Non-Isothermal Decomposition of 2-(2-Hydroxybenzylideneamino)-3-phenylpropanoic Acid in Nitrogen Atmosphere

M. VENNILA, G. MANIKANDAN,
V. THANIKACHALAM and J. JAYABHARATHI*

Department of Chemistry, Annamalai University
Annamalai Nagar - 608 002, India
pvt1998@yahoo.co.in

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Abstract: The non-isothermal decomposition properties of 2-(2-hydroxybenzylideneamino)-3-phenylpropanoic acid [HBAPPA] have been studied using microanalysis, FT-IR, UV, DTA, DTG and TG techniques. The TG studies were carried out at different heating rates of 10, 15 and 20 K/min. The Schiff base decomposed in three stages. The kinetic parameters were deduced for each stage. A probable mechanism has been proposed for the decomposition process.

Keywords: Non-isothermal decomposition, Schiff base, Kinetic parameters.

Introduction

The well established thermogravimetric analysis (TGA), differential thermal analysis (DTA) and differential thermogravimetric analysis (DTG) techniques have been widely used for studying the thermal behaviour of various types of materials and the thermodynamic parameters for the decomposition processes could be evaluated. A method to determine the activation energy by using integral dynamic curves from TG at multiple heating rates has been proposed by Flynn-Wall¹ and Ozawa². Several studies have been carried out for the determination of kinetic parameters *viz.*, activation energy, pre-exponential factor and life time of several materials such as polymers, organic and inorganic compounds³⁻⁶.

The Schiff base derived from salicylaldehyde and *L*-phenylalanine and its complexes are used as antibacterial⁷, antifungal^{7,8}, antimalarial⁹ agents and also for DNA cleavage¹⁰, amino oxidase¹¹, deamination antiradical activity¹², bio-distribution and blood clearance¹³. We are reporting here, the non-isothermal decomposition of 2-(2-hydroxybenzylideneamino)-3-phenylpropanoic acid at different heating rates in nitrogen atmosphere.

Experimental

Phenylalanine, salicylaldehyde and other chemicals used were of AnalaR grade from BDH.

Preparation of 2-(2-hydroxybenzylideneamino)-3-phenylpropanoic acid

The compound was synthesized by mixing an aqueous alcoholic solution of sodium salt of *L*-phenylalanine (0.01 M) and salicylaldehyde (0.01 M) (Scheme 1). The reaction mixture was heated for about 4 h. The resultant solution was cooled to room temperature and treated with 1:1 HCl. The pale yellow Schiff base was filtered, washed thoroughly with deionised water and dried in vacuum. The solid obtained was recrystallized using DMSO-water (50%). The melting point of the compound is 189 °C (lit: 189¹⁴). Micro anal calcd % for C₁₆H₁₅NO₃: C, 71.37; H, 5.57; N, 5.20; found: C, 70.41; H, 5.34; N, 5.73. λ_{max} (DMF) = 303nm, FT-IR (KBr): ν 3071 (C – H), 1624 (C = N), (C = O) 1488 (C – N), 1504 (C – O), 1036 (C – O) and 747 (C – H) cm⁻¹.

Scheme 1

Measurements

Microanalysis of the compound was carried out in a HERAEUS Carlo Erba 1108 model at Central Drug Research Institute, Lucknow, India. The UV-Visible spectrum of the sample was recorded on a HITACHI 2001 UV-Visible spectrophotometer in DMF medium. The FT-IR spectrum was recorded on a AVATAR model 360 using KBr pellets. Thermogravimetric analysis was carried out using a NETZSCH - Gerate bare GMBH thermal analysis, STA 409 PC. The weight of the sample was maintained constant (10 mg) for all the heating rates.

