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## 丁香油- $\beta$ -环糊精包合物中残存态环糊精的热分解动力学

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**摘要:** 采用双外推法确定了丁香油- $\beta$ -环糊精(CD)包合物中残存态  $\beta$ -CD 最可能的热分解机制. 基于 Flynn-Wall-Ozawa 方法对残存态  $\beta$ -CD 热分解反应过程的计算结果发现, 活化能( $E_a$ )变化曲线可划分为三个阶段. 第一和第三阶段的曲线轮廓近似平行, 并且都被推定为按照 Avrami-Erofe'ev A1.5 模型发生热分解反应. 但是在曲线的第二阶段, 出现了一个  $E_a$  值近似相等的平台. 为此, 采用确定反应级数的方法考察了该阶段的热分解过程. 研究表明, 反应级数随着温度升高呈现规律性的降低, 表明在这个阶段残存态  $\beta$ -CD 分解反应的复杂性. 最后, 比较了游离态  $\beta$ -CD 和残存态  $\beta$ -CD 在分解过程中红外光谱的变化情况. 结果显示, 它们在  $1000\text{ cm}^{-1}$  以下的谱图轮廓存在明显差异, 这与计算给出的二者具有不同  $E_a$  值的结果是一致的.

**关键词:** 环糊精; 包合物; 双外推法; 热分解动力学

**中图分类号:** O643

## Thermal Decomposition Kinetics of Survived $\beta$ -Cyclodextrin from an Inclusion Complex of $\beta$ -Cyclodextrin with Clove Oil

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**Abstract:** A double extrapolation method was employed to determine the most probable mechanism for the thermal decomposition reaction of the survived  $\beta$ -cyclodextrin ( $\beta$ -CD) from the inclusion complex of  $\beta$ -CD with clove oil. The activation energy ( $E_a$ ) curve calculated by Flynn-Wall-Ozawa method was clearly divided into three stages for the thermal decomposition process of the survived  $\beta$ -CD. The nearly parallel linear relationship between first and last stages was assessed as an Avrami-Erofe'ev A1.5 model. Furthermore, the platform in the second stage of the decomposition of the survived  $\beta$ -CD in which each point has approximately equivalent  $E_a$  was carefully investigated using the reaction order ( $n$ ) method. A regular decline in  $n$  as the temperature increased implied a complicated decomposition reaction mechanism for the survived  $\beta$ -CD in this stage. Infrared spectroscopic profiles from the thermal decomposition of free  $\beta$ -CD and survived  $\beta$ -CD were also compared. The changes in IR spectra below  $1000\text{ cm}^{-1}$  between free  $\beta$ -CD and survived  $\beta$ -CD in the decomposition process were quite different which agreed with the calculated  $E_a$  values.

**Key Words:**  $\beta$ -Cyclodextrin; Inclusion complex; Double extrapolation; Thermal decomposition kinetics

Connected with seven  $\alpha$ -1,4-glucoses,  $\beta$ -cyclodextrin ( $\beta$ -CD) possesses both a hydrophobic cavity and a hydrophilic surface. This special structure makes it possible to interact with many kinds of organic molecules to form stable inclusion complexes<sup>[1-3]</sup>, so it has been widely used in many industries such as food, spice, drug, and agriculture<sup>[4-7]</sup>. The preparation method, spectral characterization, and thermal stability of  $\beta$ -CD inclusion com-

plexes have been studied a lot<sup>[8,9]</sup>, but there is a conceptual confusion, i.e., to confuse one thing with another, in description and interpretation of the thermal stability, especially the thermal decomposition kinetics, between the inclusion complex of  $\beta$ -CD with an organic guest and the survived  $\beta$ -CD from the inclusion complex of  $\beta$ -CD with the guest<sup>[10,11]</sup>.

So far, the reports on the thermal decomposition kinetics of

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the survived  $\beta$ -CD from inclusion complexes of  $\beta$ -CD have not been found. Clearly, the thermal stability of  $\beta$ -CD inclusion complexes should be considered as that of the molecular aggregate of  $\beta$ -CD and an included guest. Once the guest extricated itself from an inclusion complex, the inclusion complex will be simultaneously destroyed and superseded in favor of the survived  $\beta$ -CD. Most of the guests are usually small organic molecules with low boiling point. During the heating process of sample, guest molecules will melt down and volatilize before the melting/decomposition of  $\beta$ -CD. In view of the intermolecular interaction between  $\beta$ -CD and a guest, it may be reasonable to guess tentatively that the thermal decomposition behaviors of  $\beta$ -CD as a host before and after inclusion would be different.

In one recent paper, we showed that an organic guest, clove oil, released from its inclusion complex of  $\beta$ -CD far before decomposition of  $\beta$ -CD<sup>[12]</sup>. So it is necessary to find out whether physical and chemical properties of  $\beta$ -CD have changed between before inclusion and after exclusion of clove oil. The present research makes an effort to answer the following questions: what are the differences in TG profiles at five heating rates, as well as in IR curves at different temperatures between free  $\beta$ -CD and the survived  $\beta$ -CD? How to exert double extrapolation method on the decomposition process of the survived  $\beta$ -CD from the inclusion complex of  $\beta$ -CD with clove oil.

