Thermochimica Acta, 170 (1990) 107–119
Elsevier Science Publishers B.V., Amsterdam

KINETICS OF THERMAL DECOMPOSITION OF $[Co(NH_3)_6]Cl_3$

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(Received 7 March 1990)

ABSTRACT

The thermal decomposition of $[Co(NH_3)_6]Cl_3$ was studied under non-isothermal conditions in dynamic air and argon atmospheres and under isothermal conditions in flowing air. Dissociation of the above complex occurs in three stages. The kinetics of the particular stages of $[Co(NH_3)_6]Cl_3$ thermal decomposition have been evaluated from both dynamic and isothermal weight loss data. The R_n models were selected as those best fitting the experimental TG curves. These models suggest that the kinetics and macromechanism of the $[Co(NH_3)_6]Cl_3$ dissociation can be governed by phase boundary processes. The activation energies, E_α, of the particular stages of the thermal decomposition were calculated. The results have corroborated the view that combination of isothermal and non-isothermal measurements facilitates the selection of the models best fitting experimental TG curves.

INTRODUCTION

Investigations of the kinetics of thermal decomposition of solids have been approached from two directions: using single crystals and crystalline powder materials. The latter studies have been carried out much more extensively than the former, probably on account of their practical significance. Numerous authors [1–20] have extensively discussed the usefulness of the different methods of thermal analysis which have been employed in kinetic research on the dissociation of solids. Dynamic methods seem to be the most debatable if one uses them to determine the reaction mechanisms and kinetic parameters. On the other hand, some authors (e.g., in Refs. 2, 10 and 17) have pointed out the practical importance of these methods. Tanaka (in, e.g., Ref. 10) has stated that “comparisons of thermal stabilities and/or kinetics among homologous series by means of dynamic thermal analyses should be meaningful, if they were made under identical conditions”. Wendlandt’s [2] point of view is that, in analyzing solid decomposition kinetics, the conventional isothermal method is important for estimating the kinetic model and parameters, but dynamic methods have advantages in several respects. In spite of all objections, non-isothermal methods are, as

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hitherto, largely used in thermal analysis (as reported in a dozen or so percent of the published articles) and are more often used than isothermal methods. Kinetic studies of the thermal decomposition of solids make up about 15% of all research on thermal dissociation, as Liptay [18] has reported.

For the last two decades, kinetic analysis of dynamic TG curves has been the most popular method for estimation of the kinetic parameters. The differential and integral kinetic equations connected with the 'mechanism' of the thermal decomposition of solids presented in numerous publications (e.g., refs. 3, 19 and 20) have been used for this estimation. The fact that more than one functional form, $f(\alpha)$ or $g(\alpha)$, fits the experimental results is the general disadvantage of all the suggested methods. The selection of a proper model is then practically impossible, leading to inability to estimate the real kinetic parameters (E, A).

Numerous attempts have been made to find a means of choosing one kinetic expression that best fits the experimental, non-isothermal TG curve. Then, on the basis of this single, functional form $f(\alpha)$ or $g(\alpha)$, reliable kinetic parameters could be calculated. Phadnis and Deshpande undertook one of these attempts [19]. In the present paper the method of ref. 19 has been compared with the frequently employed modified Coats and Redfern method [21,22] using as an example the thermal decomposition of the simple complex compound $[Co(NH_3)_6]Cl_3$.

Recently, the view that the combined used of isothermal and non-isothermal methods for kinetic determinations is the proper solution [1,10,23–28] has been more and more frequently expressed. The kinetic analysis of weight loss curves of the thermal decomposition of $[Co(NH_3)_6]Cl_3$ under isothermal conditions has therefore also been made, and the results are presented in this paper.

EXPERIMENTAL

Materials

Hexaamminecobalt(III) chloride was prepared by the method described in Ref. 29. The complete analytical data for this compound have been given previously [30].

Methods

Simultaneous TG–DTG–DTA curves under non-isothermal conditions were recorded with a Derivatograph C (MOM, Budapest) between 293 and 1273 K, with linear heating rate $\beta = 1.2$ K min^{-1} in flowing air and argon atmospheres (4 dm^3 h^{-1}).