Kinetic theory

The degree of conversion of the decomposition process is expressed as

$$\alpha = \frac{m_0 - m_t}{m_0 - m_\infty} \quad (1)$$

Where, m_0 is the initial mass of the sample, m_t the mass of the sample at time t and m_∞ , the final mass of the sample in that reaction. The general kinetic equation is written as

$$\frac{d\alpha}{dt} = k(T) f(\alpha) \quad (2)$$

Where α is the degree of conversion of the sample and t is time, T in the absolute temperature, $f(\alpha)$ is a function, the type of which depends on the reaction mechanism, $k(T)$, the temperature dependent rate constant, usually described by Arrhenius equation as,

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad (3)$$

Where, A is pre-exponential or frequency factor. E_a is the activation energy and R is the universal gas constant. Inserting Eqn (2) into Eqn (1) gives

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (4)$$

An integration function is shown as

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T \exp\left(-\frac{E}{RT}\right) dT \quad (5)$$

Where $g(\alpha)$ is the integral kinetic function or integral reaction model when its form is mathematically defined, $\beta = dT/dt$, the heating rate of decomposition. The kinetic parameters were calculated using model-fitting Coats and Redfern method^{15,16}, model-free Flynn-Wall-Ozawa^{1,2} (FWO), Kissinger-Akahira and Sunose^{17,18} (KAS) and Tang^{19,20} (T) methods.

Model-free method

The following procedures are used for the determination of kinetic parameters by isoconversional methods.

Flynn-Wall-Ozawa method^{1,2}

The isoconversional integral method suggested independently by Flynn- Wall¹ and Ozawa² uses Doyle's approximation of $p(x)$. This method is based on the Eqn (6).

$$\log \beta = \log \frac{AE_a}{Rg(\alpha)} - 2.315 - 0.4567 \frac{E_a}{RT} \quad (6)$$

Thus, for a constant α value, the plot $\log \beta$ versus $(1/T)$, obtained from thermograms recorded at several heating rates should be a straight line whose slope can be used to evaluate the apparent activation energy.

Kissinger-Akahira and Sunose method^{17,18}

This method is based on the Eqn (7).

$$\ln \left[\frac{\beta}{T^2} \right] = \ln \left[\frac{AR}{E_a g(\alpha)} \right] - \frac{E_a}{RT} \quad (7)$$

Thus, for a fixed α value, the plot of $\ln \left[\frac{\beta}{T^2} \right]$ versus $(1/T)$ should be a straight line whose slope can be used to evaluate the apparent activation energy.

Tang method^{19,20}

This is based on the eqn. (8)

$$\ln \left[\frac{\beta}{T^{1.894661}} \right] = \ln \left[\frac{AE_a}{g(\alpha)} \right] - 3.635041 - 1.894661 \ln E_a - 1.001450 \frac{E_a}{RT} \quad (8)$$

Thus, for constant α , the plot of $\ln \left[\frac{\beta}{T^{1.894661}} \right]$ versus $1/T$, should be a straight line whose slope can be used to calculate E_a .

Model-fitting method (Coats and Refern)^{15,16}

Modified Coats-Redfern equation is used for the determination of Arrhenius parameters.

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

Different models are used for the calculation of kinetic parameters (Table 1).

Kissinger method^{17,21}

Kissinger proposed a kinetic analysis method for thermal reactions. Models with different orders, [$f(\alpha) = 1 - \alpha^n$] are based on taking the derivative of Eqn. (10) generating $\frac{d^2\alpha}{dT^2}$.

According to Kissinger, the maximum reaction rate occurs when the second derivative is zero from which the following equation can be obtained:

$$\frac{E_a \beta}{RT_m^2} = A (n(1 - \alpha_m)^{n-1}) e^{-\frac{E_a}{RT_m}} \quad (10)$$

Where, T_m is the temperature of the maximum rate and α_m is the conversion value at that rate. The maximum reaction rate represents the peak (*i.e.* inflection point) of a DSC or DTG curve. Taking the natural logarithm of Eqn. (10) and rearranging gives,

$$\ln \left(\frac{\beta}{T_m^2} \right) = \ln \left(\frac{AR(n(1 - \alpha_m)^{n-1})}{E_a} \right) - \frac{E_a}{RT_m} \quad (11)$$

The activation energy is obtained by plotting the left-hand side of the above equation versus $\frac{1}{T_m}$ for a series of runs at different heating rates. Eqn. (11) has been generalized to any

reaction model ($f(\alpha)$). The peak temperatures are noted from DTG curves at different heating rates^{22,23}. The thermodynamic parameters can be calculated using the following equations:

$$A \exp(-E/RT) = \nu \exp(-\Delta G^\ddagger/RT) \quad (12)$$

$$\Delta H^\ddagger = E - RT \quad (13)$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (14)$$

Where $\Delta G^\ddagger$ is the Gibbs free energy of activation, $\Delta H^\ddagger$ the enthalpy of activation, $\Delta S^\ddagger$ the entropy of activation and ν the Einstein vibrational frequency, $\nu = k_B T/h$ (where k_B and h are Boltzmann and Planck's constants, respectively). The values of entropy, enthalpy and free energy of activation at the peak temperatures are obtained on the basis of Eqns. (12) - (14).

