.9967	4708	0.0252
	R_1	3.082±0.054	0.9952	3204	0.0291
588.3	R_1	4.040±0.026	0.9993	24980	0.0098
	A_3	4.107±0.062	0.9960	4460	0.0236
	A_2	5.728±0.115	0.9929	2491	0.0441
	R_2	6.137±0.146	0.9900	1776	0.0560
597.2	A_3	6.470±0.041	0.9994	25317	0.0104
	B_1	34.038±0.492	0.9970	4788	0.1260
	R_1	6.143±0.089	0.9970	4745	0.0228
	A_2	8.803±0.180	0.9940	2402	0.0460
	(R_2)	9.136±0.302	0.9845	919	0.0773
573.9	$R_{1.6}{}^b$	2.927±0.030	0.9982	9233	0.0232
	$A_{1.9}{}^b$	3.204±0.069	0.9921	2128	0.0528
584.1	$R_{1.4}{}^b$	3.917±0.022	0.9995	33605	0.0114
	$A_{2.2}{}^b$	4.182±0.040	0.9986	10953	0.0214
588.3	$R_{1.1}{}^b$	4.336±0.022	0.9995	39743	0.0084
	$A_{2.8}{}^b$	4.349±0.064	0.9961	4549	0.0248
597.2	$A_{3.2}{}^b$	6.150±0.036	0.9995	29608	0.0092
	$R_{1.0}{}^b$	6.143±0.089	0.9970	4745	0.0228

[a] F_{cr} values are within the range 4.17–4.24; $P(F>F_{cr})=0.05$

[b] The best between tested R_N and A_M models

Table 2 Values of kinetic parameters for the best fitting models selected by means of integer values of n and/or m – conventional method; isothermal experiments; argon and air; $0.05\leq\alpha\leq0.95$

Stage (Atm.)	Model	E /kJ mol^{-1}	ln(A/min^{-1})	Statistical parameter		
				r	F[a]	S
I	R_3	62.1±1.4	15.03±0.45	0.9974	1899	0.0235
(Ar)	R_2	58.8±1.8	13.82±0.57	0.9952	1027	0.0303
II	R_1[b]	85.9±2.1	18.00±0.59	0.9978	1611	0.0227
(Ar)	R_2	88.1±2.4	19.01±0.67	0.9962	1296	0.0393
	R_3	92.4±2.6	20.38±0.71	0.9961	1274	0.0416
III	A_3	135.3±4.1	22.17±0.83	0.9955	1113	0.0413
(Ar)	A_2	129.5±4.0	21.31±0.82	0.9953	1059	0.0406
	R_1	133.2±4.3	21.72±0.88	0.9949	967	0.0437
I	R_1[c]	121.1±3.1	31.92±0.96	0.9999	1505	0.0123
(air)	R_2	93.2±2.1	23.76±0.63	0.9976	2050	0.0305
	R_3	89.7±1.9	22.87±0.60	0.9976	2107	0.0289
	A_2	91.7±2.9	23.24±0.89	0.9950	989	0.0432
II	R_2	103.6±2.5	30.58±0.70	0.9970	1664	0.0295
(air)	A_2	98.2±2.5	29.04±0.68	0.9969	1580	0.0288
III[d]	A_4	184.8±15.0	39.48±3.40	0.9684	151	0.2416
(air)	A_3	184.9±15.2	39.79±3.45	0.9677	147	0.2447
	B_1	186.3±15.4	41.68±3.48	0.9675	146	0.2472
	R_1	181.5±15.0	39.08±3.40	0.9674	146	0.2412

[a] F_{cr} values are within the range 4.96–18.5; P $(F>F_{cr})=0.05$
[b] For 3 values of temperature only; [c] for 2 values of temperature only
[d] only for $0.28\leq\alpha\leq0.84$

Table 2 lists the values of the apparent kinetic parameters (E, A) estimated for the best fitting models, $g(\alpha)$, selected by the conventional method. The data reported in Table 2 show that within each the stage of the dissociation the values of both E and lnA for all the listed models are close to each other though the models are different. Thus it is possible to determine their average values in argon: E_{av}(I)=60.4 kJ mol^{-1}, A_{av}(I)=1.84×106 min^{-1}; E_{av}(II)=88.8 kJ mol^{-1}, A_{av}(II)=2.03×10^{8} min^{-1}; E_{av}(III)=132.7 kJ mol^{-1}, A_{av}(III)=2.75×10^{9} min^{-1}. In air the average values are: E_{av}(I)= 98.9 kJ mol^{-1}, A_{av}(I)=1.13×10^{11} min^{-1}, E_{av}(II)= 100.9 kJ mol^{-1}, A_{av}(II)=8.84×10^{12} min^{-1}, E_{av}(III)≅184 kJ mol^{-1}, A_{av}(III)≅

2.37×10^{17} min^{-1}. Generally, it is shown that the E_{av} and A_{av} values for the particular stages of the sample decomposition in air are higher than for the decomposition in argon. One should notice the low accuracy of estimation of E and A values for stage III in air ($r\cong0.97$; Table 2). It is probably connected with the fact that this stage of the decomposition in air is accompanied by a sharp exothermic effect which clearly disturbs the isothermal run of the process. The several degree jump of temperature of the sample is observed in a large range of α, and this is illustrated in Fig. 3. So the determined E and A values are rather doubtful. To estimate E and A values there was used: $T_{av}=(T_{onset}+T_{jump\ peak})/2$ within the α range of 0.28–0.84.

