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Non-isothermal decomposition kinetics of theobromine in nitrogen atmosphere

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ABSTRACT

The non-isothermal decomposition process of theobromine under nitrogen atmosphere was studied using the differential thermal analysis (DTA), from room temperature up to 500 °C, at heating rates, 5, 15 and 20 °C/min. The results showed that theobromine decomposes in two steps. The kinetic analysis of the first decomposition step was performed using Kissinger, Friedman, Flynn-Wall-Ozawa, and Kissinger-Akahira-Sunose isoconventional methods. The kinetic model was determined using Šatava-Šesták method. Results showed that the non-isothermal decomposition mechanism of theobromine corresponds to nucleation and growth, following the Avrami-Erofeev equation. The forms of the integral and differential equations for the mechanism function are $g(\alpha)=(-\ln(1-\alpha))^{2/3}$ and $f(\alpha)=(3/2)(1-\alpha)(-\ln(1-\alpha))^{1/3}$, respectively. Thermodynamic parameters of the non-isothermal decomposition process, change of enthalpy (ΔH), change of entropy (ΔS), and change of Gibbs free energy (ΔG) values were calculated.

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1. Introduction

Methylxanthines have important pharmacological properties and are commonly used as therapeutic agents. Stimulatory effects on the central nervous system as well as on the gastrointestinal, cardio-vascular, renal and respiratory systems have been ascribed to these compounds [1]. Theobromine (TB), 3,7-dimethylxanthine, is an alkaloid of the cacao plant and TB is a caffeine derivative and metabolite, Figure 1. TB is the second most important methylxanthine in the diet and TB has the same caffeine effects. Both TB and caffeine improve alertness without inducing irregular heartbeat or hypertension [2]. TB also has diuretic and bronchial muscle relaxing effects [1].

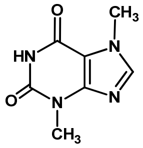

Figure 1. Structural formula of theobromine.

The thermal decomposition of TB have been studied [3,4], using TG/DTG, DTA and DSC methods. To our knowledge, the thermodynamic and kinetic data of the thermal decomposition of TB have not been reported. In this paper, the kinetic parameters such as activation energy, E, and apparent pre-exponential factor, A, of the thermal decomposition of TB were calculated using Kissinger, Friedman, Flynn-Wall-Ozawa, Kissinger-Akahira-Sunose and Šatava-Šesták methods. Šatava-Šesták method was used to establish the kinetic model of the thermal decomposition of TB.

The thermodynamic data, such as enthalpy change (ΔH), entropy change (ΔS) and Gibbs free energy change (ΔG) for the non-isothermal decomposition process were calculated. These data can play an important role to understand the physico-chemical interactions and thermodynamic properties for TB at high temperatures.

2. Experimental

2.1. Materials

TB was supplied by Sigma (St. Louis, MO). It is used without any further purification.

2.2. Physical measurements

The thermogravimetric measurements were carried out at three different heating rates (5, 15 and 20 °C/min), from room temperature up to 500 °C under dynamic nitrogen atmosphere

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Table 1. The algebraic expression of g(α) for the various kinetic reaction models.

No	g(α)	No	g(α)
1	α^2	9	$-\ln(1-\alpha)$
2	$\alpha+(1-\alpha)\ln(1-\alpha)$	10-16	$[-\ln(1-\alpha)]^n$, $(n = \frac{2}{3}, \frac{1}{2}, \frac{1}{3}, 4, \frac{1}{4}, 2, 3)$
3	$\left(1-\frac{2}{3}\alpha\right)(1-\alpha)^{2/3}$	17-22	$1-(1-\alpha)^n$, $(n = \frac{1}{2}, 3, 2, 4, \frac{1}{3}, \frac{1}{4})$
4-5	$[1-(1-\alpha)^{1/3}]^n$, (n = 2, ½)	23-27	α^n, $(n = 1, \frac{3}{2}, \frac{1}{2}, \frac{1}{3}, \frac{1}{4})$
6	$[1-(1-\alpha)^{1/2}]^{1/2}$	28	$(1-\alpha)^{-1}$
7	$[(1-\alpha)^{1/3}-1]^2$	29	$(1-\alpha)^{-1}-1$
8	$[(1/(1+\alpha)^{1/3}-1]^2$	30	$(1-\alpha)^{-1/2}$

(20 mL/min), using about 2 mg of powdered samples contained in an alumina crucible.