Results and Discussion

TG, DTA and DTG curves of salicylidene-phenylalanine are shown in Figure 1 at various heating rates, *i.e.* 10, 15 and 20 K/min. As can be seen from Figure 1, the compound is stable up to 200 °C in all heating rates. After the endothermic process of melting at 104.8 °C at the heating rate of 10 K/min, it shows three decomposition stages of mass loss. The first stage starts at 480 K and ends at about 550 K with the corresponding mass loss of 68.71, 62.27 and 65.90% at different heating rates. It is probably due to the partial release of phenylalanine (found 62.27; calculated 60.57%) characterized by a strong endothermic peak. The second stage starts at 550 K and ends at 693 K, with the mass loss of 16.48, 16.78 and 22.48% respectively for different heating rates (weak endothermic) attributed to the partial decomposition of salicylaldehyde (cyclobutadione) (found 16.46; calculated 19.33%) with weak endothermic peak observed at 387.3 °C. In the third stage, which starts at 694 K ends at 1073 K. This is due to the mass loss of cyclopropanic oxide. Similar trends are observed for other heating rates also.

Figure 1. TG, DTA and DTG curves of HBAPPA at a) 10 K min^{-1} ; b) 15 K min^{-1} and c) 20 K min^{-1} heating rates in nitrogen atmosphere.

Kinetic analysis

TG, DTG, DTA curves of the title compound are shown in Figure 1. The data obtained for the non-isothermal decomposition process at 10, 15 and 20 K/min were processed according to equation (1). The variation of E_a with α for all the three decomposition stages are given in Figures. 2-4. It is seen that E_a value depends upon the extent of conversion in stages I and III (Figures 2 & 4), whereas in stage II (Figure 3) it is independent of the extent of conversion ($0.2 \leq \alpha \leq 0.8$). The data indicate that the kinetics are likely to be governed by a single step reaction *i.e.*, F_1 mechanism for state II, whereas as multi-step reactions are involved in stages I and III. It is seen from the Figures 2 and 4, that there is a decrease in activation energy for stage I and for the stage III it increases up to $\alpha \leq 0.5$ and then decreases. This suggests that it follows a multi-step kinetics. Conversely, in stage II, the E_a values do not significantly vary with α ($0.1 \leq \alpha \leq 0.8$). Figure 2 shows a decrease in activation energy from 200 to 102 kJ/mol as α increases. In second stage, the E_a value increases from 93 to 190 kJ/mol (Figure 3). In the third stage, the E_a value increases from 26 to 96 kJ/mol ($0.1 \leq \alpha \leq 0.5$) (Figure 4).

Figure 2. Variation of the E_a with α for the first stage decomposition of HBAPPA by FWO method

Figure 3. Variation of E_a with α for the second stage decomposition of HBAPPA by FWO method

Figure 4. Variation of E_a with α for the third stage decomposition of HBAPPA by FWO method

Invariant kinetic parameters

The invariant kinetic parameters, E_{inv} and A_{inv} are calculated using Coats-Redfern method^{15,16,24} (Table 1). The values of E_a and $\ln A$ depend on the kinetic model as well as on the heating rate, as shown in Tables 2-4. The evaluation of the invariant parameters is performed using supper correlation equation and the values are listed in Table 5.

$$a_{\beta} = \ln A_{inv} - b_{\beta} E_{inv}$$

Table 1. Algebraic expressions of $f(\alpha)$ and $g(\alpha)$ for the reaction models considered in the present work^{15,16}