The doubts relating to the reality of the kinetic parameters estimated by the conventional method, as described above, as well as the fact of two R_n and/or A_m models existing among the best fitting ones have suggested the use of non-integer N and/or M values in the tested model equations. Therefore the method presented in [11] was also employed. The procedure of choice of the model fitting best the experimental data was like that one described for the conventional method. The dissimilarity in practice consists in using fractional 'N' and 'M' instead of the integer ones 'n' and 'm' in the tested functions. For the operating temperature the best R_N or A_M model was selected by 'scanning' the exponent N and/or M in steps of 0.1 from 3 to 1 and from 4 to 1, respectively.

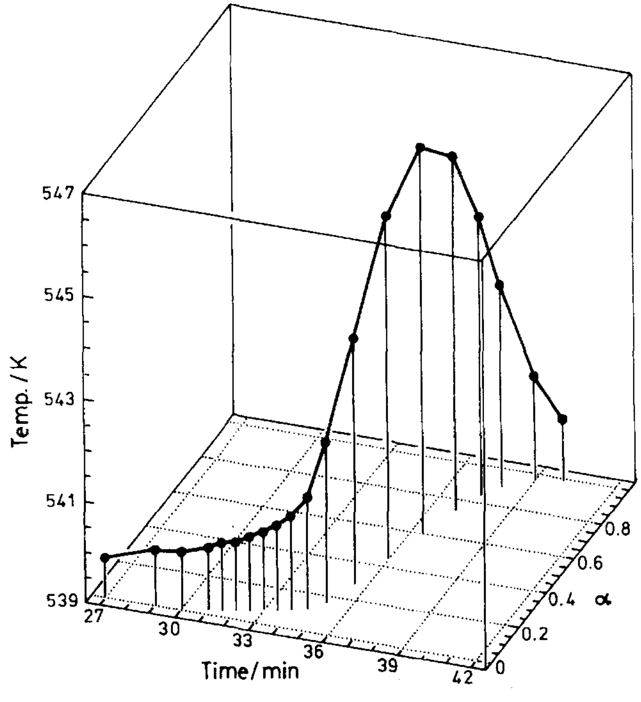

Fig. 3 The temperature jump of the sample observed in the third stage of decomposition

For comparison, the best models chosen with the latter mentioned method are listed in Table 1 together with the best fitting models, $g(\alpha)$, selected by the conventional method. Some differences and also similarities can be seen. The greatest dissimilarity exists at temperature 584.1 K. The conventional method points out A_2, R_2, A_3 and R_1 models as the best fitting. The values of the statistical parameters, r, F and S, do not vary very much so one is not entitled to choose one physicogeometrical model suggesting the obeyed macrokinetic law. By using non-integer values of N and/or M the only one model, $R_{1.4}$, is pointed out as the best fitting at T=584.1 K. The r and F values are clearly highest for $R_{1.4}$. Additionally, one can see that the best among Avrami-Erofee'v models, $A_{2.2}$, has r and F values clearly lower than $R_{1.4}$. At the temperature 573.9 K the conventional method points to R_2, D_1, R_3 and A_2 models as well fitting the experimental data. As in the previous example, r, F and S values vary also not much. Employing the non-conventional method allows to choose a single model, i.e. $R_{1.6}$. For the two higher temperatures i.e. 588.3 K and 597.2 K each of the used methods choices the single best model. The R_1 and A_3 or $R_{1.1}$ and $A_{3.2}$ models have been selected with the conventional or non-conventional methods, respectively. It should be noticed that in

Table 3 Values of the apparent rate constants from isothermal TG curves in argon and air for the best fitting R_N and A_M models selected by means of non-integer values of N and/or M in kinetic model functions; $0.05 \leq \alpha \leq 0.95$

