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A thermal decomposition study on cobalt(II) complexes of 1,2-di(imino-4′-antipyrinyl)ethane

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Abstract

The phenomenological, kinetic and mechanistic aspects of thermal decomposition of perchlorate, nitrate, chloride, bromide and iodide complexes of cobalt(II) with the Schiff base 1,2-di(imino-4′-antipyrinyl)ethane (GA) have been studied by TG and DTG analyses. The kinetic parameters like the activation energy, pre-exponential factor and entropy of activation were calculated. The decomposition reactions follow “random nucleation with one nucleus on each particle—Mampel model”.

Keywords: Coats-Redfern; Decomposition; Kinetics; Cobalt(II) complexes

1. Introduction

A plethora of references describing the metal complexes of Schiff bases have appeared in the literature during the past few decades [1–3,7]. However, little is known on the thermal studies of such complexes [4,5]. In view this and as part of our continuing interest on the thermal studies of Schiff base-metal complexes [6,12], we report here the phenomenological, kinetic and mechanistic aspects of thermal decomposition of the perchlorate, nitrate, chloride, bromide and iodide complexes of cobalt(II) with the Schiff base derived from antipyrine, viz., 1,2-di(imino-4′-antipyrinyl)ethane (GA), empirical formula: $C_{24}H_{24}N_6O_2$ (Fig. 1).

2. Experimental

The Schiff base, 1,2-di(imino-4′-antipyrinyl)ethane (GA) and its cobalt(II) complexes were prepared and characterized as reported earlier [7]. Thermogravimetric analyses were undertaken on Delta Series TGA 7 thermal analyzer in nitrogen atmosphere, sample mass: 10 mg; heating rate: 10 °C min^{-1}. The kinetic evaluation of the thermal decomposition of the complexes was done using a computer program in Qbasic.

3. Results and discussions

The elemental analysis, electrical conductance in non-aqueous media, magnetic moments and infrared as well as electronic spectra show [7] that the five complexes have the formulae: $[Co(GA)(ClO_4)]ClO_4$, $[Co(GA)(NO_3)]NO_3$, $[Co(GA)Cl_2]$, $[Co(GA)Br_2]$ and

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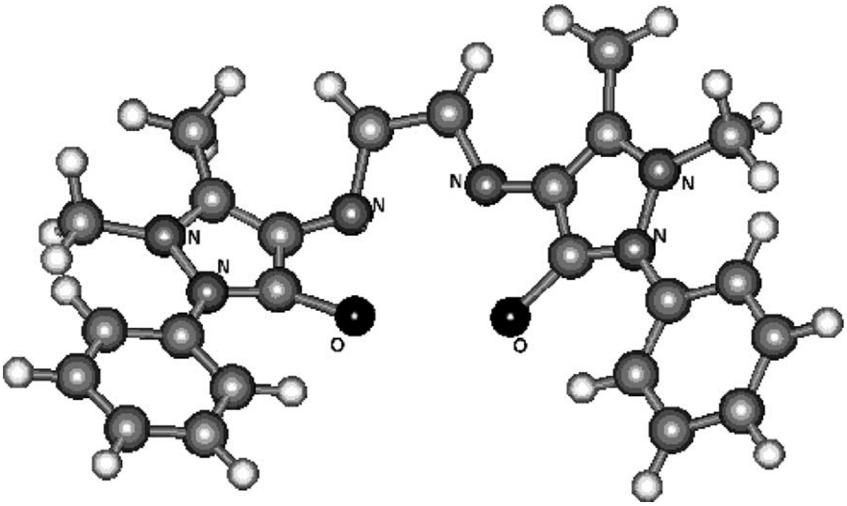

Fig. 1. 1,2-Di(imino-4′-antipyrinyl)ethane.

[Co(GA)I$_2$]. GA acts as a neutral tetradentate ligand coordinating through both carbonyl oxygens and both azomethine nitrogens in all these complexes. In the perchlorate and nitrate complexes, one of the anions is coordinated in a bidentate fashion, whereas in the halide complexes both the anions are coordinated to the metal, generating an octahedral geometry around the cobalt(II) ion (Fig. 2). The TG and DTG curves of all five complexes are given in Figs. 3–7.