Clove oil has been extensively used as a natural flavoring agent in food industry. In consideration of the volatility and instability, it may be feasible to use a molecular envelope against oxygen and other diffusion, with the aid of forming its inclusion complex of  $\beta$ -CD. After they are released from the inclusion complex at a moderate temperature, how the residue, i.e., the survived  $\beta$ -CD from the inclusion complex of  $\beta$ -CD with clove oil, behaves in even hotter surroundings? How to comprehend completely and correctly the fastest and largest mass loss process of the survived  $\beta$ -CD is the focus of our present work. So the thermal decomposition kinetics of the survived  $\beta$ -CD is estimated by a double extrapolation method under nonisothermal condition<sup>[13,14]</sup>. The structures of  $\beta$ -CD and the main component of clove oil are presented in Scheme 1.

On one hand, when the model free methods of Flynn-Wall-Ozawa and Friedman are employed to calculate activation energy ( $E_a$ ), the value of  $E_a$  differs depending on the change of conversion degree ( $\alpha$ ). And the regulation of such change relates to different reaction type.  $\alpha$  represents the develop stage of the

crystal nucleus for new particles. Thus the calculated  $E_a$  is the value for different develop stage of the new crystal nucleus. Only when  $\alpha$  is extrapolated to zero, the value of  $E_{a, \alpha \rightarrow 0}$  would be nucleation formation activation energy of the new particles.

On the other hand, if the thermal process of a sample is dealt with the method of model function fitting, the calculated  $E_a$  and  $\alpha$  varied with the heating rate for a certain function. The thermal conduction between the sample and the surroundings, the endothermic and exothermic of the sample, as well as the deviation of sample heating rate from programmed heating rate all have influences on the assessment of reaction mechanism. Nevertheless, if heating rate ( $\zeta$ ) is extrapolated to zero, the sample would be at the ideal thermal equilibrium state and the calculated  $E_{a, \zeta \rightarrow 0}$  would be close to the real value.

According to these views, the double extrapolation method is employed to determine the most probable mechanism function for the thermal decomposition reaction of the survived  $\beta$ -CD at both thermal equilibrium and original state.

## 1 Experimental

### 1.1 Materials

$\beta$ -CD is purchased from Shanghai Chemical Reagent Company and recrystallized twice from deionized distilled water. Clove oil, a seminatural and semisynthetic product, is purchased from Shanghai Feixiang Chemical Company and used without further purification. All other chemicals are of analytical-reagent grade unless otherwise stated.

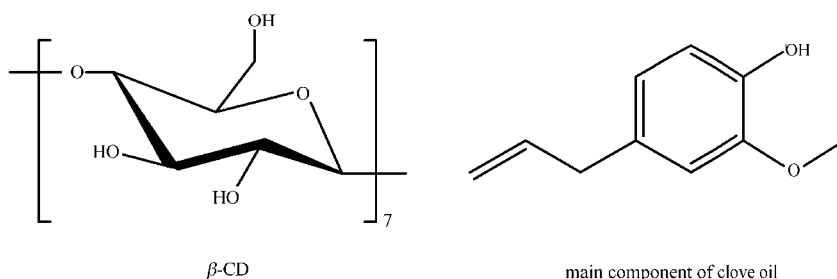
### 1.2 Preparation of $\beta$ -CD inclusion complex of clove oil

Inclusion complex of  $\beta$ -CD with clove oil is prepared by mixing clove oil with  $\beta$ -CD and stirring for 48 h at 298.2 K. The initial molar ratio of clove oil to  $\beta$ -CD (1 mmol) is about 10:1 in deionized water.

The separated crude product is washed using small amounts of deionized water (3×5 mL) and alcohol (95%, 3×3 mL) to remove the unreacted  $\beta$ -CD and clove oil. The obtained sample is dried for 24 h at 383.2 K in vacuo, and then stored in a vacuum desiccator over silica gel<sup>[12]</sup>. In aqueous solution, the chemical stoichiometry and formation constant of the inclusion complex of  $\beta$ -CD with the main component of clove oil of  $\beta$ -CD were determined to be one-to-one and  $3.55 \times 10^4 \text{ mol}^{-1} \cdot \text{L}$ , respectively<sup>[15]</sup>.

### 1.3 Instrument and method

TG curves are recorded on a Shimadzu TGA-50 (Shimadzu Co., Ltd., Japan) thermogravimetric analyzer at the heating rates



Scheme 1 Chemical structure of  $\beta$ -CD and main component of clove oil

of 5.0, 10.0, 15.0, 20.0, 25.0 K·min<sup>-1</sup> under a nitrogen gas flow of 25 mL·min<sup>-1</sup>. The crystallite powder is about 5.5 mg for the various TG measurements.

The samples are heated by MTI GSL1600X (Hefei Kejing Materials Technology Co., Ltd., China) in vacuo under the heating rate of 10.0 K·min<sup>-1</sup> to 573.2 and 623.2 K, respectively. Fourier transform infrared (FT-IR) spectra are recorded on a Bruker EQUINOX55 spectrometer with KBr pellets.