Isothermal TG experiments were performed with the same apparatus in flowing air (4 dm^3 h^{-1}). A preheating step at a constant heating rate $\beta = 20$ K min^{-1} was followed by an isothermal stage. The temperatures studied in these measurements were: 498.5, 502, 506, 552, 561, 583 and 761.5 K.

The sample weight was 100 mg, and the sieve mesh was $\leqslant 0.056$ mm (specific surface 5.74 m^2 g^{-1}). Alumina crucibles 7.5 mm in diameter and 15.0 mm tall were used both for the specimen and for the reference material, which was calcined alumina.

RESULTS AND DISCUSSION

The thermal decomposition of $[Co(NH_3)_6]Cl_3$ proceeds in three stages in both air and argon gaseous atmospheres, as was proved earlier [30]. On the basis of the experimental data (thermal and chemical analyses, X-ray diffraction, reflectance spectroscopy, scanning electron microscopy) the probable decomposition sequences of $[Co(NH_3)_6]Cl_3$ presented in ref. 30 are as follows.

Stage I (air, argon)

$$6[Co(NH_3)_6]Cl_3(s) \rightarrow 3CoCl_2(s) + 3(NH_4)_2[CoCl_4](s) + N_2(g) + 28NH_3(g) \qquad (1)$$

Stage II (air, argon)

$$3(NH_4)_2[CoCl_4](s) \rightarrow 6NH_4Cl(g) + 3CoCl_2(s) \qquad (2)$$

Stage III (air)

$$3CoCl_2(s) + 2O_2(g) \rightarrow Co_3O_4(s) + 3Cl_2(g) \qquad (3)$$

Stage III (argon)

$$CoCl_2(s) \rightarrow CoCl_2(g) \qquad (4)$$

The reactions (1) and (2) are compatible with those of Wendlandt and Smith [31].

Non-isothermal experiments

Kinetic analysis of the experimental TG curves obtained under non-isothermal conditions was performed by means of the methods of Phadnis and

Deshpande [19] [eqns. (5) and (6)] and of Coats and Redfern [21,22] (eqn. (7)).

$$f(\alpha)g(\alpha) = \frac{RT^2}{E_\alpha}\frac{\mathrm{d}\alpha}{\mathrm{d}T} \tag{5}$$

$$g'(\alpha) = -\frac{E_\alpha}{RT} \tag{6}$$

where

$$g'(\alpha) = \int \frac{\mathrm{d}\alpha}{f(\alpha)g(\alpha)}$$

$$\ln\left(\frac{g(\alpha)}{T^2}\right) = \ln\frac{AR}{\beta E_\alpha}\left(1 - \frac{2RT}{E_\alpha}\right) - \frac{E_\alpha}{RT} \tag{7}$$

where α is the degree of conversion, A is the pre-exponential factor, R is the gas constant, β is the linear heating rate (K min^{-1}), T is the temperature (K) and E_α is the activation energy.

The degree of conversion, α, and $\Delta\alpha/\Delta T \approx \mathrm{d}\alpha/\mathrm{d}T$ were determined for each stage of dissociation of the complex compound (about 20 values of α for each stage).

The algebraic expression of differential $f(\alpha)$ and integral $g(\alpha)$ functions for the most common mechanism operating in solid-state decompositions [3,19,20] are presented in Table 1.

TABLE 1

Kinetic models investigated

Symbol [a]	$f(\alpha)$	$g(\alpha)$	$g'(\alpha)$
D_1	$\frac{1}{2}\alpha^{-1}$	α^2	$2\ln\alpha$
D_2	$1/[-\ln(1-\alpha)]$	$(1-\alpha)\ln(1-\alpha)+\alpha$	$\ln[(1-\alpha)\ln(1-\alpha)+\alpha]$
D_3	$(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$	$\frac{3}{2}[1-(1-\alpha)^{1/3}]^2$	$2\ln[1-(1-\alpha)^{1/3}]$
D_4	$1/(1-\alpha)^{-1/3}-1$	$\frac{3}{2}[1-\frac{2}{3}\alpha-(1-\alpha)^{2/3}]$	$\ln[1-\frac{2}{3}\alpha-(1-\alpha)^{2/3}]$
F_1	$(1-\alpha)$	$-\ln(1-\alpha)$	$\ln[-\ln(1-\alpha)]$
A_2	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$	$\frac{1}{2}\ln[-\ln(1-\alpha)]$
A_3	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$	$\frac{1}{3}\ln[-\ln(1-\alpha)]$
R_1	1	α	$\ln\alpha$
R_2	$(1-\alpha)^{1/2}$	$2[1-(1-\alpha)^{1/2}]$	$\ln[1-(1-\alpha)^{1/2}]$
R_3	$(1-\alpha)^{2/3}$	$3[1-(1-\alpha)^{1/3}]$	$\ln[1-(1-\alpha)^{1/3}]$

