Thermal Degradation Kinetics and Stability Study of Chrysin by Thermal Analysis

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Chrysin is one of the natural flavonoids possessing many biological activities. Research in thermal decomposition of chrysin is of great interest in developing its derivants. thermal analysis study was carried out by thermogravimetric analyser unit, microscopic melting point apparatus and differential scanning calorimetry instrument. The results showed chrysin began melting at 558 K and then evaporate. The evaporation process was analyzed by the Ozaw-Flynn-Wall (OFW) equation, Kissinger-Akahira-Sunose (KAS) equation, Tang equation, Starink equation, iterative Ozaw-Flynn-Wall equation and iterative Kissinger-Akahira-Sunose equation. The evaporation process of chrysin was a single-step kinetic process. The average value of activation energies, pre-exponential A and thermodynamic functions ($\Delta S^{\neq}$, $\Delta H^{\neq}$ and $\Delta G^{\neq}$) of the transition state were calculated. The most probable mechanism for the thermal decomposition stage also was found.

Keywords: Chrysin, Thermal degradation kinetics, Ozaw-Flynn-Wall equation, Kissinger-Akahira-Sunose equation.

INTRODUCTION

Chrysin (5,7-dihydroxy flavone) is one of the natural flavonoids that is widely distributed in *Passiflora* (passion flower), medicinal herb[1,2], flowers and honey of many other plant species[3]. It has been shown to possess several biological activities, including anticancer[4-6], antioxidant[7,8], antiinflammatory[9,10], vasodilatory[11], and estrogenic effects[12,13]. Lots of experiments have been done on the pharmacological characters of chrysin. But few investigations concern its thermal stability. Research in thermal decomposition of drugs is of great interest in developing new products, because it is often necessary to predict the drug's degradation rates at room temperatures from data collected on accelerated processes studied at elevated temperatures[14,15]. In pharmaceutical sciences thermal methods of analysis have found important applications, among them the determination of kinetics parameters[16,17].

Thermogravimetry (TG) is an important tool to study thermal stability and determine the kinetic parameters of the decomposition of drugs and medicines in which the sample is heated and the weight changes are recorded as a TG curve. The aim of the present work is to determine the decomposition reaction mechanism and to calculate the Arrhenius parameters by rising temperature methods on a thermal analysis. The values of the transition state changes of the entropy $\Delta S^{\neq}$, enthalpy $\Delta H^{\neq}$ and Gibbs free energy $\Delta G^{\neq}$ of the decomposition reaction of chrysin are discussed for the first time.

EXPERIMENTAL

The material used in the present study is chrysin which was obtained from Ciyuan Biotech Co. Ltd. Shaanxi (China). The melting point of chrysin was measured on an X-4 microscopic melting point apparatus made by Beijing Tech Instruments.

TG-DTG (Netzsch 40PC thermogravimetric analyser) run from 303.15 to 873.15 K were carried out with four different linear heating rates (5, 8, 11 and 15 K/min). High purity nitrogen gas (99.999 %) was used as protective atmosphere, flowing at 20 mL min^{-1}. The results present in this paper were calculated by the programs compiled by ourselves.

The differential scanning calorimetry (DSC) experiment was conducted on a DSC instrument (DSC 200F3, NETZSCH, Germany). The instrumental sensitivity and temperature were calibrated previously with a set of Hg, In, Sb, Bi and Zn standards. The 7.6 mg chrysin was enclosed in an aluminum crucible and heated from room temperature to 592.48 K (heating rate 11 K min^{-1}) under the gas flow of high-purity nitrogen (protection gas flow: 60 mL min^{-1} and purge gas: 20 mL min^{-1}).

Methodology: According to non-isothermal kinetic theory, kinetic equation of thermal decomposition of solid-state materials[18,19] can be expressed as eqn (1):

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \tag{1}$$

where α is the fraction decomposed, T is absolute temperature, β is the heating rate (K min^{-1}), A is the pre-exponential factor, E_a is the apparent activation energy, R is the gas constant (8.314 J mol^{-1} K^{-1}) and f(α) is the conversion function. In order to obtain α and T values TG curves has been carried out.