## 2 Results and discussion

### 2.1 A comparison in the TG profiles between free $\beta$ -CD and the survived $\beta$ -CD

The TG profiles of the thermal decomposition process of the survived  $\beta$ -CD from the inclusion complex of  $\beta$ -CD with clove oil are displayed in Fig.1A, corresponding to the residual mass fraction ( $w$ ) range from 70% to 30%. At this stage, the guest, clove oil, has already been released from its inclusion complex of  $\beta$ -CD, and the fastest mass loss process is caused by the thermal decomposition of the survived  $\beta$ -CD<sup>[12]</sup>. After the  $w$  of less than 30%, it is reckoned as the carbonization and cineration processes of the survived  $\beta$ -CD. In order to evaluate the effect of clove oil on the thermal decomposition behavior of  $\beta$ -CD, the TG profiles of free  $\beta$ -CD in the same  $w$  range are given in Fig.1B.

Obviously, the thermal decomposition temperature of the survived  $\beta$ -CD in Fig.1A rises accompanying the increase of the heating rate. A very similar situation is observed in Fig.1B. On the other hand, although all guest molecules should have escaped after mass loss of more than 30%, the effect of the guest molecules on the thermal behavior of  $\beta$ -CD can still be seen from the distinction of the TG profiles between Fig.1A and Fig.1B.

The influence, resulting from the released clove oil, makes a smaller temperature span of 58.5 K (577.9–636.4 K in Fig.1A) for the survived  $\beta$ -CD than 82.4 K (578.1–660.5 K in Fig.1B) for free  $\beta$ -CD during the decomposition process in  $w$  from 70% to 30%. The difference in temperature interval between any two of the five heating rates is also apparently different from each other between free  $\beta$ -CD and the survived  $\beta$ -CD. For example, when the  $w$  value of the sample is 50%, the temperature differences between the heating rates of 5.0 and 10.0, 10.0 and 15.0, 15.0 and 20.0, 20.0 and 25.0 K·min<sup>-1</sup> are 13.20, 9.20, 9.83, and 6.48

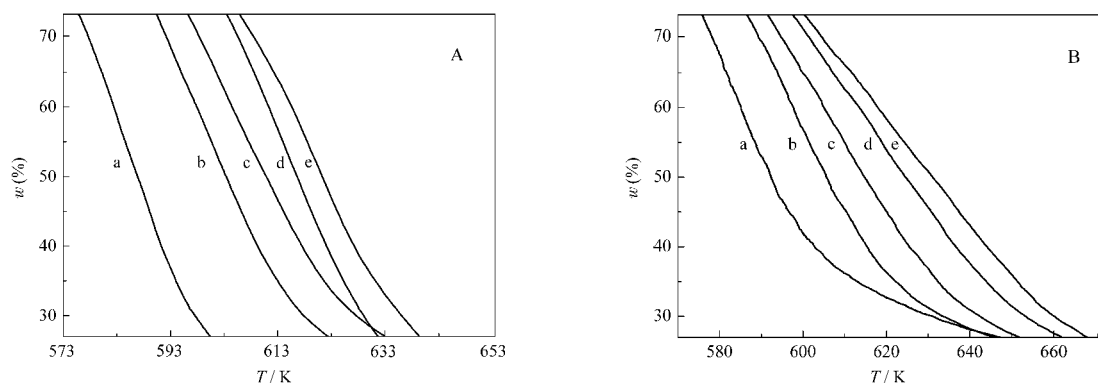


Fig.1 TG profiles of (A) the survived  $\beta$ -CD and (B) free  $\beta$ -CD in  $w$  range from 70% to 30% at different heating rates ( $\zeta$ )  $\zeta$ /(K·min<sup>-1</sup>): (a) 5.0, (b) 10.0, (c) 15.0, (d) 20.0, (e) 25.0

K for the survived  $\beta$ -CD, whereas they are 13.64, 9.66, 9.16, and 4.28 K for free  $\beta$ -CD, respectively.

These observations give a strong impression on the influence of the existence and disappearance of clove oil on the thermal decomposition process of  $\beta$ -CD. In the following sections, we will undertake to determine thermal decomposition kinetic parameters and kinetic mechanism functions for the survived  $\beta$ -CD.

### 2.2 Basic theory of thermal decomposition kinetics

Continuous distribution kinetics can be employed to analyze the thermal decomposition processes of  $\beta$ -CD and  $\beta$ -CD complexes on the basis of many analysis methods, such as integral Flynn-Wall-Ozawa<sup>[16,17]</sup>, Coats-Redfern<sup>[18,19]</sup>, and differential isoconversional Friedman methods<sup>[20,21]</sup>. Eq.(1) represents the kinetics of thermal decomposition reactions of the survived  $\beta$ -CD:

$$\frac{d\alpha}{dt} = \zeta \frac{d\alpha}{dT} = k \cdot f(\alpha) = A \exp\left(\frac{-E_a}{RT}\right) \cdot f(\alpha) \quad (1)$$

where  $\alpha$  is the degree of conversion at heating time  $t$ ,  $\zeta$  is the heating rate, and  $k$  is the rate constant.  $E_a$  is the apparent activation energy.  $A$ ,  $R$ , and  $T$  are the frequency factor, molar gas constant, and absolute temperature, respectively. And  $f(\alpha)$  relating to the reaction mechanism described in this paper only depends on the value of  $\alpha$ . It should be noted that Eq. (1) has been proposed as the beginning to deal with the kinetics process by many kinds of analysis methods. The methods can be classified according to either the experimental conditions selected (isothermal or nonisothermal condition) or the mathematical analysis performed (model-fitting or isoconversional model-free method)<sup>[22–24]</sup>. In the present work, the values of  $E_a$  for the decomposition processes of survived  $\beta$ -CD are calculated both by the isoconversional model-free and model-fitting methods under the nonisothermal condition.