[a] D_1: one-dimensional diffusion (power law); D_2: two-dimensional diffusion; cylindrical symmetry; D_3: three-dimensional diffusion; spherical symmetry; Jander eqn.; D_4: three-dimensional diffusion; spherical symmetry; Ginstling–Brounshtein eqn.; F_1: random nucleation; only one nucleus on each particle; A_2: random nucleation; Avrami I eqn.; A_3: random nucleation; Avrami II eqn.; R_1: phase boundary reaction (zero-order); Polanyi–Wigner eqn.; R_2: phase boundary reaction; cylindrical symmetry; R_3: phase boundary reaction; spherical symmetry.

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

The activation energies, E_α, for the particular stages of decomposition were determined in the following coordinate systems, respectively

$$f(\alpha)g(\alpha) \text{ vs. } T^2\frac{\mathrm{d}\alpha}{\mathrm{d}T}$$

$$g'(\alpha) \text{ vs. } \frac{10^3}{T}$$

and

$$\ln\frac{g(\alpha)}{T^2} \text{ vs. } \frac{10^3}{T}$$

It was initially assumed that linearity of plots of the above mentioned dependences suggests the 'mechanism' connected with a particular functional form of α.

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

$$F = \frac{r^2(N-2)}{1-r^2} \tag{8}$$

where r is the linear regression coefficient, and N is the number of measuring points.

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

Values of the apparent activation energy E_α, the linear regression coefficient r, Snedecor's test variable F, and the standard error of estimation S obtained from analysis of the dynamic TG curves on the basis of eqns. (5)–(7) are listed in Tables 2 and 3. The values presented in these tables have been obtained from the tested equations which fit best the experimental TG curves. For comparison, values of E_α evaluated by the Arnold–Somogyvari–Paulik–Paulik (ASPP) method [32] (using the software of the Derivatograph C) have been included. From Table 2 it can be seen that the best fitting expressions for the first and third stages of $[\mathrm{Co(NH_3)_6}]\mathrm{Cl_3}$ decomposition in air, selected on the basis of all the tested methods [eqns. (5)–(7)], are the same. These are the R_2, D_4, R_3 and D_3 functions for stage I