Symbol	Reaction Model	Differential form ^a	
		$f(\alpha) = \frac{1}{k} \frac{d\alpha}{dt}$	Integral form ^a $g(\alpha) = kt$
P2	Power law	$3\alpha^{(2/3)}$	$\alpha^{(1/3)}$
P3	Power law	$2\alpha^{(1/2)}$	$\alpha^{(1/2)}$
D1	1-D Diffusion	$1/2\alpha$	α^2
P4	Power law	$2/3\alpha^{(-1/2)}$	$\alpha^{(3/2)}$
F1	First-order (mampel)	$(1-\alpha)$	$-\ln(1-\alpha)$
A4	Avrami-Erofe'ev (n=4)	$4(1-\alpha)[- \ln(1-\alpha)]^{3/4}$	$[- \ln(1-\alpha)]^{1/4}$
A3	Avrami-Erofe'ev (n=3)	$3(1-\alpha)[- \ln(1-\alpha)]^{2/3}$	$[- \ln(1-\alpha)]^{1/3}$
A2	Avrami-Erofe'ev (n=2)	$2(1-\alpha)[- \ln(1-\alpha)]^{1/2}$	$[- \ln(1-\alpha)]^{1/2}$
D3	3-D Diffusion-Jander Eqn.	$3/2(1-\alpha)^{2/3}/2[1-(1-\alpha)^{1/3}]^{-1}$	$[1-(1-\alpha)^{1/3}]^2$
R3	Contracting area	$3(1-\alpha)^{2/3}$	$[1-(1-\alpha)^{1/3}]$
R2	Contracting area	$2(1-\alpha)^{1/2}$	$[1-(1-\alpha)^{1/2}]$
F2	Second-order	$(1-\alpha)^2$	$(1-\alpha)^{-1}-1$
D2	2-D Diffusion	$(1-\alpha) \ln (1-\alpha)^{+2}$	$(- \ln(1-\alpha))^{-1}$
D4	Ginstling-Brounshtein	$(1-2\alpha/3) - (1-\alpha)^{2/3}$	$3/2((1-\alpha)^{-1/3}-1)^{-1}$

^a In some references $f(\alpha)$ and $g(\alpha)$ have opposite designations

Table 2. Kinetic parameters for the first stage decomposition of HBAPPA

Kinetic model	$\beta = 10, \text{ K min}^{-1}$			$\beta = 15, \text{ K min}^{-1}$			$\beta = 20, \text{ K min}^{-1}$		
	E_a kJ mol ⁻¹	ln A, s ⁻¹	r	E_a kJ mol ⁻¹	ln A, s ⁻¹	r	E_a kJ mol ⁻¹	ln A, s ⁻¹	r
P2	68.71	14.50	-0.990	60.14	12.60	-0.987	53.46	11.08	-0.983
P3	42.92	8.13	-0.988	37.18	6.94	-0.984	32.70	5.96	-0.980
P4	30.09	4.85	-0.986	25.76	4.00	-0.982	22.38	3.29	-0.976
F1	209.78	48.61	-0.999	186.11	42.88	-0.999	167.61	38.35	-0.999
F2	298.86	70.30	-0.987	265.97	62.22	-0.988	240.19	55.83	-0.989
F3	409.34	97.03	-0.968	365.04	86.04	-0.970	330.24	77.36	-0.971
D1	315.62	79.96	-0.992	280.80	71.41	-0.990	253.73	64.72	-0.988
D2	335.44	76.81	-0.996	297.79	67.53	-0.995	268.46	60.26	-0.993
D3	380.20	86.16	-0.999	337.92	75.70	-0.999	304.93	67.49	-0.997
D4	374.89	84.62	-0.997	332.87	74.24	-0.995	300.16	66.11	-0.993
A2	100.63	22.55	-0.999	88.75	19.81	-0.999	79.45	17.62	-0.998
A3	63.61	13.50	-0.999	55.72	11.77	-0.999	49.55	10.37	-0.998
A4	46.05	9.11	-0.999	40.07	7.85	-0.999	35.38	6.82	-0.998
R2	174.78	39.34	-0.998	154.73	34.53	-0.997	139.10	30.74	-0.995
R3	164.91	37.19	-0.996	145.89	32.64	-0.995	131.06	29.05	-0.993