### 2.3 Evaluation of the activation energy of thermal decomposition reaction

One of the most popular integral methods to calculate the  $E_a$  values is Flynn-Wall-Ozawa method<sup>[25]</sup>. This method involves isoconversional type analysis and multiple heating rates. It has the presentation form as follows:

$$\lg \zeta = \lg\left(\frac{AE_a}{R}\right) - \lg F(\alpha) - 2.315 - 0.4567 \frac{E_a}{RT} \quad (2)$$

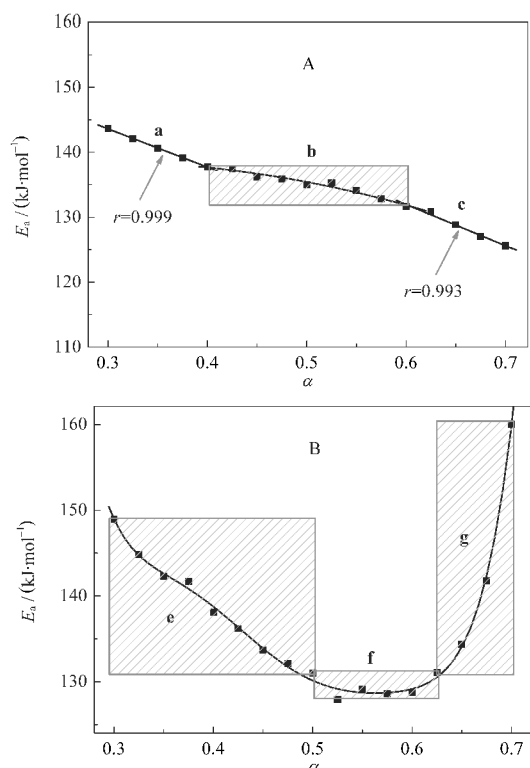
where  $F(\alpha)$  is a power series expansion for the integration of the exponential term of Eq.(1). At the same value of  $\alpha$ ,  $F(\alpha)$  will be a constant, and  $E_a$  can be determined from the slope ( $0.4567E_a/R$ ) of a plot of  $\lg \frac{d\alpha}{dt}$  versus  $(-1/T)$ .

The  $E_a$  values are related to  $\alpha$  values. The variations of  $E_a$  in the  $\alpha$  range from 0.30 to 0.70 for both the survived  $\beta$ -CD and free  $\beta$ -CD are presented in Fig.2. The varied curves of  $E_a$  for the survived  $\beta$ -CD and free  $\beta$ -CD are just coincident with the fastest mass loss processes of their respective thermal decomposition reactions.

There are three stages in Fig.2A for the thermal decomposition process of the survived  $\beta$ -CD. An approximate platform appears in stage **b**, and the  $E_a$  values fluctuate around a mean of  $135.1 \text{ kJ}\cdot\text{mol}^{-1}$  in the  $\alpha$  range from 0.40 to 0.60. Stages **a** and **c**, respectively corresponding to the  $\alpha$  range from 0.30 to 0.40 and from 0.60 to 0.70, relate to the linear parts of the  $E_a$  curve.

The curve in Fig.2B can also be divided into three stages, i.e., a descent stage **e**, an approximate platform stage **f**, and an ascent stage **g**. The former two are somewhat similar to stages **a** and **b** in Fig.2A except for the difference of  $\alpha$  range and the detailed values of  $E_a$ . However, there exists a significant difference between stage **g** and stage **c**. The reverse trend might indicate the different decomposition mechanism between free  $\beta$ -CD and the survived  $\beta$ -CD. Otherwise, the values of  $E_a$  differ between the two curves even at the same value of  $\alpha$ , and the difference escalates as  $\alpha$  is increased.

The linear relationships in stage **a** and stage **c** are rather good,



**Fig.2**  $E_a$  profiles of the thermal decomposition processes of (A) the survived  $\beta$ -CD and (B) free  $\beta$ -CD in the  $\alpha$  range from 0.30 to 0.70 based on Flynn-Wall-Ozawa method

with the correlation coefficients ( $r$ ) of 0.999 and 0.993, respectively. Furthermore, it is very interesting that the slopes ( $-58.92$  in stage **a** and  $-63.52$  in stage **c**) of the two straight lines are also quite close. The approximately parallel relationship suggests that there might be a similar reaction mechanism in the two stages, because the decrease trend of  $E_a$  in the two stages seems to obey a similar rule. Consequently, it is very important to further elucidate the thermal behavior of the survived  $\beta$ -CD in stages **a** and **c**. So the isoconversional type analysis and model-fitting method are employed to investigate the two processes.

The differential isoconversional method suggested by Friedman is based on the general form of rate Eq.(3)<sup>[21]</sup>. It can be written in the natural logarithmic form as follows:

$$\ln \frac{d\alpha}{dt} = \ln A f(\alpha) - \frac{E_a}{RT} \quad (3)$$

When  $\alpha$  keeps constant, the plot of  $\ln(d\alpha/dt)$  versus  $1/T$ , which is obtained from TG analysis results recorded at several heating rates, should be a straight line whose slope allows an evaluation of  $E_a$ . The calculated values of  $E_a$  for the survived  $\beta$ -CD under five heating rates with varied  $\alpha$ , according to Friedman method, are listed in Table 1.