2.3. Theoretical analysis

The kinetic analysis of solid state thermal decomposition is usually described by the following Equation (1) [5].

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

where , dα/dt is the rate of conversion, α is the conversion of the reaction which is defined as $\alpha = (m_0-m_t)/(m_0-m_f)$, where m_0 and m_f are the initial and final masses of the sample at each stage of decomposition, respectively, and m_t is the mass of the sample at time t (or temperature T), *f*(α) is a mathematical model function of kinetics which depends on the reaction type and reaction mechanism, k(T) is the specific rate constant, whose temperature dependence is commonly described by the Arrhenius Equation (2).

$$k(T) = Ae^{-\frac{E}{RT}} \tag{2}$$

by combining Equation (1) and (2), taking into consideration the heating rate β = dT/dt (°C/min), under non-isothermal condition, the kinetic analysis of solid state thermal decomposition is described by Equation (3).

$$\frac{d\alpha}{dt} = \beta\frac{d\alpha}{dT} = Ae^{-\frac{E}{RT}}f(\alpha) \tag{3}$$

Most of the methods that describe the kinetics of reactions in solids use Equation (3) as well as several approximation of its integral form.

$$g(\alpha) = \frac{A}{\beta}\int_0^T e^{-\frac{E}{RT}}\,dT \tag{4}$$

where

$$g(\alpha) = \int_0^\alpha \frac{1}{f(\alpha)}\,d\alpha \tag{5}$$

is the integral form of the model function that does not depend on the heating rate used.

2.3.1. Kissinger (K) method

Kissinger method [6-9] is expressed by Equation (6)

$$\ln\frac{\beta_i}{T_{pi}^2} = \ln\frac{A_K R}{E_K} - \frac{E_K}{R}\frac{1}{T_{pi}} \tag{6}$$

where i= 1, 2, 3 …….., by plotting $\ln\frac{\beta_i}{T_{pi}^2}$ versus $\frac{1}{T_{pi}}$, E_K and A_K can be calculated from slope $(-E_K/R)$ and intercept $\ln(A_K R/E_K)$, respectively.

2.3.2. Friedman (FR) method

FR method [10], a linear differential method based on Equation (7).

$$\ln\frac{d\alpha}{dt} \equiv \ln\beta\frac{d\alpha}{dT} = \ln A\,f(\alpha)\frac{E}{RT} \tag{7}$$

2.3.3. Flynn-Wall-Ozawa (FWO) method

FWO method [6,7,11,12], a linear integral method based on Equation (8).

$$\ln\beta = \ln\frac{AE}{Rg(\alpha)} - 5.331 - 1.052\frac{E}{RT} \tag{8}$$

2.3.4. Kissinger-Akahira-Sunose (KAS) method

KAS method [9,13], a linear integral method based on Equation (9).

$$\ln\frac{\beta}{T^2} = \ln\frac{AR}{Eg(\alpha)} - \frac{E}{RT} \tag{9}$$

For α = constant, the plot of ln(dα/dt) *vs* 1/T, or lnβ *vs* 1/T, or $\ln(\beta/T^2)$ *vs* 1/T from the experimental thermogravimetric curves recorded for several constant heating rates, should be a straight line, the activation energy, E, being evaluated from these slopes, by means of FR, FWO, and KAS methods, respectively.

2.3.5. Šatava-Šesták method

The expression from Šatava-Šesták method [14] is given by Equation (10).

$$\ln g(\alpha) = \ln\frac{A_s E_s}{R\beta} - 5.330 - 1.0516\frac{E_s}{RT} \tag{10}$$

where g(α) comes from one of 30 forms of integral formula in the literature [15,16].These forms of integral formula are given in Table 1. For every fixed β_i (i =1, 2, 3, 4, …), and each mechanism functions g(α), the values of activation energy (E_s) and pre-exponential factor (A_s), can be obtained using Equation (10), respectively. The model of the reaction can be identified as long as $0 < E_s < 400$ kJ/mol. It is necessary that E_s values compared with the values of E_0 where E_0 is the average activation energy calculated by FR, KAS, and FWO methods. If E_s meets with the condition of $|(E_0 - E_s)/E_0| \leq 0.1$, the E_s is acceptable. $\ln A_s$ calculated need to be compared with $\ln A_k$ calculated by Kissinger method, if $\ln A_s$ meets with the condition $|(\ln A_s - \ln A_k)/\ln A_s| \leq 0.46$, the $\ln A_s$ is acceptable. If g(α) meets the above mentioned requirements, then it will be an integral form of the most probable mechanism function of reaction.