Calculation of activation energy by isoconversional procedures: From eqn. (1), the Ozaw-Flynn-Wall (OFW) equation[20-23], Kissinger-Akahira-Sunose (KAS) equation[24,25], Tang equation[26,27], and Starink equation[28] are deduced by the corresponding transforms:

OFW equation:

$$\ln \beta = \ln \frac{0.0048 A E_a}{g(a)R} - 1.0516 \frac{E_a}{RT} \qquad (2)$$

KAS equation:

$$\ln \frac{\beta}{T^2} = \ln \frac{AR}{g(a)E_a} - \frac{E_a}{RT} \qquad (3)$$

Tang equation:

$$\ln \frac{\beta}{T^{1.894661}} = C_1 - 1.001450 \frac{E_a}{RT} \qquad (4)$$

Starink equation:

$$\ln \frac{\beta}{T^{1.92}} = C_2 - 1.008 \frac{E_a}{RT} \qquad (5)$$

The iterative procedure[29-33] was used to calculate the approximate value of E_a approaching to the exact value; the equations are expressed as:

$$\ln \frac{\beta}{H(x)} = \ln \frac{0.0048 A E_a}{g(\alpha)R} - 1.0516 \frac{E_a}{RT} \qquad (6)$$

and

$$\ln \frac{\beta}{H(x)T^2} = \ln \frac{AR}{g(\alpha)E_a} \frac{E_a}{RT} \qquad (7)$$

where $x = E_a/RT$, h(x) is expressed by the fourth Senum and Yang approximations and H(x) is also calculated[34] from x, g(α) is the mechanism function depend on the conversion mechanism and its mathematical model.

The iterative procedure performed involved the following steps:[30,34,35] (i) Assume h(x) = 1 or H(x) = 1 to estimate the initial value of the activation energy E_{a1}. The conventional isoconversional methods stop the calculation at this step; (ii) using E_{a1}, calculate a new value of E_{a2} for the activation energy from the plot of ln[β/H(x)] *versus* 1/T or ln[β/(h(x)T^2)] *versus* 1/T; (iii) repeat step (ii), replacing E_{a1} with E_{a2}. When $|E_{ai} - E_{a(i-1)}| <$ 0.01 kJ mol^{-1}, then the last value of E_{ai} was considered to be the exact value of the activation energy of the study decomposition reaction. These plots are model independent because the estimation of the apparent activation energy does not require selection of particular kinetic model [type of g(α) function]. Therefore, the activation energy values obtained by this method are usually regarded as more reliable than those obtained by a single TG curve.

Determination of the most probable decomposition mechanism function: Eqn (8) was used to estimate the most correct reaction mechanism[32].

$$\ln g(a) = \left[\ln \frac{AE_a}{R} + \ln \frac{e^{-x}}{x^2} + \ln(hx) \right] - \ln \beta \qquad (8)$$

For determination of the most probable decomposition mechanism function, the values of conversion α corresponding to multiple rates taken at the same temperature were put into the left side of eqn. (8); combined with thirty-one types of mechanism functions[32], the slope k_m of the straight line and the linear correlation coefficient r were obtained from the curve of ln[g(α)] *versus* ln β. The most probable mechanism function was assumed to be the one for which the value of the slope k_m was near -1.00000 and the correlation coefficient r was better. If several g(α) functions conform to this requirement, the values of conversion α corresponding to multiple heating rates at same temperatures were applied to calculate the probable mechanism by the same method. The function, whose k_m value was the closest to -1.000 and the correlation coefficient r that was also high at all these temperatures, was considered to be the most probable mechanism function.

Calculation of pre-exponential factor A: The pre-exponential factor A can be calculated from the intercept of the curves of eqn (6) or (7), inserting the most probable g(α) function determined.