Stage (Atm.)	T/K	Model	Rate const. $k \times 10^3$/min^{-1}	Statistical parameters		
				r	F[a]	S
I	376.0	$R_{1.8}$	6.404±0.047	0.9995	18618	0.0117
(Ar)		$A_{1.7}$	7.078±0.111	0.9979	4043	0.0279
	381.5	$R_{1.7}$	8.566±0.032	0.9997	73660	0.0100
		$A_{2.2}$	8.215±0.114	0.9964	5233	0.0369
	386.1	$A_{1.3}$	15.191±0.107	0.9992	20133	0.0272
		$R_{3.0}$	13.094±0.125	0.9985	11059	0.0317
	391.9	$A_{1.2}$	22.797±0.125	0.9996	32997	0.0205
		$R_{3.0}$	17.990±0.282	0.9970	4081	0.0460
II	427.1	$A_{1.9}$	2.886±0.009	0.9998	108996	0.0073
(Ar)		$R_{1.6}$	2.691±0.023	0.9986	14108	0.0189
	437.3	$A_{2.1}$	5.155±0.028	0.9994	33378	0.0140
		$R_{1.5}$	4.887±0.027	0.9993	32131	0.0136
	439.9	$A_{1.9}$	6.266±0.015	0.9999	180725	0.0060
		$R_{1.8}$	6.040±0.061	0.9986	9660	0.0249
	447.7	$A_{1.4}$	12.031±0.131	0.9983	8486	0.0374
		$R_{3.0}$	11.357±0.156	0.9975	5318	0.0413

Table 3 Continued

Stage (Atm.)	T/K	Model	Rate const. k×10^3/min^{-1}	Statistical parameters		
				r	F[a]	S
III (Ar)	see Table 1					
I (air)	384.7	$R_{1.9}$	4.423±0.083	0.9974	2871	0.0333
		$A_{2.1}$	4.053±0.151	0.9897	719	0.0611
	390.0	$R_{1.2}$	5.054±0.032	0.9996	24467	0.0090
		$A_{2.4}$	5.452±0.134	0.9943	1661	0.0371
	394.1	$R_{1.3}$	7.713±0.043	0.9994	31845	0.0117
		$A_{2.1}$	8.742±0.137	0.9957	4084	0.0369
	399.6	$R_{1.9}$	13.041±0.088	0.9993	21802	0.0169
		$A_{2.0}$	12.206±0.174	0.9969	4934	0.0323
II (air)	431.2	$A_{2.3}$	4.711±0.030	0.9994	24094	0.0151
		$R_{1.5}$	4.687±0.050	0.9984	8944	0.0247
	433.6	$A_{1.8}$	6.369±0.028	0.9996	50728	0.0129
		$R_{1.6}$	5.471±0.043	0.9988	15971	0.0196
	439.1	$A_{1.4}$	11.700±0.082	0.9994	20470	0.0193
		$R_{3.0}$	11.013±0.136	0.9982	6522	0.0322
	445.1	$A_{1.4}$	17.665±0.249	0.9981	5017	0.0373
		$R_{3.0}$	16.516±0.328	0.9963	2542	0.0490
III[b] (air)	516.0	$R_{1.0}$	32.21±0.69	0.9980	2198	0.0125
		$A_{4.0}$	22.75±0.50	0.9978	2055	0.0091
	528.0	$A_{1.2}$	314.0±4.9	0.9983	4023	0.0228
		$R_{3.0}$	268.6±5.1	0.9975	2755	0.0236
	539.1	$A_{4.0}$	187.8±7.7	0.9958	596	0.0204
		$R_{1.2}$	291.0±15.6	0.9929	350	0.0412
	544.0	$A_{2.4}$	333.5±2.3	0.9996	21052	0.0063
		$R_{1.5}$	392.0±4.6	0.9988	7238	0.0126

[a] F_{cr} values are within the range 4.08–6.61; $P(F>F_{cr})=0.05$

[b] only for $0.28\le\alpha\le0.84$

each case a clearly better fitting of the experimental data is obtained by using fractional values of N and M.

Table 3 lists the apparent rate constant values together with corresponding statistical parameters estimated for the best from the midst of the tested R_N and

A_M models selected by means of non-integer values of N and/or M in the kinetic model functions. As it can be seen it is mostly possible to choose only the single best model operating at a set temperature basing on statistical parameters values.

The data presented in Table 3 show that the best models for dehydration (stage I) in air are R_N models but the N values selected at different temperatures are varied. For dehydration in argon R_N models are clearly the best, like in air, but only at two lower temperatures. At higher temperatures A_M law obeys.

The experimental data of the second stage of the sample decomposition in both gaseous atmospheres are best fitted by the nucleation-growth, A_M, functions.