TABLE 2

Values of kinetic parameters from dynamic TG experiments in an air atmosphere

Stage	Range of α	Model [a]	E_α (kJ mol^{-1})	A (min^{-1})	Statistical parameters			Method [c]
					r	F [b]	S	
I	0.01–0.92	R_2	146.4	–	0.9986	4677	0.009932	PD(5)
		D_4	276.5	–	0.9975	2594	0.007061	
		R_3	167.0	–	0.9922	827	0.020707	
		D_3	334.0	–	0.9922	827	0.040356	
		R_2	157.1	–	0.9996	18136	0.043794	PD(6)
		R_3	161.3	–	0.9996	17697	0.045501	
		D_3	322.6	–	0.9996	17697	0.091916	
		D_4	311.3	–	0.9995	14473	0.094117	
		R_3	153.1	8.67×10^{13}	0.9996	16993	0.044019	CR
		D_3	313.9	1.74×10^{29}	0.9996	16667	0.091248	
		R_2	148.8	2.93×10^{13}	0.9996	16291	0.043741	
		D_4	302.4	9.94×10^{27}	0.9995	14037	0.095804	
			147.2	1.72×10^{13}	–	–	–	ASPP
II	0.02–0.95	D_2	217.2	–	0.9912	616	0.014163	PD(5)
		D_1	147.0	–	0.9715	185	0.038183	
		R_1	73.5	–	0.9715	185	0.076366	
		D_4	256.4	–	0.9674	161	0.023489	
		F_1	211.8	–	0.9912	614	0.193661	PD(6)
		A_2	105.9	–	0.9912	614	0.096821	
		A_3	70.6	–	0.9912	614	0.064548	
		D_3	387.7	–	0.9868	409	0.434733	
		R_3	193.8	–	0.9868	409	0.217366	
		F_1	202.0	2.46×10^{16}	0.9902	556	0.194192	CR
		A_2	96.1	8.64×10^{6}	0.9892	501	0.097353	
		A_3	60.8	2.10×10^{4}	0.9880	449	0.065031	
		D_3	377.2	5.74×10^{31}	0.9865	400	0.427608	
		R_3	184.0	5.15×10^{14}	0.9853	366	0.218094	
			154.6	8.72×10^{11}	–	–	–	ASPP
III	0.04–0.90	D_2	278.6	–	0.9937	862	0.011451	PD(5)
		D_1	197.3	–	0.9873	424	0.023063	
		R_1	98.6	–	0.9873	424	0.046126	
		R_1	109.9	–	0.9994	9248	0.033908	PD(6)
		D_1	219.7	–	0.9994	9248	0.067827	
		D_2	234.8	–	0.9984	3447	0.118681	
		D_1	205.5	7.24×10^{9}	0.9994	8635	0.065649	CR
		R_1	95.7	3.32×10^{3}	0.9993	7854	0.032039	
		D_2	220.6	3.68×10^{10}	0.9983	3261	0.114646	
			98.1	1.17×10^{4}	–	–	–	ASPP

[a] Models as in Table 1.

[b] F_{cr} values are within the range 9.07–9.65.

[c] PD(5), Phadnis–Deshpande method, eqn. (5); PD(6), Phadnis–Deshpande method, eqn. (6); CR, Coats–Redfern method, eqn. (7); ASPP, Arnold–Somogyvari–Paulik–Paulik method.

TABLE 3

Values of kinetic parameters from dynamic TG experiments in argon atmosphere

Stage	Range of α	Model [a]	E_α (kJ mol^{-1})	A (min^{-1})	Statistical parameters			Method [c]
					r	F [b]	S	
I	0.01–0.93	D_3	318.9	–	0.9942	1204	0.008966	PD(5)
		R_3	159.4	–	0.9942	1204	0.017935	
		R_2	141.0	–	0.9913	799	0.024911	
		D_4	267.3	–	0.9853	468	0.017169	
		D_1	244.8	–	0.9896	662	0.462729	PD(6)
		R_1	122.4	–	0.9896	662	0.231368	
		D_2	255.1	–	0.9884	591	0.510397	
		D_4	259.2	–	0.9877	557	0.534025	
		R_2	130.6	–	0.9873	541	0.273372	
		D_1	236.8	7.27×10^{21}	0.9891	631	0.458382	CR
		R_1	114.1	4.47×10^{10}	0.9883	586	0.229223	
		D_2	246.6	3.65×10^{23}	0.9876	553	0.509837	
		D_4	251.4	4.03×10^{23}	0.9873	539	0.526691	
		R_2	122.5	5.03×10^{10}	0.9858	482	0.271378	
			131.4	2.93×10^{11}	–	–	–	ASPP
II	0.02–0.95	D_2	181.6	–	0.9882	794	0.015427	PD(5)
		D_4	215.8	–	0.9765	391	0.018498	
		R_2	118.4	–	0.9590	218	0.045156	
		F_1	197.9	–	0.9889	838	0.020547	PD(6)
		A_2	99.0	–	0.9889	838	0.102736	
		A_3	66.0	–	0.9886	838	0.068484	
		F_1	188.1	1.60×10^{15}	0.9876	752	0.206223	CR
		A_2	89.2	2.14×10^{6}	0.9861	670	0.103520	
		A_3	56.2	2.01×10^{3}	0.9844	595	0.069211	
			130.7	7.91×10^{9}	–	–	–	ASPP
III	0.01–0.94	D_1	328.8	–	0.9812	389	0.028785	PD(5)
		R_1	164.4	–	0.9812	389	0.057568	
		D_3	483.1	–	0.9976	3077	0.217603	PD(6)
		R_3	241.6	–	0.9976	3077	0.108787	
		F_1	255.7	–	0.9974	2917	0.118287	
		A_2	127.8	–	0.9974	2917	0.059141	
		A_3	85.2	–	0.9974	2917	0.039429	
		D_3	466.6	1.72×10^{21}	0.9974	2831	0.219104	CR
		R_3	225.1	5.05×10^{9}	0.9971	2593	0.110460	
		F_1	239.3	3.24×10^{10}	0.9971	2536	0.118708	
		A_2	111.7	6.76×10^{3}	0.9965	2147	0.060228	
		A_3	68.8	2.11×10^{2}	0.9960	1872	0.039746	
			305.8	1.18×10^{14}	–	–	–	ASPP

[a] See Table 1.