3.1. Phenomenological aspects

The phenomenological aspects of the present complexes are presented in (Table 1). The perchlorate complex is represented as Co(GA)(ClO$_4$)]ClO$_4$. It undergoes a three-stage decomposition in the range 252–641 °C. The first stage starts at 252 °C and ends at 374 °C. The observed mass loss (31.42%) is attributed to the decomposition of half a molecule of GA. The infrared spectrum of the residue after this stage shows the presence of GA indicating only partial removal of the ligand. The DTG peak corresponding to this stage is observed at 305 °C. The second stage starts at 374 °C and ends at 540 °C. The corresponding mass loss (18.56%) is due to the conversion of two perchlorates into chlorides. Absence of perchlorate ion after this stage is confirmed by infrared spectral analysis of the intermediate compound obtained at 540 °C. The

Table 1
Phenomenological data for the thermal decomposition of cobalt(II) complexes

Complex	Stage of decomposition	TG plateaux (°C)	DTG peak (°C)	Mass loss found (calculated %)
[Co(GA)(ClO$_4$)]ClO$_4$	I	252–374	305	31.42 (31.21)
	II	374–540	431	18.56 (18.65)
	III	540–641	580	31.78 (31.21)
[Co(GA)(NO$_3$)]NO$_3$	I	156–327	270	35.07 (35.03)
	II	327–423	389	19.92 (20.28)
	III	423–499	440	35.35 (35.03)
[Co(GA)Cl$_2$]	I	172–463	354	38.64 (38.37)
	II	463–636	610	38.36 (38.37)
[Co(GA)Br$_2$]	I	283–450	372	33.60 (33.09)
	II	450–	–	Continuous
[Co(GA)I$_2$]	I	179–461	326	59.56 (59.98)
	II	461–539	483	35.71 (35.53)

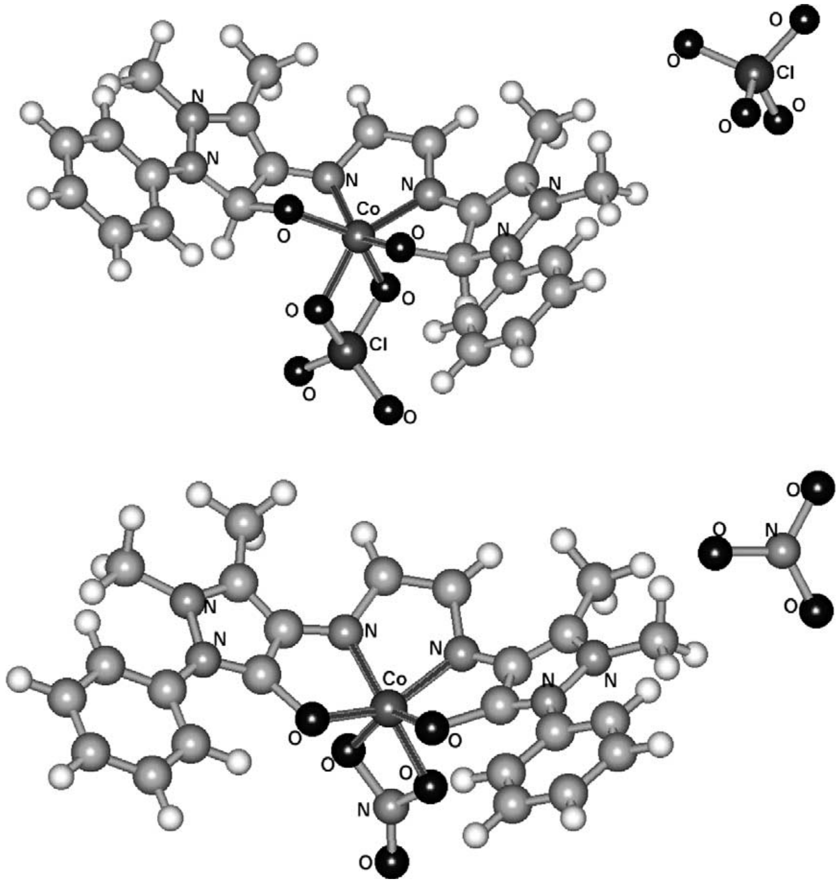

Fig. 2. Tentative structures of cobalt(II) complexes of 1,2-di(imino-4′-antipyrinyl)ethane.