Also, the values of  $E_a$ , when  $\alpha$  are extrapolated to 0 for stages **a** and **c** based on Friedman method, are exhibited in Table 1. It is  $135.2 \text{ kJ}\cdot\text{mol}^{-1}$  for stage **a** and  $69.9 \text{ kJ}\cdot\text{mol}^{-1}$  for stage **c**. It should be noted that the calculated values of  $E_a$  (Table 1), as well as the extrapolation data, from Friedman method are, to a certain degree, different from those (Fig.2) calculated by the modified Ozawa method.

Although the mathematical analyses for two methods are of the same basic form, i.e., Eq.(1), the detailed operation process, such as integral, differential and application of approximation, differs slightly under different methods, which causes the difference in the calculated or extrapolated results between the methods. In order to strictly assess the extrapolation results from Friedman method, a double extrapolation procedure, i.e., Coats-Redfern method, is also employed to further inspect the kinetic mechanism function of the thermal decomposition in stages **a** and **c**.

Model-fitting methods involve fitting different model functions to temperature integral process and simultaneously determining the value of  $E_a$ . There are many nonisothermal model-fitting methods, and the most popular one is Coats-Redfern method<sup>[19]</sup>.

Applying a first order integration to Eq.(1) gives Eq.(4) as fol-

**Table 1** Calculated results of  $E_a$  (in  $\text{kJ}\cdot\text{mol}^{-1}$ ) for the survived  $\beta$ -CD from Friedman method

$\alpha$	$E_a$	$r$	$\alpha$	$E_a$	$r$
0.300	$121.7 \pm 5.3$	0.997	0.600	$110.8 \pm 21.9$	0.946
0.325	$121.3 \pm 6.1$	0.996	0.625	$112.0 \pm 25.1$	0.932
0.350	$120.4 \pm 6.9$	0.995	0.650	$112.8 \pm 27.3$	0.922
0.375	$119.0 \pm 7.7$	0.994	0.675	$113.8 \pm 32.5$	0.896
0.400	$117.4 \pm 8.9$	0.991	0.700	$118.3 \pm 41.9$	0.852
extrapolate	$135.2 \pm 3.7$	0.986	extrapolate	$69.9 \pm 16.3$	0.922

lows:

$$G(\alpha) = \frac{A}{\zeta} \int_0^T \exp(-E_a/RT) dT \quad (4)$$

Then utilizing an asymptotic series expansion for approximating the exponential integral in Eq.(4) gives Coats-Redfern representation in Eq.(5):

$$\ln \left[ \frac{G(\alpha)}{T^2} \right] = \ln(AR/\zeta E_a) - E_a/RT \quad (5)$$

At a constant heating rate of  $\zeta$ , plotting the left side of Eq.(5) with varied  $\alpha$ , which includes the model function  $G(\alpha)$  versus  $1/T$  gives the value of  $E_a$  in the light of the slope of the fitted line in the plot. The most common model functions are listed in Table 2<sup>[26]</sup>.

By replacing, in turn, the expression of  $G(\alpha)$  in Eq.(5) with the listed 18 model functions, based on the original data of  $T$  and  $\alpha$ , we obtain the calculated  $E_a$  values from these functions at five heating rates and their respective extrapolation results. These data in the  $\alpha$  ranges from 0.30 to 0.40 and from 0.60 to 0.70 are listed in Table 3 and Table 4, respectively. The model function that gives the closest value of  $E_a$  in stage **a** or stage **c** to those from Friedman method is selected as the chosen model.

The obtained values of  $E_a$  by extrapolating  $\zeta$  to 0 in Coats-Redfern method are carefully compared with those by extrapolating  $\alpha$  to 0 in Friedman method. It is found that the calculated and extrapolated values of  $E_a$  from the function A1.5, i.e.,  $[-\ln(1-\alpha)]^{2.3}$  in both stages are the closest to those from the Friedman method. And among the 18 functions, the function A1.5 displays the best linear correlation coefficients under five heating rates at the two stages. Thus, both of the two stages (**a** and **c**) in Fig.2A are of the same kind of the decomposition mechanism,

**Table 2** Expression of the model functions  $G(\alpha)$  for some of the common mechanism in the solid reaction<sup>[26]</sup>

Model symbol	Model	Function $G(\alpha)$
P1	Power law	$\alpha^{32}$
P2	Power law	$\alpha^{12}$
P3	Power law	$\alpha^{13}$
P4	Power law	$\alpha^{14}$
A1.5	Avrami-Erofe'ev ( $m=1.5$ )	$[-\ln(1-\alpha)]^{2.3}$
A2	Avrami-Erofe'ev ( $m=2$ )	$[-\ln(1-\alpha)]^{1.2}$
A3	Avrami-Erofe'ev ( $m=3$ )	$[-\ln(1-\alpha)]^{1.3}$
A4	Avrami-Erofe'ev ( $m=4$ )	$[-\ln(1-\alpha)]^{1.4}$
R2	phase-boundary controlled reaction (contracting area)	$[1-(1-\alpha)^{1/2}]$
R3	phase-boundary controlled reaction (contracting area)	$[1-(1-\alpha)^{1/3}]$
D1	one-dimensional diffusion	$\alpha^2$
D2	two-dimensional diffusion Valensi Eq.	$[(1-\alpha)\ln(1-\alpha)]+\alpha$
D3	three-dimensional diffusion Jander Eq.	$[1-(1-\alpha)^{1/3}]^2$
D4	three-dimensional diffusion Ginsthing-Bronshtein	$1-(2/3)\alpha-(1-\alpha)^{2/3}$
F0	zero-order	$\alpha$
F1	first-order	$-\ln(1-\alpha)$
F2	second-order	$(1-\alpha)^{-1}-1$
F3	third-order	$0.5[(1-\alpha)^{-2}-1]$

i.e., Avrami-Erofe'ev ( $m=1.5$ ). This result is also in good accordance with the parallel relationship of the straight lines in Fig. 2A.