2.3.6. Thermodynamic parameters

After E and A values are obtained using non-isothermal method, the thermodynamic parameters can be calculated [17,18] using equations

$$\Delta S = R\ln\left(\frac{Ah}{k_B T_p}\right) \tag{11}$$

Table 2. Values of T_i, T_p and T_f for the TB decomposition determined by thermogravimetric analysis at different heating rates.

β, °C/min	T_i, °C	T_p, °C	T_f, °C
5	206.1	280.4	303.5
15	206.1	307.6	332.3
20	206.1	315.8	337.9

Table 3. The activation energy calculated using FR, FWO and KAS.

α	FR method		FWO method		KAS method	
	E (kJ/mol)	r^2	E (kJ/mol)	r^2	E (kJ/mol)	r^2
0.2	118.523	0.993	128.665	0.999	129.651	0.985
0.3	118.869	0.995	125.612	0.999	124.277	0.993
0.4	117.379	0.996	127.151	0.999	125.709	0.993
0.5	117.780	0.993	123.753	0.999	122.230	0.997
0.6	121.144	1.000	123.243	0.999	121.464	0.996
0.7	129.210	0.996	127.452	0.999	129.651	0.996
0.8	122.884	0.993	124.123	0.999	121.685	0.998
Mean	120.827		125.714		124.952	

k_B is the Boltzmann constant (1.3807×10^{-23}), and h is the Planck constant (6.625×10^{-34} J/s).

$$\Delta H = E - RT_p \tag{12}$$

$$\Delta G = \Delta H - T_p\Delta S \tag{13}$$

The change of enthalpy (ΔH), change of entropy (ΔS), and change of Gibbs free energy (ΔG), in the thermal decomposition process decomposition are calculated.

In all of the above equations, α represents the fractional conversion, β is the heating rate (°C/min), T is the temperature (K), T_p is the temperature at the maximum rate of the weight loss (differential thermogravimetry (DTG)) peak temperature, E is the apparent activation energy (kJ/mol), A is the pre-exponential factor (1/min), R is the gas constant (8.314 J/mol·K) and g(α) is the integral conversion function.

3. Results and discussion

3.1. Thermal decomposition of TB

TG/DTG and DTA curves of the thermal decomposition of TB under nitrogen atmosphere, from room temperature up to 500 °C, at the heating rates (5, 15, 20 °C/min) are shown in Figure 2 and 3, respectively. It is clear that the TG curves are shifted to higher temperatures as the heating rates increases from 5 to 20 °C/min. The shapes of the curves are quite similar, all curves showed two decomposition steps. There is no mass loss up to 240 °C, as temperature increases the TG curves of TB exhibit a sharp mass loss of about 90% in the temperature range 260-330 °C, which corresponds to the endothermic peak as shown in the DTA curves, Figure 3, in the temperature range 289-320 °C. This mass loss may be due to the loss of the xanthine group. In the second step, the TG curves show a mass loss of about 10%, in the temperature range 345-400 °C, where an endothermic peak appears in the DTA curves, Figure 3, in the range 369-403 °C. The first step was chosen as the main object of discussion.

Values of initial temperature (T_i), inflection temperature (T_p) and final temperature (T_f) from thermogravimetric curves for the chosen step at various heating rates are presented in Table 2.

3.2. Non-isothermal kinetic of TB

The non-isothermal decomposition of the first decomposition step of TB was investigated using Kissinger, FR, KAS, FWO and Šatava-Šesták methods. The activation energy values were calculated in the conversion range 0.2 ≤ α ≤ 0.8. This range is strongly recommended because most reactions, especially solid-state ones, are not stable at the beginning and ending periods [19].

The values of activation energy E_k and pre-exponential factor ln A_k calculated by Kissinger method are 116.953 kJ/mol and 29.595/min, respectively. The linear correlation coefficient (r^2) is 0.985. Activation energy calculated by FR, KAS, and FWO methods are tabulated in Table 3. The relationship between activation energy, E, and conversion (α) are shown in Figure 4.