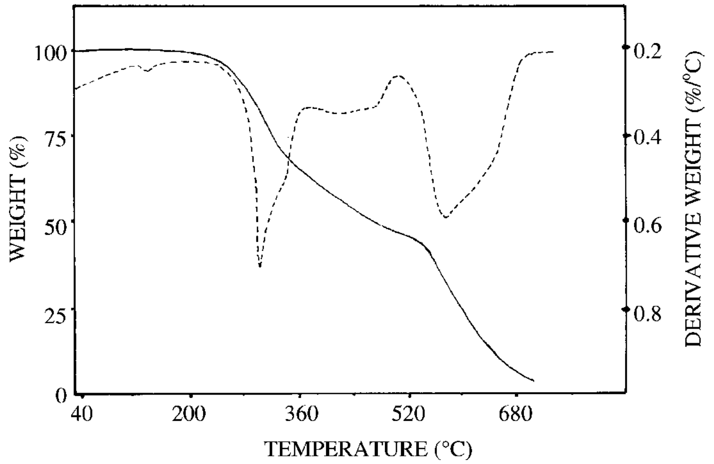

Fig. 3. TG and DTG curves of $[Co(GA)ClO_4]ClO_4$.

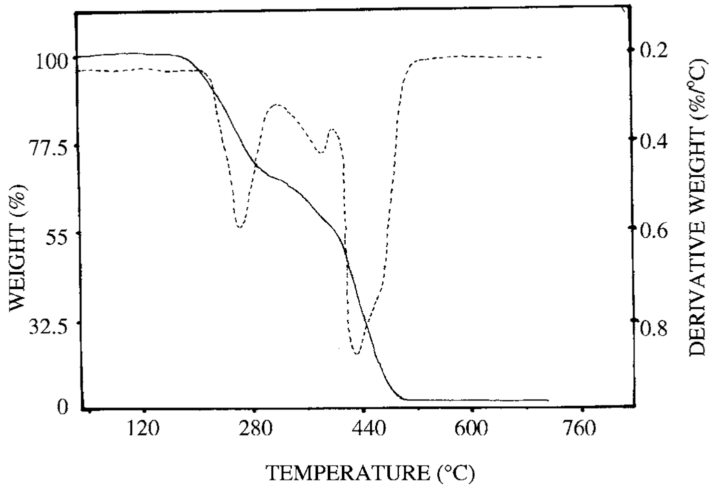

Fig. 4. TG and DTG curves of [Co(GA)NO_3]NO_3.

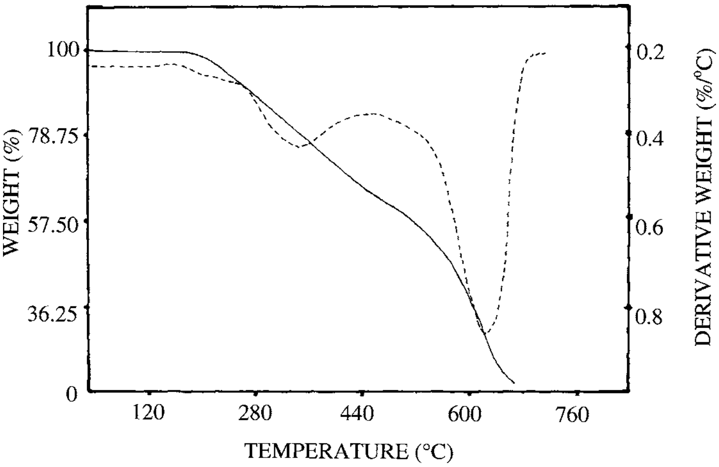

Fig. 5. TG and DTG curves of [Co(GA)Cl_2].

rate of mass loss is maximum at 431 °C as indicated by the DTG peak. The third stage, which occurs in the temperature range 540–641 °C with a DTG peak at 580 °C, corresponds to a mass loss of (31.78%) corresponding to the decomposition of the remaining half of the GA molecule. The final residue is anhydrous cobalt chloride as confirmed by qualitative analysis.