In the third stage of dissociation in argon as well as in air the contracting geometry, R_N, and nucleation-growth, A_M, model functions are found to be the best for the lower and higher parts of the investigated temperature interval, respectively. It should be noticed that the fractional values of N and/or M in most cases vary with temperature within a particular stage of the decomposition. Thus, the mean values of N and M over the investigated temperature range for each stage of the reactant decomposition were found similarly as in [18]. The values of Arrhenius parameters, E and ln$A$ determined for the R_N and/or A_M models with the mean, fractional values of N and/or M are listed in Table 4. It can be seen that for particular stages of the decomposition in both air and argon the E and ln$A$ values

Table 4 The values of kinetic parameters from the isothermal TG experiments in air and argon estimated by use the mean non-integer values of N and/or M determined for the best fitting models; $0.05 \leq \alpha \leq 0.95$

Stage (Atm.)	Model	E/kJ mol^{-1}	ln(A/min^{-1})	Statistical parameters		
				r	F^a	S
I	$R_{1.575}$	96.3±2.9	24.59±0.89	0.9955	1107	0.0429
(Air)	$(A_{2.15})$	92.2±3.3	23.32±1.02	0.9936	771	0.0492
II	$A_{1.725}$	100.8±2.8	22.97±0.76	0.9963	1331	0.0321
(Air)	$(R_{2.275})$	104.7±3.0	24.06±0.82	0.9960	1250	0.0345
III^b	$A_{2.9}$	185.3±15.2	39.90±3.44	0.9679	148	0.2439
(Air)	$(R_{1.675})$	183.4±15.4	39.88±3.49	0.9663	141	0.2476
I	$A_{1.25}$	65.7±1.4	16.35±0.44	0.9977	2168	0.0234
(Ar)	$(R_{1.75})$	57.4±2.1	13.32±0.66	0.9934	747	0.0348
II	$A_{1.825}$	87.4±3.0	18.85±0.83	0.9941	843	0.0484
(Ar)	$(R_{1.975})$	85.6±2.6	18.33±0.82	0.9939	815	0.0482
III	$A_{2.525}$	133.1±4.0	21.88±0.83	0.9954	1090	0.0411
(Ar)	$(R_{1.272})$	130.3±5.6	21.28±1.16	0.9908	534	0.0573

[a] F_{cr} values is equal 4.96; $P(F>F_{cr})=0.05$
[b] only for $0.28 \leq \alpha \leq 0.84$

estimated for R_N and A_M models are very close to one another. It is true also for stage III in air though the evaluated E and $\ln A$ values are rather doubtful ($r \cong 0.97$) what is connected with really non-isothermal conditions of the reaction caused by a self-heating effect as it was described above. Generally, the Arrhenius parameters values for all stages of the reactant decomposition in air are higher than for the respective stages in argon.

Comparison of the results of the two methods

The Arrhenius parameters values estimated by the use of mean, non-integer values of N and/or M (Table 4) are very close to the average values of E and $\ln A$ determined by the conventional method. However these former are considered to be more meaningful because of the fact that in most cases only a single model function is the best fitting the experimental data at one operating temperature. But this does not usually obey within an interval of temperature for a particular stage of the decomposition. Generally, it can be said that the overall decomposition process of $[Co(NH_3)_6]_2(C_2O_4)_3{\cdot}4H_2O$ is fitted best with R_N or A_M model equations. One can suppose that the macromechanism of dissociation is governed by contracting geometry and/or nucleation-growth processes. The author is aware that this should be complemented by other experimental observations. Particularly valuable there are microscopic examinations of the textural changes that accompany reaction [19, 20]. The scanning electron microscopy investigations of the fine powder samples (intermediates and final products) will be discussed in detail in [13].

The comparison of E values determined by the author for $[Co(NH_3)_6]_2(C_2O_4)_3{\cdot}\ H_2O$ decomposition in air in isothermal, linear rising temperature and quasi-isothermal-isobaric conditions is presented and discussed in [14]. The values of kinetic parameters determined for particular stages of thermal decomposition of $[Co(NH_3)_6]_2(C_2O_4)_3{\cdot}4H_2O$ in both gaseous atmospheres compare well with literature data [16, 21–35].

Conclusions

1. Certainty of the best model selection is increased when non-integer values of N and/or M instead of integer n and/or m are used in $g(\alpha)$ equations. It makes the estimated values of activation energy more reliable.

2. In most cases only a single model function with non-integer values of N or M is the best fitting the experimental data at one operating temperature. The conventional method does not usually allow to make such distinction.

3. Comparison of the results from two tested methods shows that the Arrhenius parameters values estimated by the use of non-integer values of N and/or M in the kinetic model function equations are very close to the average E and $\ln A$ values determined by the conventional method.

4. The similarity of the $E(A_m)$ and $E(R_n)$ values indicates that the activation energies are not sensitive to the particular model chosen.

5. The Arrhenius parameters values for all the stages of the reactant decomposition in air are higher than for the respective stages in argon.

6. The results show that the phase boundary and/or nucleation growth processes control the macroscopic mechanism of the particular stages of $[Co(NH_3)_6]_2(C_2O_4)_3\cdot 4H_2O$ thermal decomposition.

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