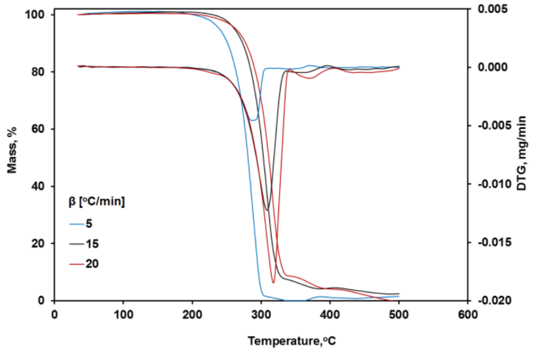

Figure 2. TG/DTG curves of the thermal decomposition of TB in nitrogen atmosphere at different heating rates (5, 15, 20 °C/min).

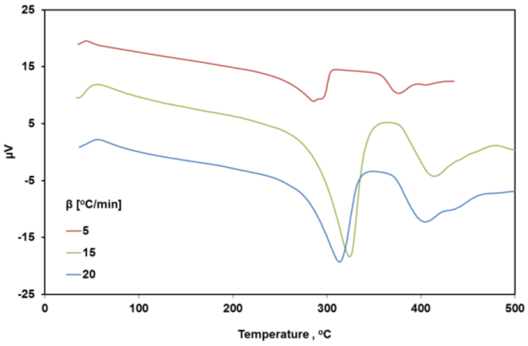

Figure 3. DTA curves for the thermal decomposition of TB in nitrogen atmosphere at different heating rates (5, 15, 20 °C/min).

By comparing the activation energies calculated by the three isoconversional methods (FR, KAS, and FWO), it is clear, that the activation energy values calculated by FWO and KAS are in good agreement, while these determined by FR differential method is slightly lower. The average of the activation energy (E_0) values calculated by the three methods (FR, KAS, and FWO) is 123.832 kJ/mol.

The kinetic parameters calculated by Šatava-Šesták method are listed in Table 4. The values of activation energy and pre-exponential factor calculated by the Šatava-Šesták method compare, respectively, with the average of activation

Table 4. Activation energy and pre-exponential factor calculated using Šatava-Šesták method.

No	β = 5 °C/min			β = 15 °C/min			β = 20 °C/min		
	E_s (kJ/mol)	ln A_s	r^2	E_s (kJ/mol)	ln A_s	r^2	E_s (kJ/mol)	ln A_s	r^2
1	264.668	62.230	0.996	255.711	59.279	0.997	256.101	58.936	0.999
2	295.255	68.611	0.998	285.552	66.771	0.999	285.347	66.989	0.999
3	307.478	69.931	0.999	297.521	66.419	0.999	296.135	65.685	0.999
4	88.222	24.161	0.996	85.236	23.933	0.997	85.367	23.720	0.999
5	22.055	10.859	0.996	21.309	11.652	0.997	21.548	11.913	0.999
6	33.083	12.902	0.996	31.963	13.524	0.997	32.012	13.732	0.999
7	332.202	75.646	0.999	321.744	71.827	0.999	320.706	70.993	0.998
8	209.641	47.189	0.991	202.443	45.064	0.993	203.332	44.975	0.996
9	185.627	45.701	0.999	180.026	44.119	0.998	179.049	43.697	0.995
10	123.751	32.151	0.999	120.017	31.473	0.998	119.366	31.289	0.995
11	92.813	25.460	0.999	90.013	25.234	0.998	89.524	25.169	0.995
12	61.875	18.888	0.999	60.008	19.113	0.998	59.683	19.168	0.995
13	742.509	169.920	0.999	720.107	160.204	0.998	716.197	157.640	0.995
14	46.406	15.687	0.999	45.006	16.138	0.998	44.542	16.328	0.995
15	371.254	86.877	0.999	360.053	82.583	0.998	356.34	82.015	0.995
16	556.882	128.340	0.999	540.081	121.335	0.998	534.511	120.330	0.995
17	66.167	19.553	0.996	63.927	18.898	0.997	64.645	19.755	0.999
18	397.002	91.201	0.996	383.565	86.208	0.997	384.152	86.222	0.999
19	264.668	62.230	0.996	255.711	59.279	0.997	256.101	59.384	0.999
20	529.336	120.289	0.996	511.420	113.254	0.997	512.203	113.180	0.999
21	44.111	15.062	0.996	42.618	15.515	0.997	42.683	15.696	0.999
22	33.083	12.902	0.996	31.963	13.524	0.997	32.012	13.732	0.999
23	132.334	33.547	0.996	127.855	32.639	0.997	128.050	32.610	0.999
24	199.172	47.960	0.996	193.606	46.240	0.997	193.937	46.041	0.999
25	66.390	19.594	0.996	64.535	19.772	0.997	64.645	19.896	0.999
26	44.260	15.088	0.996	43.023	15.583	0.997	43.097	15.761	0.999
27	33.195	12.921	0.996	32.267	13.573	0.997	32.322	13.778	0.999
28	120.947	32.563	0.923	116.298	31.693	0.913	111.534	30.649	0.896
29	253.729	61.287	0.988	245.369	58.514	0.985	240.826	57.122	0.978
30	60.473	19.106	0.923	58.149	19.239	0.913	55.767	18.882	0.896