The nitrate complex is formulated as [Co(GA)(NO_3)]NO_3. It decomposes in three stages. The first stage starts at 156 °C and ends at 327 °C. The maximum rate of mass loss is indicated by the DTG peak at 270 °C. The corresponding mass loss (35.07%) is due to the decomposition of half a molecule of GA. The infrared spectrum of the residue after this stage shows the presence of GA indicating only a partial removal of the ligand. The second stage of decomposition starts at 327 °C and ends at 423 °C with the DTG peak at 389 °C. The corresponding mass loss (19.92%) is due to the decomposition of two nitrate ions. The third stage starts at 423 °C and ends at 499 °C with the DTG peak at 440 °C. The corresponding mass loss (35.35%) is attributed to the removal of the remaining

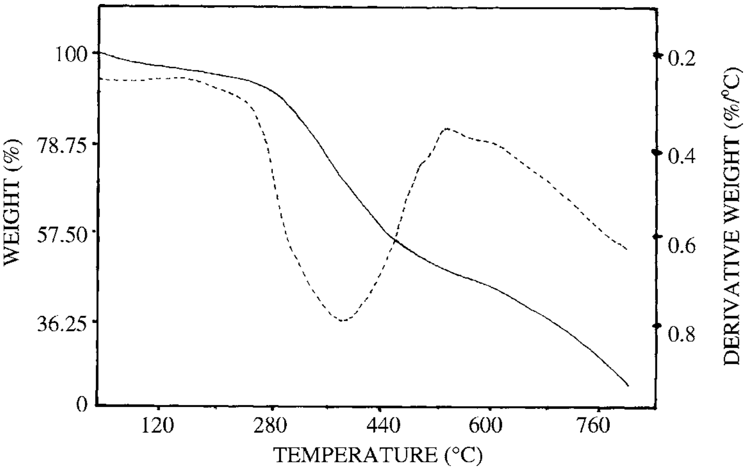

Fig. 6. TG and DTG curves of [Co(GA)Br_2].

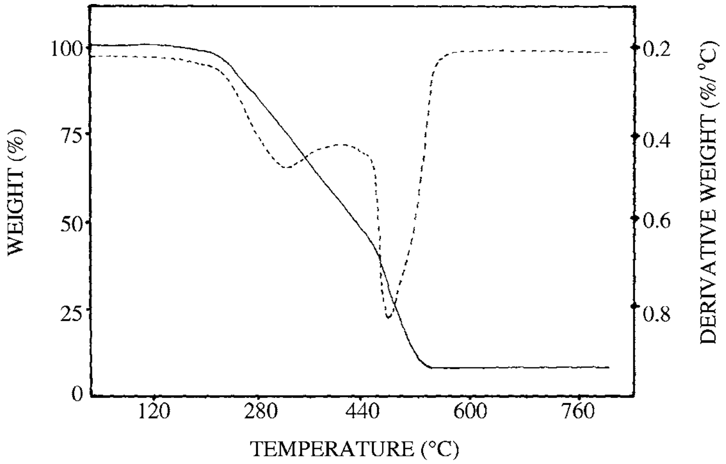

Fig. 7. TG and DTG curves of [Co(GA)I_2].

half of the molecule of GA. The decomposition complete at 499 °C and the final residue is anhydrous cobalt oxide as confirmed by qualitative analysis.

The chloride complex [Co(GA)Cl_2], undergoes a two-stage decomposition. The first stage begins at 172 °C and ends at 463 °C. The corresponding mass loss (38.64%) is due to the decomposition of half a molecule of GA. The infrared spectrum of the residue after this stage shows the presence of GA, indicating only a partial removal of the ligand. The second stage starts at 463 °C and ends at 636 °C and the corresponding mass loss (38.36%) is due to the removal of the remaining half of the molecule of GA, yielding anhydrous cobalt chloride as the final residue as confirmed by qualitative analysis. The rate of mass loss is found to be maximum at 354 and 610 °C, respectively for the first and second stages as indicated by the corresponding DTG peaks.

The bromide complex is represented as [Co(GA) Br_2]. It undergoes decomposition in two stages. The first stage starts at 283 °C and ends at 450 °C. The corresponding mass loss (33.60%) is attributed to the decomposition of half a molecule of GA. The infrared spectrum of the residue after this stage shows the presence of GA, indicating only a partial removal of the ligand. The DTG peak of this stage is observed at 372 °C. The second stage of decomposition starts at 450 °C and is a continuous one. The steady mass loss observed in this stage may be due to the expulsion of the remaining half of the molecule of GA together with volatilization of the residue of anhydrous cobalt bromide [8] above 678 °C.