## 2.4 Reaction order of thermal decomposition of the survived $\beta$ -CD in stage **b**

Stages **a** and **c** in Fig.2A studied above, indicating that the changes of the  $E_a$  values involve in the same regulation. Stage **b**

**Table 3** Calculated and extrapolated  $E_a$  for the survived  $\beta$ -CD in the  $\alpha$  range from 0.30 to 0.40 under five heating rates

Model symbol	$E_a/(kJ \cdot mol^{-1})$					Extrapolate to $\zeta \rightarrow 0$
	5.0 $K \cdot min^{-1}$	10.0 $K \cdot min^{-1}$	15.0 $K \cdot min^{-1}$	20.0 $K \cdot min^{-1}$	25.0 $K \cdot min^{-1}$	
P1	251.5±4.1	209.7±3.6	203.6±3.4	215.4±5.2	182.5±5.3	252.2±6.7
P2	78.4±1.7	62.8±0.8	61.1±1.2	65.1±1.7	54.2±1.8	78.2±6.1
P3	48.5±0.9	38.6±0.5	37.4±0.8	40.1±1.1	32.7±1.2	48.5±3.8
P4	34.0±0.7	26.6±0.3	25.6±0.5	26.6±1.2	21.9±0.8	34.1±2.6
A1.5	135.0±3.0	110.8±1.1	108.5±2.5	114.5±2.2	96.6±2.3	134.9±9.6
A2	99.2±2.3	80.6±0.9	78.7±2.1	83.7±1.7	70.1±1.8	99.0±7.3
A3	62.9±1.5	50.4±0.6	49.0±1.5	52.4±1.1	43.4±1.2	62.8±4.9
A4	44.8±1.1	35.5±0.3	34.4±1.0	36.8±0.8	30.0±0.9	44.9±3.6
R2	185.6±3.5	152.7±1.6	149.2±3.2	158.3±3.5	133.9±3.6	185.3±13.1
R3	192.9±3.9	158.8±1.5	155.1±3.6	164.6±3.5	139.3±3.6	192.5±13.6
D1	339.2±5.6	280.3±3.6	274.6±4.9	290.7±7.0	247.1±7.2	338.5±23.4
D2	365.8±6.6	302.6±3.4	296.3±6.0	313.8±7.0	266.9±7.3	365.1±25.2
D3	395.3±7.8	327.1±3.1	320.3±7.2	339.3±7.0	288.7±7.4	394.5±27.2
D4	375.5±6.9	310.7±3.4	304.3±6.3	322.2±7.1	273.6±3.6	375.0±25.9
F0	164.7±2.8	135.3±1.7	132.3±2.4	140.4±3.5	118.8±3.3	164.4±11.7
F1	208.0±4.5	171.4±1.5	167.5±4.2	177.7±3.4	150.5±3.7	207.7±14.6
F2	256.8±7.4	213.0±1.9	208.2±6.5	220.9±3.6	187.5±3.8	256.5±17.6
F3	314.4±9.9	260.0±3.1	254.3±9.2	270.2±4.5	229.3±4.1	313.7±21.9

**Table 4** Calculated and extrapolation  $E_a$  in the  $\alpha$  range from 0.60 to 0.70 under five heating rates

Model symbol	$E_a/(kJ \cdot mol^{-1})$					Extrapolate to $\zeta \rightarrow 0$
	5.0 $K \cdot min^{-1}$	10.0 $K \cdot min^{-1}$	15.0 $K \cdot min^{-1}$	20.0 $K \cdot min^{-1}$	25.0 $K \cdot min^{-1}$	
P1	98.3±6.8	73.9±5.2	64.1±5.8	98.2±5.2	76.0±3.7	88.2±18.2
P2	26.3±2.3	15.3±2.9	14.3±1.9	25.8±1.9	13.8±1.7	23.5±7.1
P3	14.3±1.5	8.7±1.1	6.1±1.2	13.7±1.3	8.7±0.8	12.2±4.1
P4	8.2±1.1	4.0±0.8	2.0±0.9	7.7±1.0	4.0±0.5	6.6±3.0
A1.5	75.4±4.1	56.2±3.2	48.4±3.8	75.2±3.1	57.7±2.1	67.5±14.3
A2	54.3±3.1	39.8±2.3	33.6±2.7	53.8±2.5	40.6±1.5	48.4±10.8
A3	32.9±2.1	23.2±1.4	18.9±1.8	4.0±0.5	23.6±1.0	28.9±7.8
A4	22.3±1.6	14.9±1.1	11.6±1.4	21.7±1.3	15.1±0.7	19.4±5.4
R2	87.4±5.4	65.6±4.0	56.4±4.6	87.1±4.2	67.2±2.7	78.4±16.4
R3	97.0±5.7	73.0±4.3	63.1±4.9	96.6±5.8	74.9±2.9	87.2±17.9
D1	134.5±9.1	102.2±6.8	88.8±7.7	134.5±7.1	104.9±4.9	121.1±24.3
D2	164.6±10.2	125.5±7.8	109.5±8.8	164.6±7.9	128.9±5.3	148.3±29.3
D3	203.8±11.3	156.1±8.7	136.7±10.0	203.9±8.7	160.2±5.8	184.0±35.9
D4	177.5±10.6	135.6±8.1	118.4±9.2	177.5±8.1	139.2±5.5	160.0±31.5
F0	62.4±4.6	46.1±3.4	39.2±3.8	62.0±3.6	47.2±2.4	55.7±12.2
F1	120.0±6.8	88.2±4.3	77.7±5.6	118.0±4.8	91.8±3.1	107.1±22.2
F2	197.7±7.5	151.3±6.0	132.4±7.7	197.5±6.4	155.0±4.0	178.5±34.8
F3	298.0±10.4	229.4±7.5	201.7±10.1	177.5±8.1	235.1±5.4	281.7±42.9