Table 3. Kinetic parameters for the second stage decomposition of HBAPPA

Kinetic model	$\beta = 10, \text{ K min}^{-1}$			$\beta = 15, \text{ K min}^{-1}$			$\beta = 20, \text{ K min}^{-1}$		
	E_a kJ mol ⁻¹	ln A, s ⁻¹	r	E_a kJ mol ⁻¹	ln A, s ⁻¹	r	E_a kJ mol ⁻¹	ln A, s ⁻¹	r
P2	23.89	1.76	-0.985	24.27	2.21	-0.983	27.56	3.16	-0.995
P3	12.57	-0.98	-0.976	12.80	-0.55	-0.973	14.94	0.24	-0.992
P4	6.94	-2.62	-0.954	7.10	-2.19	-0.950	8.67	-1.5	-0.985
F1	84.32	14.96	-1.000	85.60	15.50	-0.999	94.16	17.26	-0.996
F2	120.62	22.98	-0.988	122.52	23.59	-0.989	133.35	25.66	-0.977
F3	165.35	32.70	-0.970	168.04	33.40	-0.971	181.51	35.85	-0.954
D1	137.48	32.44	-0.993	139.35	33.04	-0.992	153.34	35.71	-0.997
D2	140.32	24.89	-0.997	142.32	25.49	-0.996	156.97	28.26	-0.999
D3	158.88	27.43	-0.999	161.19	28.06	-0.999	177.11	31.02	-0.999
D4	157.23	26.82	-0.996	159.52	27.46	-0.995	175.81	30.49	-0.999
A2	37.16	5.02	-0.999	37.76	5.50	-0.999	41.98	6.57	-0.995
A3	21.16	1.37	-0.999	21.54	1.82	-0.999	24.28	2.67	-0.994
A4	13.58	-0.54	-0.999	13.84	-0.10	-0.999	15.88	0.65	-0.993
R2	69.85	11.01	-0.998	70.89	11.53	-0.997	78.48	13.14	-0.999
R3	65.74	10.35	-0.996	66.71	10.86	-0.995	74.00	12.44	-0.999

Table 4. Kinetic parameters for the third stage decomposition of HBAPPA

Kinetic model	$\beta = 10, \text{ K min}^{-1}$			$\beta = 15, \text{ K min}^{-1}$			$\beta = 20, \text{ K min}^{-1}$		
	E_a kJ mol ⁻¹	ln A, s ⁻¹	r	E_a kJ mol ⁻¹	ln A, s ⁻¹	r	E_a kJ mol ⁻¹	ln A, s ⁻¹	r
P2	14.69	-1.95	-0.988	16.18	-1.42	-0.925	20.67	-0.39	-0.827
P3	5.31	-4.19	-0.963	5.97	-3.70	-0.793	8.77	-2.72	-0.678
P4	0.65	-6.89	-0.521	0.90	-6.22	-0.245	2.85	-4.57	-0.366

Contd...

F1	64.14	6.68	-0.973	72.80	7.91	-0.995	89.46	10.35	-0.966
F2	93.55	11.81	-0.937	109.33	13.87	-0.991	136.82	17.66	-0.994
F3	129.82	17.96	-0.903	154.71	21.08	-0.976	196.08	26.60	-0.998
D1	113.04	21.33	-0.996	123.06	22.47	-0.979	143.85	25.29	-0.932
D2	110.75	12.30	-0.992	122.10	13.59	-0.984	145.50	16.73	-0.938
D3	125.69	13.35	-0.985	140.39	15.01	-0.992	168.84	18.79	-0.957
D4	124.82	12.94	-0.991	137.61	14.33	-0.984	164.22	17.86	-0.941
A2	25.38	0.34	-0.961	29.21	1.17	-0.992	37.24	2.63	-0.951
A3	12.24	-2.22	-0.935	14.43	-1.51	-0.983	19.52	-0.33	-0.922
A4	6.00	-3.80	-0.868	7.42	-3.11	-0.963	11.13	-1.99	-0.871
R2	52.47	3.88	-0.987	58.49	4.81	-0.985	71.16	6.75	-0.937
R3	49.15	3.55	-0.990	54.46	4.39	-0.980	66.05	6.20	-0.926

Table 5. Compensation effect parameters for several combinations of kinetic models for the decomposition of HBAPPA