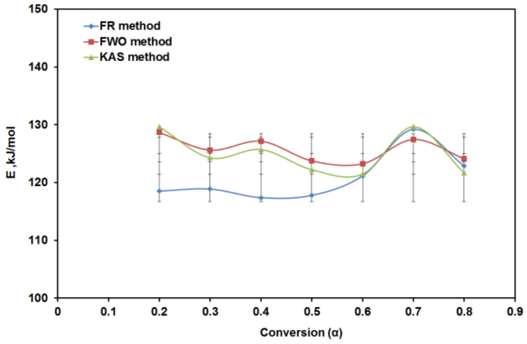

Figure 4. The relationship between activation energy, E, and conversion, α.

energy (E_0) calculated using the above mentioned methods (FR, KAS, and FWO methods), and the value of the pre-exponential factor calculated by the Kissinger method. It is clear from the results that the decomposition reaction of TB for the chosen step (first decomposition step) is consistent with the mechanism of nucleation and growth, Avrami-Erofeev equation, (that is serial-number 10 in Table 1), as the values of E_s and $\ln A_s$ meet with the conditions of both $|(E_0 - E_s)/E_0| \leq 0.1$ and $|(\ln A_s - \ln A_k)/\ln A_s| \leq 0.46$, respectively. The forms of the integral and differential equations for the mechanism function are $g(\alpha) = (-\ln(1-\alpha))^{2/3}$ and $f(\alpha) = (3/2)(1-\alpha)(-\ln(1-\alpha))^{1/3}$, respectively. The activation energy and pre-exponential factor were 121.045 kJ/mol, 5.496×10^{13} 1/min, respectively.

3.3. Thermodynamic parameters

When the values of activation energy, *E*, and pre-exponential factor, A, have been obtained, thermodynamic parameters of the reaction can be calculated from the previous Equations (11-13). The calculated values of the thermodynamic parameters, enthalpy change (ΔH), entropy change (ΔS) and Gibbs free energy change (ΔG) for the first decomposition step of TB are 116.076 kJ/mol, -45.087 J/mol·K, and 143.019 kJ/mol, respectively.

The entropy of activation, ΔS, value for the decomposition of TB is negative, which indicates a highly ordered activated complex, and the degrees of freedom of rotation as well as of vibration are less than they are in the non-activated complex. The positive value of the enthalpy, ΔH, is in good agreement with endothermic effects in DTA data. The positive values of the enthalpy, ΔH, and Gibbs free energy, ΔG, for the decomposition stage show that it is a non-spontaneous process. These thermodynamic functions are consistent with kinetic parameters and thermal analysis data.

4. Conclusion

Kinetic analysis of non-isothermal decomposition process of TB under nitrogen atmosphere was performed using Kissinger, Friedman, Flynn-Wall-Ozawa, and Kissinger-Akahira-Sunose. For the determination of kinetic model function of the considered process, the Šatava-Šesták method was used. It was found that the decomposition kinetic model of TB corresponds to nucleation and growth, following the Avrami-Erofeev equation. The activation energy and pre-exponential factor were 121.045 kJ/mol, 5.496×10^{13} 1/min, respectively. Thermodynamic parameters, change of enthalpy (ΔH), change of entropy (ΔS) , and change of Gibbs free energy (ΔG),for the first decomposition step of TB are 116.076 kJ/mol, -45.087 J/mol·K, and 143.019 kJ/mol, respectively.

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