[b] F_{cr} values are within the range 8.18 × 8.86.

[c] See footnote to Table 2.

and D_2, D_1 and R_1 for stage III. Values of the activation energy calculated for a particular model (e.g. R_2) with PD(5), PD(6) and CR methods (see Table 2) are not the same; however, they are close to one another. The E_α value (stage I) evaluated by the ASPP method is the closest to the E_α values calculated for the R_2 model. For stage III the E_α ASPP value is the nearest to E_α (R_1). Somewhat different are the results obtained for the second stage of dissociation in air. The PD(5) method indicates the models D_2, D_1 and R_1 as being the most likely, whereas integral methods PD(6) and CR point to quite other models (F_1, A_2, A_3). On the other hand the values of activation energy E_α (D_2) and E_α (F_1) are close to each other.

The results presented in Table 3 for the thermal decomposition of $[Co(NH_3)_6]Cl_3$ in an argon atmosphere show that, for all three stages of dissociation, the best fitting expressions selected with integral methods PD(6) and CR are different from those chosen by using the PD(5) method. This may suggest that the selected functions depend more on the method of mathematical treatment than on the experiment. The E_α values calculated for particular models by means of both integral methods have been approximated. For stage I the values of $E_\alpha(R_2)$ and $E_\alpha(R_1)$ are nearest to each other and in good agreement with the value obtained with the ASPP method. For stage II, the nearest values are $E_\alpha(D_2)$ from PD(5), $E_\alpha(F_1)$ from PD(6) and $E_\alpha(F_1)$ from CR. Accordingly, for stage III, it appears that $E_\alpha(D_3)$ from PD(6) $\approx E_\alpha(D_3)$ from CR and $E_\alpha(R_3)$ from PD(6) $\approx E_\alpha(R_3)$ from CR. Comparison of the best fitting expressions on the basis of the PD(5) method reveals that the same models have been selected for the first stage of the thermal decomposition of $[Co(NH_3)_6]Cl_3$ in both gaseous atmospheres, while for stage II or III only some of the models are the same (see Tables 2 and 3).

From the integral methods the following relations have been found for the two atmospheres: for stage II the same models (F_1, A_2 and A_3); for stage I only some models are the same (R_2 and D_4); for stage III, different models.

It has been observed that the E_α values for dissociation in argon (stages I and II) are lower than these in air for the corresponding models.

The dependences mentioned above are similar to those presented in Ref. 33 and are in agreement with the sequences of $[Co(NH_3)_6]Cl_3$ thermal decomposition presented earlier.

If the assumption is made that the form of $f(\alpha)$ or $g(\alpha)$ is connected with the reaction mechanism, then it may be considered that the pairs of mechanisms R_nD_n selected for stages I and III do not conflict with the results of morphological studies presented in Ref. 30.

The principal conclusion resulting from the data reported above is that, on the basis of dynamic measurements, the selection of only one kinetic model is practically impossible using the presented methods, i.e. PD(5), PD(6) or CR. Of course, it is possible to force a selection of one model with the highest value of Snedecor's test F, or the regression coefficient r, but small differences in their values presented in Tables 2 and 3 do not justify this being done.

Results from the performed experiments and the data presented above confirm the problem, mentioned many times, that it is impossible to choose one kinetic model from dynamic measurements.

The Phadnis–Deshpande method has an additional disadvantage, as pointed out earlier [33], that the following relations of the activation energy values exist

$$E_\alpha(D_1) = 2E_\alpha(R_1)$$

$$E_\alpha(F_1) = 2E_\alpha(A_2) = 3E_\alpha(A_3)$$

$$E_\alpha(D_3) = 2E_\alpha(R_3)$$

In consideration of the above mentioned problems in choosing one proper kinetic model followed by evaluation of the real kinetic parameters, investigations under isothermal conditions have been performed.