The iodide complex, $[Co(GA)I_2]$, undergoes a two stage decomposition. The first stage begins at 179 °C and ends at 461 °C with the DTG peak at 326 °C. The corresponding mass loss (59.56%) is due to the decomposition of the GA molecule. The second stage starts at 461 °C and ends at 539 °C with the DTG peak at 483 °C. The corresponding mass loss (35.71%) is due to the decomposition of two iodide ions. The decomposition complete at 539 °C and the final residue is anhydrous cobalt oxide as confirmed by qualitative analysis.

3.2. Structure and thermal stability correlation

The TG and DTG data reveal that although the molecular composition of the complexes is the same, viz., $Co(GA)X_2$ ($X = ClO_4^-$, NO_3^-, Cl^-, Br^- or I^-), the nature of the decomposition pattern is different. The perchlorate and nitrate complexes exhibit a three-stage decomposition whereas a two-stage decomposition is observed in the case of chloride, bromide and iodide complexes. Within the series the nitrate complex is the least stable and the bromide complex is the most stable. The difference in thermal stability of the complexes is in the order bromide > perchlorate > iodide > chloride > nitrate.

3.3. Kinetic aspects

All the well-defined stages were selected for the study of the kinetics of decomposition of the complexes. The kinetic parameters (the activation energy E and the pre-exponential factor A) were calculated using the Coats-Redfern equation [9].

$$\log\left[\frac{g(\alpha)}{T^2}\right] = \log\frac{AR}{\phi E}\left[1-\frac{2RT}{E}\right] - \frac{E}{2.303RT}$$

In the present case, a plot of L.H.S of this equation against 1/T gives straight line (Figs. 7 and 8) whose slope and intercept are used for calculate the kinetic parameters by the least-square method. The goodness of fit was checked by calculating the correlation coefficient.

The entropy of activation ΔS can be calculated using the equation

$$A = \frac{kT_s}{h}e^{\Delta S/R}$$

where, k is the Boltzmann constant, h the Planck's constant and T_s the peak temperature.

The various kinetic parameters calculated are given in Table 2. The activation energy (E) in the different stages are in the range 30.16–306.99 kJ mol^{-1}. The respective values of the pre-exponential factor (A) vary from 2.72×10^{-2} to 7.84×10^{7} s^{-1}. The corresponding values of the entropy of activation (ΔS) are in the

Table 2
Kinetic parameters for the thermal decomposition of cobalt(II) complexes

Complex	Stage	E (kJ mol^{-1})	A (s^{-1})	ΔS (J mol^{-1})
$[Co(GA)(ClO_4)]ClO_4$	I	97.94	45.79	−218.61
	II	174.90	1.01	−251.88
	III	232.48	1.46×10^{3}	−173.89
$[Co(GA)(NO_3)]NO_3$	I	66.49	3.73	−238.94
	II	114.15	55.96	−218.07
	III	306.99	7.84×10^{7}	−100.89
$[Co(GA)Cl_2]$	I	30.16	2.72×10^{-2}	−281.02
	II	187.53	6.33×10^{2}	−200.45
$[Co(GA)Br_2]$	I	49.88	0.15	−266.63
$[Co(GA)I_2]$	I	35.66	4.84×10^{-2}	−275.78
	II	221.64	5.30×10^{4}	−162.08