in Fig.2A can be approximately considered as a platform because all of the nine points in the shadowed area in Fig.2A have very close values of  $E_a$ , i.e., these  $E_a$  values are within a narrow range of  $(135.1 \pm 3.2)$  kJ·mol<sup>-1</sup>. An evaluation method of reaction order is utilized to investigate whether the stage is a simple thermal decomposition process. According to the extended theory of Avrami<sup>[27]</sup> under nonisothermal condition, the variation of  $\alpha$  with temperature and heating rate can be described in Eq.(6) as follows:

$$\alpha(T) = 1 - \exp(-k/\zeta^n) \quad (6)$$

where,  $k$  and  $n$  are the reaction rate and reaction order, respectively. And  $k$  can be defined based on Arrhenius Equation, i.e., Eq.(7):

$$k = A \exp(-E_a/RT) \quad (7)$$

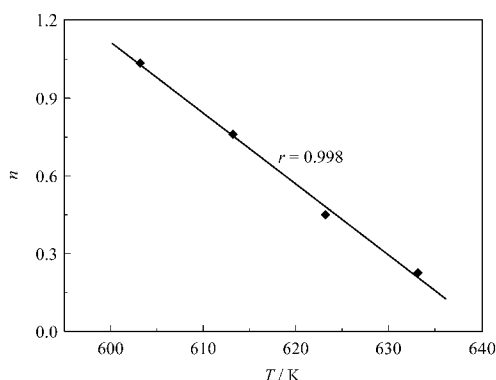
Substituting it into Eq.(6), then taking double natural logarithm for both sides in Eq.(6) gives Eq.(8) as follows:

$$\ln\{-\ln[1-\alpha(T)]\} = \ln A - \frac{E_a}{RT} - n \ln \zeta \quad (8)$$

Plotting the left side in Eq.(8) against  $\ln \zeta$  under isothermal condition<sup>[26]</sup>, we can obtain a figure, in which the slope of the straight line is just the reaction order of the survived  $\beta$ -CD. It should be emphasized that the value of  $n$  is changed with temperature. A plot describing the  $n$  values for the thermal decomposition of the survived  $\beta$ -CD in stage **b** as a function of temperature is shown in Fig.3.

A survived  $\beta$ -CD should be also composed of seven glucose units joined by  $\alpha$ -1,4-glucosidic bonds, and the scission of the chemical bonds would not be occurred at a single location. From our recent work with gas chromatography coupled to time-of-flight mass spectrometry to make tracks for the thermal decomposition behavior of  $\beta$ -CD inclusion complexes, it is found that many small fragment ions from the loop backbone of the survived  $\beta$ -CD could be produced, and the small fragments could still form some larger fragments. These complicated the decomposition process of the survived  $\beta$ -CD.

The considered temperature range in Fig.3 just corresponds to the center area of the thermal decomposition of the survived  $\beta$ -CD under five heating rates (Fig.1A). The continuously decreasing trend of  $n$  implies the complexity of the thermal decomposi-



**Fig.3** Changing trend of  $n$  with enhanced temperature for the thermal decomposition of the survived  $\beta$ -CD in stage **b**

tion process of the survived  $\beta$ -CD in stage **b**, even with an approximately constant value of  $E_a$  in the stage.

For the four black points in Fig.3, the fit to a linear relationship between  $n$  and  $T$  from 603.2 to 633.2 K is quite good, with correlation coefficient ( $r$ ) value of 0.998. Combined with the TG profiles in Fig.1A, the value of  $\alpha$  from 0.40 to 0.60 is included in this temperature range except for the heating rate of 5.0 K·min<sup>-1</sup>. Then fitting this area to Fig.2A, it is found that  $E_a$  is kept approximately constant in stage **b**. This phenomenon is abnormal but very interesting. Because a continuously varying value of  $n$  suggests that there should exist changing reaction mechanisms with the escalation of the decomposition process. The approximate invariability of  $E_a$  in Fig.2A may result from the superposition result supplied by the different decomposition mechanism functions.