Calculation of thermodynamic functions ($\Delta S^{\neq}$, $\Delta H^{\neq}$ and $\Delta G^{\neq}$) of the transition state complex of thermal decomposition reaction: From the theory of the activated complex (transition state) of Eyring[36-38], the values of the transition state changes of the entropy $\Delta S^{\neq}$, enthalpy $\Delta H^{\neq}$ and Gibbs free energy $\Delta G^{\neq}$ may be calculated according to the following eqns. (9-11):

$$\Delta S^{\neq} = R \ln \left(\frac{Ah}{e \chi k_B T_p} \right) \qquad (9)$$

$$\Delta H^{\neq} = E^{\neq} - RT_p \qquad (10)$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T_p \Delta S^{\neq} \qquad (11)$$

where e is the Neper number (2.7183), χ is the transition factor, which is unity for monomolecular reactions, k_B is the Boltzmann constant (1.381 × 10^{-23} J K^{-1}), h is the Plank constant (6.626 × 10^{-34} J s) and T_P is the DTG peak temperature. $E^{\neq}$ is the activation energy E_a, which is obtained from eqn. (7).

RESULTS AND DISCUSSION

TG-DTG Analysis: Fig. 1 shows the TG-DTG curves of chrysin at four different heating rates from ambient temperature to 860 K, respectively. The overlay plots show the heating rate effect on the rate of thermal decomposition. They are stable at 508.95, 519.20, 528.10, 533.00 K. At these temperatures, thermal decomposition of examined samples began and were nearly completed at about 558.70, 571.85, 582.05, 588.60 K (mass loss 99 %).

The DTG curve with the presence of only one decomposition step centered at about 553.45 K (565.19, 577.05 and 582.25 K). The observed mass loss starts at about 553.45 K and ends at about 560 K in the DTG curve (β = 5 K min^{-1}).

DSC analysis: The DSC/DDSC curves of chrysin at heating rates of 11 K min^{-1} in nitrogen atmosphere are presented in Fig. 2. According to DSC curve, there is a strong endothermic peak at 581 K. The onset reaction temperature is 558 K and end temperature is 597 K, which corresponds to the decomposition peak.
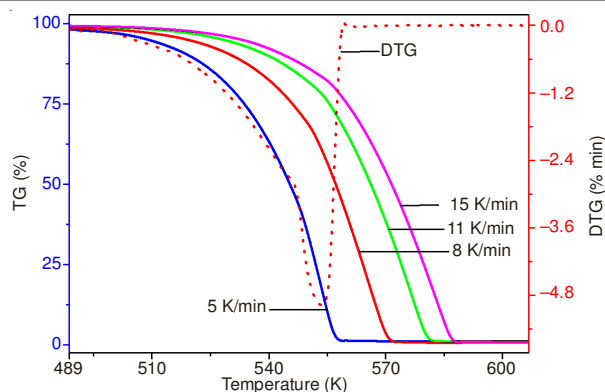
Fig. 1. Experimental TG/DTG curves for the nonisothermal decomposition of chrysin at different heating rates
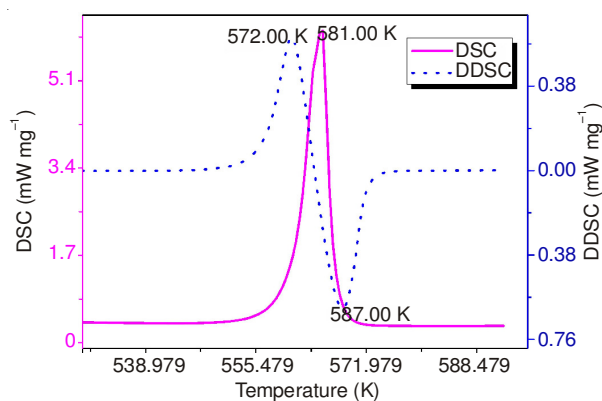

Fig. 2 DSC/DDSC curves of chrysin

The melting range of chrysin is 558-560 K which was measured by X-4 microscopic melting point apparatus. It indicates that it was an evaporation process of chrysin.

On the DDSC curve two well-defined peaks can be distinguished. The first peak occurs at 572 K, which suggested that chrysin rapidly evaporate at this moment. Other peak 581 K is a negative peak, which means that chrysin quickly finish evaporating.

Kinetic parameters and thermodynamic functions of chrysin evaporation

Calculation of activation energy E_a: According to eqns 2-7, the isoconversional calculation procedures were used. The corresponding of OFW and KAS method lines obtained at

different fraction conversion α and different heating rates β is presented in Fig. 3. The figures of other methods (Tang, Starink, iterative of OFW and KAS method, Eqn. 4-7) are similar to Fig. 3, so they have been omitted for brevity. The E_a values ofthe chrysin evaporation corresponding to different degrees of conversion a for β = 5, 8, 11 and 15 K min^{-1} were obtained from the isoconversional calculation procedures and are listed in Table-1

The relative errors of activation energy values obtained from different calculation procedures for the chrysin evaporation at different degrees of conversion are showed in Table-2.