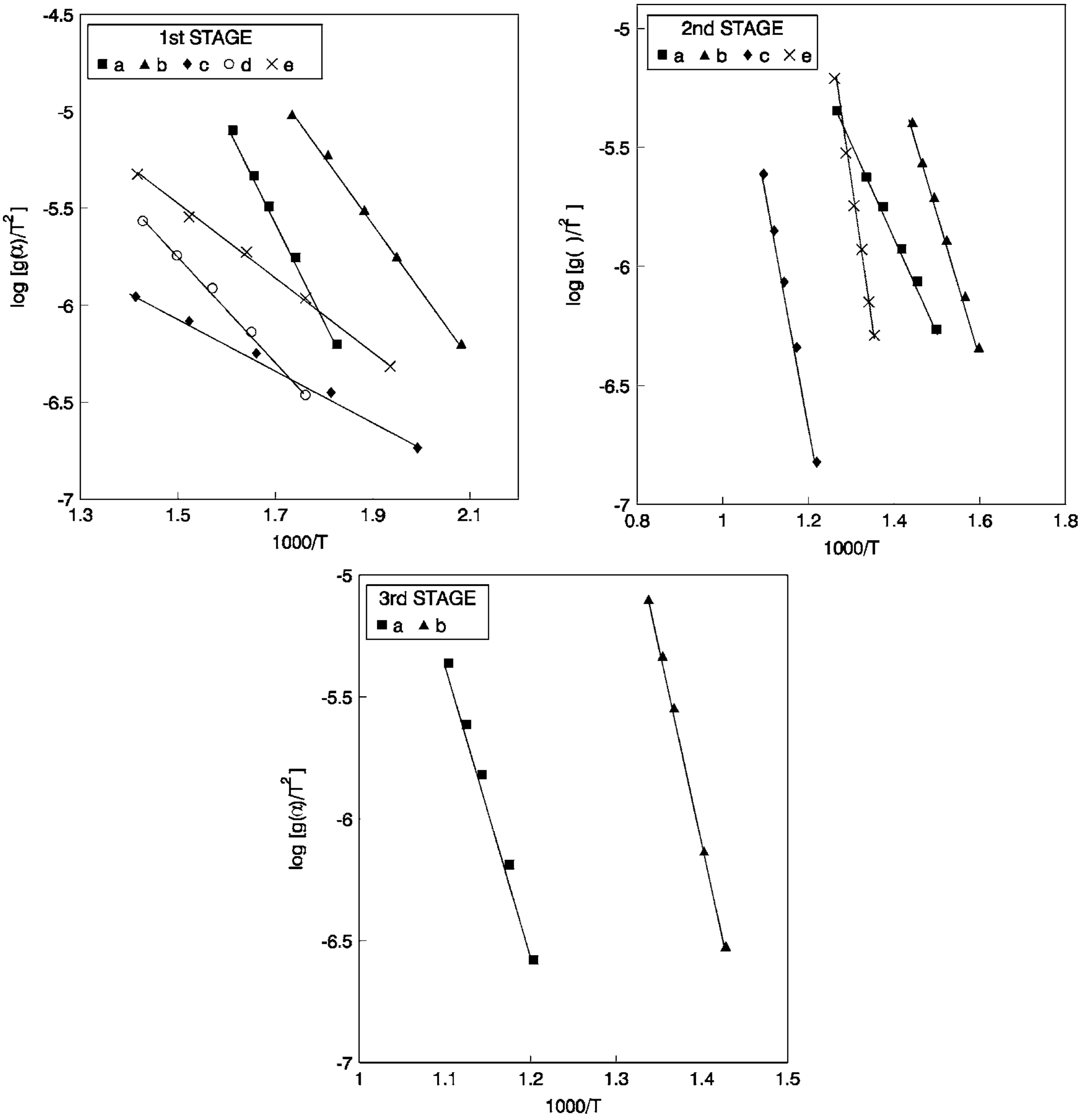

Fig. 8. Plots ($\log[g(\alpha)/T^2]$ vs. $1000/T$) for the thermal decomposition of cobalt(II) complexes. (a) $[Co(GA)(ClO_4)]ClO_4$; (b) $[Co(GA)(NO_3)]NO_3$; (c) $[Co(GA)Cl_2]$; (d) $[Co(GA)Br_2]$; (e) $[Co(GA)I_2]$.

range −281.02 to −100.89 J mol^{-1}. There is no definite trend either in the values of A or ΔS among the different stages in the present series. But the activation energy for the second stage is greater than that of the first stage, may due to the less steric strain occurring at that stage. However, the negative values of entropy of activation indicate that the activated complex has a more ordered structure than the reactants [11,12].

3.4. Mechanistic aspects

The assignment of the mechanism is based on the assumption that the form of $g(\alpha)$ depends on the reaction mechanism. Here in the present investigation, nine forms of $g(\alpha)$, suggested by Satava [10] are used to enunciate the mechanism of thermal decomposition in each stage. The correlation coefficient for all these nine forms were calculated and the form of $g(\alpha)$ for which the correlation has a maximum value is chosen as the mechanism of reaction. In the present investigation, the highest value of correlation coefficient is obtained for

$$g(\alpha) = -\ln(1-\alpha)$$

in all stages of decomposition. Hence, the mechanism is "random nucleation with one nucleus on each particle" representing 'Mampel model'.

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