Stage I						
β , K min ⁻¹	AKM			AKM-{D1; D3; D4}		
	a_β , A/s ⁻¹	b_β /mol J ⁻¹	r	a_β , A/s ⁻¹	b_β /mol J ⁻¹	r
10	-1.78774	0.23857	0.997	-2.07343	0.23999	0.999
15	-1.54495	0.23678	0.997	-1.82566	0.23885	0.999
20	-1.40395	0.23506	0.996	-1.67965	0.23676	0.999
β , K min ⁻¹	AKM-{F2; F3; D1; D2; D3; D4}			AKM - {D1; D2; D3; D4}		
	a_β , A/s ⁻¹	b_β /mol J ⁻¹	R	a_β , A/s ⁻¹	b_β /mol J ⁻¹	r
10	-2.01378	0.2395	0.999	-2.23121	0.24207	0.999
15	-1.77254	0.2379	0.999	-1.97946	0.24068	0.999
20	-1.63184	0.23634	0.999	-1.82942	0.23932	0.999
Stage II						
β , K min ⁻¹	AKM			AKM - {D1; D3; D4}		
	a_β , A/s ⁻¹	b_β /mol J ⁻¹	r	a_β , A/s ⁻¹	b_β /mol J ⁻¹	r
10	-3.30911	0.21189	0.985	-3.51601	0.21417	0.998
15	-2.90037	0.21008	0.985	-3.10825	0.21252	0.998
20	-2.50933	0.20563	0.987	-2.72024	0.20785	0.998
β , K min ⁻¹	AKM - {F3; D1; D2; D3; D4}			AKM - {P2; P3; P4; D1; D2; D3; D4; A2; A3; A4}		
	a_β , A/s ⁻¹	b_β /mol J ⁻¹	r	a_β , A/s ⁻¹	b_β /mol J ⁻¹	r
10	-3.64362	0.21882	0.998	-4.40125	0.22536	0.999
15	-3.2368	0.21713	0.998	-3.97938	0.22341	0.999
20	-2.85093	0.21196	0.999	-3.68962	0.2187	0.999
β , K min ⁻¹	AKM - {P2; A2}					
	a_β , A/s ⁻¹	b_β /mol J ⁻¹	r			
10	-3.13797	0.20397	0.999			
15	-2.73394	0.2026	0.999			
20	-2.33566	0.19852	0.999			

Contd...

Stage III						
β , K min ⁻¹	AKM			AKM – {P2; P3; P4; D1; D2; D3; D4; A2; A3; A4; R2; R3}		
	a_β , A/s ⁻¹	b_β /mol J ⁻¹	r	a_β , A/s ⁻¹	b_β /mol J ⁻¹	r
10	-4.83949	0.16998	0.962	-4.30115	0.17166	0.999
15	-4.34544	0.16031	0.966	-3.75791	0.16071	0.999
20	-3.65528	0.15106	0.974	-3.24571	0.15235	0.999
β , K min ⁻¹	AKM – {P3; P4; D1; D2; D3; D4; A2; R2}			AKM – {P2;P3; P4; D1; D2; D3; D4; A2; A3; A4; R2}		
	a_β , A/s ⁻¹	b_β /mol J ⁻¹	r	a_β , A/s ⁻¹	b_β /mol J ⁻¹	r
10	-4.62622	0.17428	0.999	-4.90202	0.17706	0.999
15	-4.13248	0.16336	0.999	-4.34541	0.16517	0.999
20	-3.59587	0.15428	0.999	-3.82654	0.15584	0.999
β , K min ⁻¹	AKM – {P2; P3; P4; D1; D2; D3; D4; A3; A4}			AKM – {P4; D1; D2; D3; D4}		
	a_β , A/s ⁻¹	b_β /mol J ⁻¹	r	a_β , A/s ⁻¹	b_β /mol J ⁻¹	r
10	-4.61892	0.17354	0.999	-4.69687	0.17455	0.998
15	-4.12506	0.1628	0.998	-4.21698	0.16379	0.998
20	-3.64697	0.15427	0.998	-3.67827	0.15458	0.999

The plot of a_β versus b_β , obtained for three constant heating rates, is a straight line whose parameters allow the computation of $\ln A_{\text{inv}}$ and E_{inv} (Table 6). For several groups of apparent activation parameters listed in Table 5, obtained by different kinetic models, we tried to establish the best correlation and the closest value to the mean isoconversional activation energies [FWO; $E_a = 138.97 \pm 4.31$ kJ/mol]. For AKM–{D₁–D₄}, the plot of $\ln A$ versus E_a has the highest correlation coefficient $E_a = 146.23$ kJ/mol; $\ln A = 33.18$; ($r = -0.990$) and is a straight line for stage I.