Isothermal experiments

The kinetic model functions in integral form $g(\alpha)$ listed in Table 1 were examined for the particular stages of $[Co(NH_3)_6]Cl_3$ thermal decomposition by conventional isothermal analysis according to the following kinetic equation

$$g(\alpha) = kt \qquad (9)$$

where α is the degree of conversion, k is the rate constant and t is the isothermal time.

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.

Figures 1a–c show the α vs. t curves obtained from the isothermal TG experiments for the different stages of $[Co(NH_3)_6]Cl_3$ decomposition. The form of the curves in Fig. 1a (stage I) suggests deceleratory models, i.e. contracting area (R_2) or volume (R_3). The rectilinear parts of the curves in the range of α up to 0.95 in Fig. 1b (stage II) indicate the R_1 model. As can be seen in Fig. 1c (stage III), the experimental points fall fairly close to the straight line, which may suggest the R_1 model as well.

Table 4 gives values of the rate constant calculated for the best fitted models, together with the statistical parameters r, F and S. In Table 5 approximate values of the kinetic parameters A and E_α are presented.

The data reported in Table 4 show that, for the first stage of dissociation, the best models are R_3 and R_2, which are compatible with the results from non-isothermal experiments. The approximate E_α, $A(R_3)$ values calculated from the isothermal experiments (see Table 5) are close to E_α, $A(R_2)$ from

TABLE 4

Values of kinetic parameters from isothermal TG curves in air atmosphere.

Stage	Range of α	Temperature (K)	Model	Rate constant $k \times 10^3$ (min^{-1})	Statistical parameters		
					r	F [a]	S
I	0.07–0.80	498.5	R_3	10.176	0.9967	3186	0.030467
			R_2	8.965	0.9945	1891	0.034838
			D_1	5.848	0.9940	1742	0.023678
			D_2	4.300	0.9908	1133	0.021589
	0.02–0.95	502.0	R_3	12.080	0.9985	4696	0.032503
			R_2	10.013	0.9975	2838	0.034659
			D_1	6.469	0.9969	2247	0.025161
			D_2	5.490	0.9909	756	0.036832
	0.10–0.95	506.0	R_2	13.844	0.9995	16002	0.014047
			R_3	16.787	0.9988	6788	0.026152
			A_2	12.653	0.9980	4002	0.025673
			D_1	9.183	0.9971	2817	0.022208
II	0.06–0.95	552.0	R_1	4.014	0.9996	25138	0.008054
			A_3	4.121	0.9934	1586	0.032921
	0.07–0.96	561.0	R_1	4.611	0.9988	7430	0.013795
			A_3	4.834	0.9932	1319	0.034330
			R_2	7.613	0.9900	888	0.065865
	0.13–0.95	583.0	R_1	12.535	0.9992	7124	0.011200
			R_2	19.990	0.9956	1348	0.041055
			A_2	18.673	0.9904	615	0.056782
III	0.02–0.62	761.5	R_1	1.350	0.9974	4322	0.014808
			A_2	1.778	0.9966	3363	0.022110
			R_2	1.664	0.9965	3235	0.021096

[a] F_{cr} values are within the range 7.88–9.33.

TABLE 5

Approximate values of kinetic parameters for selected models: isothermal experiments

Stage	Model	E_α (kJ mol^{-1})	A (min^{-1})	r
I	R_3	144.4	1.35×10^{13}	0.986929
	R_2	125.6	1.25×10^{11}	0.966782
II	R_1	102.9	1.98×10^{7}	0.982454
	A_2	103.8	3.56×10^{7}	0.988316
	A_3	112.7	1.71×10^{8}	0.983522
	R_2	102.8	3.1×10^{7}	0.988614

PD(5) and CR methods and E_α, A from ASPP methods. Therefore it may be concluded that, for the first stage of thermal decomposition in air, the best models are R_3 and R_2. It is emphasized that the isothermal kinetic characteristics of solid state decomposition reactions are often determined by the progressive changes of interface geometry as the reaction advances [34].