The approximate values of E_{a5} and E_{a6} by iterative procedure (eqns 6 and 7) were more approaching the exact value. As listed in Tables-1 and 2, compared with the relative errors of the values of E_a obtained by the iterative method and the Ozaw-Flynn-Wall (OFW), Kissinger-Akahira-Sunose (KAS), Tang and Starink methods, the activation energies calculated according to the all six calculation procedures discussed are practically equal. While the results obtained from the iterative method and the KAS or Tang or Starink methods are closer to each other. Meanwhile, it can be discovered that the values obtained from the plot of $\ln[\beta/H(x)]$ *vs.* $1/T$ are almost the same as that obtained from the plot of $\ln[\beta/(h(x)T^2)]$ *vs.* $1/T$. So, the values of E_a obtained from the iterative method or the Starink or Tang methods are more reliable[18].

The activation energy value of chrysin evaporation was determined to be 93.03 ± 4.71 kJ mol^{-1} (5.06 %) in the range of $0.10 \le \alpha \le 0.90$ and listed in Table-1. If E_a values are independent of α, the evaporation process is dominated by a single reaction step[39,40]; on the contrary, a significant variation of E_a with a should be interpreted in terms of multi-step reaction mechanisms[39,41,42]. It is considered that the E_a values are independent of α if the relative error of the slope of straight lines of iterative equation is lower than 10 %[18,43]. From Table-1, it is obvious that activation energies at different degrees of conversion vary here by about 5.06 % (less than 10 %), which indicates that the evaporation process of chrysin could be considered as single-step reaction mechanism and can be adequately described by a unique kinetic triplet (activation energy, reaction mechanism and pre-exponential factor). Furthermore, the obtained results of activation energy reveal that the dependence of the activation energy (E_a) on the degrees

TABLE-1
ACTIVATION ENERGIES FOR CHRYSIN EVAPORATION, Ea (kJ mol^{-1}), AND THE INTERCEPT, B, AT DIFFERENT DEGREES OF CONVERSION α AND CALCULATION PROCEDURES

α	E_a (kJ mol^{-1})						B
	E_{a1}	E_{a2}	E_{a3}	E_{a4}	E_{a5}	E_{a6}	
0.1	95.2178	91.2999	91.6322	91.5799	91.6603	91.6603	10.41
0.2	92.2034	87.9343	88.2817	88.2248	88.3216	88.3216	9.19
0.3	96.1845	92.0188	92.3656	92.3101	92.3994	92.3993	9.82
0.4	98.8388	94.7311	95.0782	95.0234	95.1084	95.1084	10.22
0.5	100.3821	96.2873	96.6357	96.5811	96.6645	96.6644	10.41
0.6	100.8019	96.6707	97.0215	96.9664	97.0509	97.0508	10.35
0.7	98.4012	94.1008	94.4578	94.4004	94.4933	94.4933	9.70
0.8	95.9450	91.4765	91.8394	91.7798	91.8817	91.8813	9.05
0.9	93.8888	89.2742	89.6424	89.5809	89.6910	89.6906	8.50
Average	96.8737	92.6437	92.9950	92.9385	93.0301	93.0300	10.41