Table 6. IKP for several combinations of kinetic models for HBAPPA

Kinetic model	E_{inv} kJ mol ⁻¹	$\ln A_{\text{inv}}$	r
Stage I			
AKM	109.52	24.35	-0.990
AKM – {D1; D3; D4}	122.06	27.23	-0.990
AKM – {F2; F3; D1; D2; D3; D4}	120.99	26.98	-0.989
AKM – {D1; D2; D3; D4}	146.23	33.18	-0.990
AKM – {F1; F2; F3; D1; D2; D3; D4}	104.13	22.85	-0.990
Stage II			
AKM	128.76	23.99	-0.935
AKM – {D1; D3; D4}	116.54	21.53	-0.960
AKM – {F3; D1; D2; D3; D4}	105.94	19.63	-0.955
AKM – {P2; P3; P4; D1; D2; D3; D4}	98.47	17.88	-0.942
AKM – {P2; A2}	135.84	24.66	-0.960
Stage III			
AKM	62.50	5.74	-0.994
AKM – {P2; P3; P4; D1; D2; D3; D4; A2; A3; A4; R2; R3}	54.40	5.02	-0.998
AKM – {P3; P4; D1; D2; D3; D4; A2; R2}	51.30	4.29	-0.997
AKM – {P2; P3; P4; D1; D2; D3; D4; A2; A3; A4}	50.50	4.02	-0.998
AKM – {P2; P3; P4; D1; D2; D3; D4; A3; A4}	50.24	4.08	-0.998
AKM – {P4; D1; D2; D3; D4}	50.82	4.15	-0.996

For AKM- $\{F_3, D_1-D_4\}$, the plot of $\ln A$ versus E_a has the highest correlation coefficient ($E_a = 105.94$ kJ/mol; $\ln A = 19.63$; $r = 0.950$) and is true straight line for the second stage (FWO; $E_a = 131.42 \pm 3.02$ kJ/mol). Whereas for AKM- $\{P_2-P_4, D_1-D_4, A_2-A_3, R_2, R_3\}$, the plot of $\ln A$ versus E_a has the highest correlation coefficient $E_a = 54.4$ kJ/mol; $\ln A = 5.02$ ($r = 0.998$) and is a straight line for the third stage (FWO; $E_a = 70.75 \pm 3.26$ kJ/mol).

Thermodynamic parameters

As can see from the Table 7, the value of $\Delta S^\ddagger$ is positive for the first stage and negative for the second and third stages. The negative values suggest that the activated complexes have a higher degree of arrangement than the initial stage. The positive values of enthalpy and free energy of activation for this compound show that the process is connected with absorption of heat is non-spontaneous in nature^{25,26}.

Table 7. Kinetic and thermodynamic parameters for the thermal behaviour of HBAPPA by Kissinger method

Stage	Peak Temp, K	E_a , kJ/mol	$\ln A$, min ⁻¹	$\Delta S^\ddagger$, J K ⁻¹ mol ⁻¹	$\Delta H^\ddagger$, kJ mol ⁻¹	$\Delta G^\ddagger$, kJ mol ⁻¹	$-r$
I	516.84	139.97	31.88	15.51	134.72	126.65	0.9700
	520.74						
	527.14						
	619.14						
II	628.28	104.43	19.16	-91.77	99.21	156.87	0.986
	639.14						
	861.74						
III	879.54	77.37	8.77	-180.95	70.03	229.180	0.9685
	909.34						

Conclusion

The title compound is decomposed in three stages. The energy of activation of first stage is more than that of the other two stages, which indicates that the first stage decompose in rather slow. $\Delta G^\ddagger$ is more positive indicating that the decomposition process is non-spontaneous in nature.

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