For the second stage of $[Co(NH_3)_6]Cl_3$ decomposition in air, the best model within the whole temperature range is R_1. This model appeared among the best fitted ones only with the PD(5) method when the dynamic experiments were made. The approximate E_α, A values for the best models of stage II presented in Table 5 are very close to each other. The values of E_α, $A(A_2)$ from isothermal experiments are near to E_α, $A(A_2)$ determined by integral methods for non-isothermal measurements (see Table 2).

For the third stage of $[Co(NH_3)_6]Cl_3$ decomposition the TG isothermal curve is fitted best by the R_1 model, which is compatible with the results of dynamic experiments.

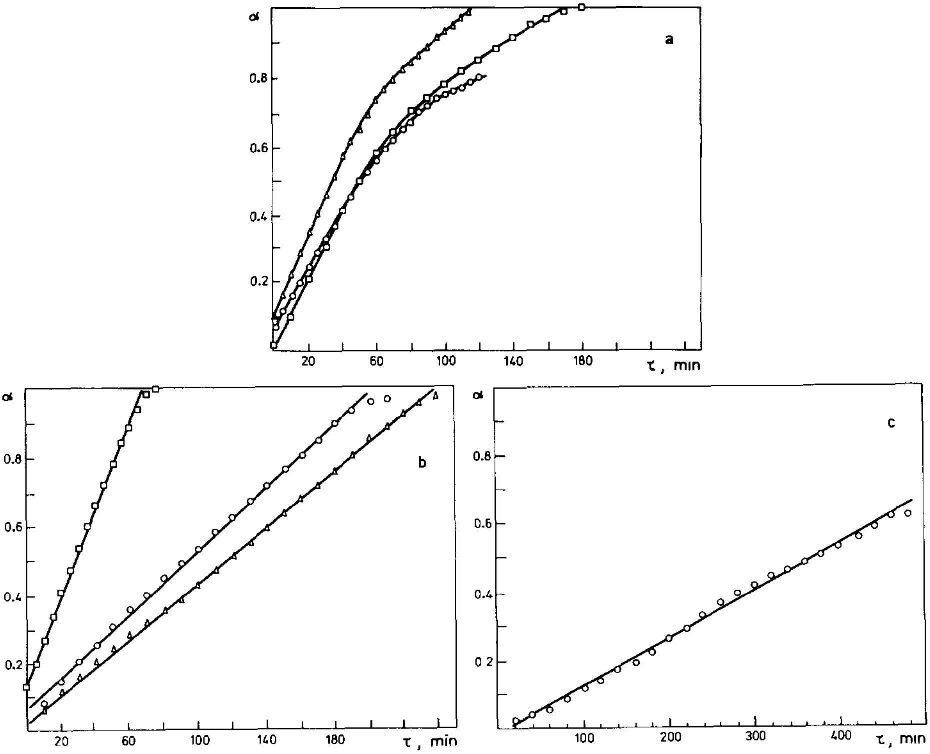

Fig. 1. Isothermal conversion–time curves. (a) First stage of dissociation: ○, 498.5 K; □, 502 K; △ 506 K. (b) Second stage of dissociation: △, 552 K; ○, 561 K; □, 583 K. (c) Third stage of dissociation: ○, 761.5 K.

CONCLUSIONS

The various results obtained have confirmed the view expressed earlier by Arnold et al. [35–38] that the mathematical method of treatment of experimental results influences the choice of the best fitted model. In this paper the second stage of thermal decomposition of $[Co(NH_3)_6]Cl_3$ is a good illustration of this fact.

The results corroborate the opinion given in the introduction of this paper that it is advisable to combine isothermal and non-isothermal measurements. This approach simplifies the selection of the models best fitting the experimental TG curves followed by the calculation of reliable kinetic parameters.

The R_n models selected as those best fitting the experimental TG curves suggest that the kinetics and macromechanism of the thermal decomposition of $[Co(NH_3)_6]Cl_3$ could be governed by phase boundary processes. This has been confirmed by morphological observations [30,39]. Similarly, the results of Oswald and co-workers [8,40] revealed that the phase boundary process controlled the macroscopic mechanism of the thermal decomposition of single crystals of some nickel complex compounds.

ACKNOWLEDGEMENT

This work was supported by the CPBP 03.08 Program.

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