E_{a1} is the result of the OFW method. E_{a2} is the result of the KAS method. E_{a3} is the result of the Tang method. E_{a4} is the result of the Starink method.
E_{a5} is the iterative result of the OFW method. E_{a6} is the iterative result of the KAS method. B is the intercept of the plot of equation (7)
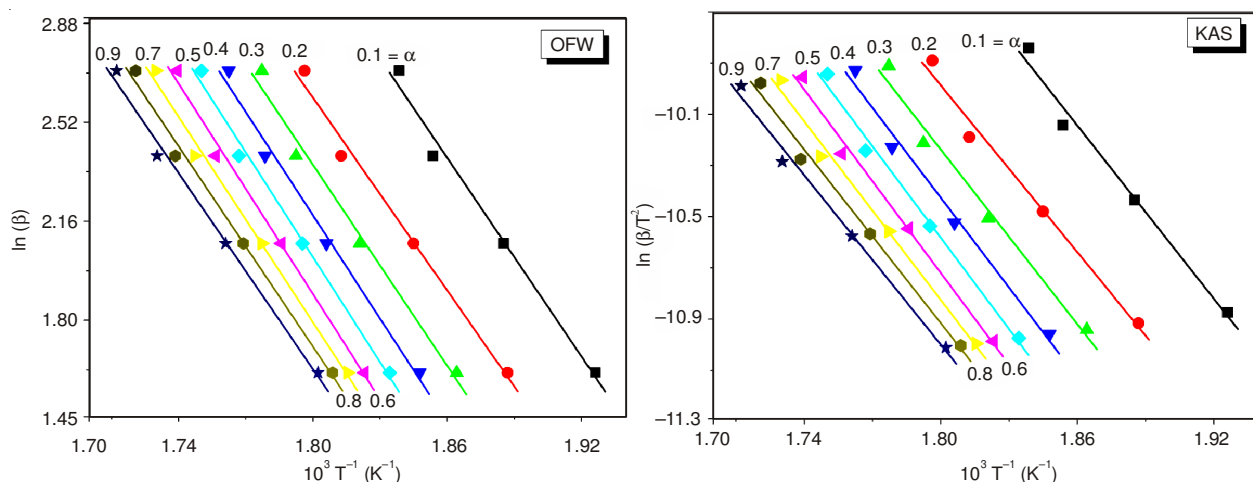
Fig. 3. Isoconversional plots at various conversion degrees for chrysin draw according OFW and KAS calculation procedure (eqns. 2-3)

TABLE-2
RELATIVE ERRORS OF ACTIVATION ENERGY FOR CHRYSIN EVAPORATION WITH DIFFERENT CALCULATION PROCEDURES AT DIFFERENT DEGREES OF CONVERSION

α	RE* (%)					
	RE_{a1}	RE_{a2}	RE_{a3}	RE_{a4}	RE_{a5}	RE_{a6}
0.1	3.88	-0.39	-0.03	-0.09	0.00	0.00
0.2	4.39	-0.44	-0.05	-0.11	0.00	0.00
0.3	4.09	-0.41	-0.03	-0.10	0.00	0.00
0.4	3.92	-0.40	-0.03	-0.09	0.00	0.00
0.5	3.85	-0.38	-0.02	-0.08	0.00	0.00
0.6	3.86	-0.39	-0.03	-0.08	0.00	0.00
0.7	4.14	-0.41	-0.03	-0.10	0.00	0.00
0.8	4.42	-0.44	-0.04	-0.11	0.00	0.00
0.9	4.68	-0.47	-0.06	-0.12	0.00	0.00

*$RE_{ai} = 100 \times (E_{ai}-E_{a5})/E_{a5}$

of conversion (a) help to identify kinetic scheme of the evaporation process.

Determination of most probable mechanism: We used eqn (8) to find the most probable evaporation mechanism. Degrees of conversion for β = 5, 10, 11 and 15 K min⁻¹ at the same temperature are listed in Table-3. Appropriate temperatures were randomly selected and the range of the degrees of conversion corresponding to the temperature should be within 0.1-0.9. The corresponding degrees of conversion of four temperatures were chosen as examples to put into 31 types of mechanism functions[32]. The slope k_m, correlation coefficient r and intercept B of linear regression of ln[g(α)] *versus* ln β were obtained. The results of the linear regression show that the slopes of No. 9 (g(α) = [-ln(1-α)]^{1/2}) and No. 31 (g(α) = [1-(1-α)^{1/3}]^{1/2}) mechanism functions were the most adjacent to -1.00000 and the correlation coefficients r are better, which are listed in Table-3. Therefore, No. 9 (g(α) = [-ln(1-α)]^{1/2}) was determined to be the most probable mechanism function of the chrysin evaporation, which is a Avrami-Eroféev equation. It belongs to the mechanism of sigmoid rate equations or random nucleation and subsequent growth.