The varied mechanism could be attributed to the different thermal behaviors of the sample at different stages. One of our recent studies<sup>[12]</sup> described the detailed decomposition process of the survived  $\beta$ -CD from its inclusion complex of clove oil. First, at stage **a**, a few fragments of the survived  $\beta$ -CD were observed, implying that its main component was still left in the sample. Second, the survived  $\beta$ -CD began to decompose rapidly at stage **b**, since there was a very large mass loss in TG curve corresponding to the stage. Then it is the carbonization process of the survived  $\beta$ -CD with a few fragments released which related to stage **c**. The different decomposition behaviors in different stages resulted in the variation of the thermal decomposition kinetics of the survived  $\beta$ -CD.

### 2.5 Difference in FT-IR spectra between free $\beta$ -CD and the survived $\beta$ -CD

FT-IR spectra of free  $\beta$ -CD and the survived  $\beta$ -CD at 573.2 and 623.2 K, as well as IR spectrum of free  $\beta$ -CD at 298.2 K, are displayed in Fig.4, aiming to give a direct comparison of the structural difference between them.

The absorptions at about 3390, 2298, and 1200–1000 cm<sup>-1</sup> for free  $\beta$ -CD at 298.2 K are due to the vibration of —OH group, —CH<sub>2</sub> group, and C—O bond, respectively. The absorption at 943 cm<sup>-1</sup> is the breathing vibration of  $\beta$ -CD backbone, and 854 cm<sup>-1</sup> is the characteristic absorption of glucose.

On the whole, many fine absorption peaks at finger print region between 1300–700 cm<sup>-1</sup> for free  $\beta$ -CD at 298.2 K disappear both at 573.2 K and at 623.2 K for free  $\beta$ -CD and the survived  $\beta$ -CD. And the two IR curves of the survived  $\beta$ -CD show more similarity than those of free  $\beta$ -CD. In other words, the IR curve of free  $\beta$ -CD at 623.2 K is simpler than that at 573.2 K. For example, the single peak at 1639.8 cm<sup>-1</sup> for free  $\beta$ -CD at 298.2 K has been split into two peaks at 1705.3 and 1612.6 cm<sup>-1</sup> at 573.2 K, however, only a single peak at 1598.6 cm<sup>-1</sup> is observed at 623.2 K. As for the survived  $\beta$ -CD, the single peak appears at 1642.7 cm<sup>-1</sup> at 623.2 K and 1631.9 cm<sup>-1</sup> at 573.2 K. Moreover, the vibration absorptions of —OH and —CH<sub>2</sub> groups are not readily observable for both free  $\beta$ -CD and the survived  $\beta$ -CD at higher temperatures. It should be noted that at 623.2 K, the ab-

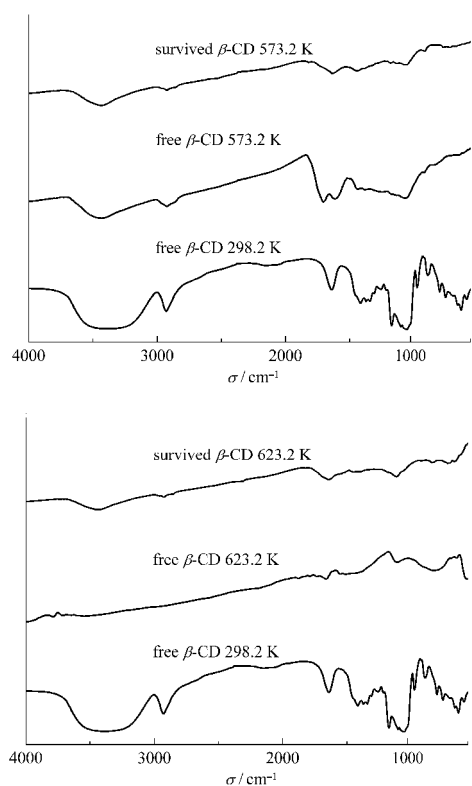


Fig.4 FT-IR spectra of free  $\beta$ -CD and the survived  $\beta$ -CD at different temperatures

sorption curve trend of free  $\beta$ -CD below  $1000\text{ cm}^{-1}$  is quite different with that of the survived  $\beta$ -CD.

These observations mean that there exists a difference in thermal decomposition mechanisms or rates between free  $\beta$ -CD and the survived  $\beta$ -CD from the inclusion complex of  $\beta$ -CD with clove oil. In other words, clove oil as guest affects the decomposition rates of  $\beta$ -CD as host to a certain extent, which are in good accordance with the calculated results of  $E_a$  values.

### 3 Conclusions

The calculation method of double extrapolation was employed and the obtained results from both isoconversional model-free and model-fitting methods under the nonisothermal condition displayed the complexity of thermal decomposition process of the survived  $\beta$ -CD from its inclusion complex of clove oil. The difference of the thermal decomposition behaviors of the survived  $\beta$ -CD in different stages was discussed. It was interesting that the initial stage and the final stage of the decomposition process for the survived  $\beta$ -CD were of the same reaction model while the platform stage in the middle presented a regular decline value of reaction order ( $n$ ). Different methods were used to calculate the activation energy and the method of Coats-Redfern with the model function of Avrami-Erofe'ev ( $m=1.5$ ) was found to be the best to explain the whole process of the thermal decomposition reaction.

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