Calculation of pre-exponential factor A the constant of reaction rate k: The pre-exponential factors A for the chrysin evaporation can be estimated from the intercept of the plots of eqn 7 (the intercept, B, are listed in Table-1), inserting the determined most probable g(α) function (No. 9). The results showed that the ranges of pre-exponential factor A were 1.03×10^8–5.00×10^8 s⁻¹ and the average value of A was 2.95×10^8 s⁻¹. The pre-exponential factor (A) values in the Arrhenius equation for solid phase reactions are expected to be over a wide range (6 or 8 orders of magnitude), even after the effect of surface area is taken into account[37,38]. For first order reactions, the pre-exponential factor may vary from 10^5 to 10^{18} s⁻¹. The low factors will often indicate a surface area, but if the reactions are not dependent on surface area, the low factor may indicate a "tight" complex[37].

On the basis of the apparent activation energy E_a (93.03 ± 4.71 kJ mol⁻¹) and the pre-exponential factor A (2.95×10^8 s⁻¹) of evaporation, the constant of reaction rate k for every one temperature can be calculated using Arrhenius equation (eqn.12)

TABLE 3
RELATION OF TEMPERATURE AND DEGREES OF CONVERSION α AT DIFFERENT HEATING RATES β (K min⁻¹) AND RESULTS OF lg G (α) *vs.* ln β CURVES OF TWO TYPES OF PROBABLE MECHANISM FUNCTIONS

T/K	α				Function No.	B	$-k_m$	$-r$
	β = 5	β = 8	β = 11	β = 15				
551.20	0.72	0.34	0.19	0.15	9	1.60	0.96	0.99
					31	0.84	0.88	0.99
552.40	0.78	0.37	0.21	0.16	9	1.76	1.01	0.98
					31	0.95	0.91	0.99
553.60	0.84	0.40	0.22	0.17	9	1.95	1.07	0.98
					31	1.08	0.95	0.99
554.85	0.90	0.43	0.24	0.18	9	2.16	1.14	0.98
					31	1.23	0.99	0.99

$$k = A \exp(-E_a/RT) \qquad (12)$$

The value of kinetic constant k_p at T_p temperature is 0.283 s^{-1}.

Determination of some thermodynamic functions of evaporation process: Eqns. 9-11 were used to calculate the transition state thermodynamic functions ($\Delta S^{\neq}$, $\Delta H^{\neq}$ and $\Delta G^{\neq}$). The average values of the functions are as follow: $\Delta S^{\neq} = -96.21$ J mol^{-1} K^{-1}, $\Delta H^{\neq} = 88.66$ kJ mol^{-1} and $\Delta G^{\neq} = 143.03$ kJ mol^{-1}. As seen from the results, the value of entropy ($\Delta S^{\neq} < 0$) indicate that the activated complex has a more ordered structure than its original state and the positive value of $\Delta G^{\neq}$ means the evaporation process of chrysin was not spontaneous at room temperature.

Conclusion

The thermodynamic properties of chrysin were studied by microscopic melting point apparatus and DSC. The results showed chrysin began melting at 558 K and then evaporate. The OFW equation, KAS equation, Tang equation, Starink equation, iterative OFW method and iterative KAS method were used to analyze the evaporation process. The evaporation process of chrysin involved one stage, which indicated that the stage was a single-step kinetic process and can be adequately described by a unique kinetic triplet [E_a, A, g(α)]. The values of activation energies estimated with six comparative isoconversional procedures, its average value was determined to be 93.03 ± 4.71 kJ mol^{-1} (5.06 %) in the range of $0.10 \leq \alpha \leq 0.90$. The average value of A was 2.95×10^8 s^{-1}. The most probable mechanism for chrysin evaporation stage was g(α) = $[-\ln(1-\alpha)]^{1/2}$, which is a sigmoid rate equations or random nucleation and subsequent growth. The calculated thermodynamic functions ($\Delta S^{\neq}$, $\Delta H^{\neq}$ and $\Delta G^{\neq}$) of the transition state complex were -96.21 J mol^{-1} K^{-1}, 88.66 kJ mol^{-1} and 143.03 kJ mol^{-1}, respectively. The activated complex of chrysie has a more ordered structure than its original state and the evaporation process of chrysin was not spontaneous at room temperature.

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