KINETIC STUDIES ON THE THERMAL DISSOCIATION OF THE INCLUSION COMPLEX OF β-CYCLODEXTRIN WITH CINNAMIC ALDEHYDE

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Abstract

The stability of the inclusion complex of β-CD with cinnamic aldehyde was investigated by means of TG and DSC. The mass loss takes place in three stages: dehydration occurs at 50–120°C; dissociation of β-CD·C_9H_8O proceeds in the range 200–260°C; and decomposition of β-CD begins at 280°C. The kinetics of the dissociation of β-CD·C_9H_8O was studied by means of thermogravimetry both at constant temperature and with linearly increasing temperature. The results demonstrate that the dissociation of β-CD·C_9H_8O is dominated by a one-dimensional diffusion process. The activation energy E is 160 kJ mol^{-1}, and the pre-exponential factor A is 5.8×10^{14} min^{-1}. Scanning electron microscope observations and the results of crystal structure analysis are in good agreement with those of thermogravimetry.

Keywords: β-cyclodextrin, cinnamic aldehyde, kinetics, thermal analysis

Introduction

β-Cyclodextrin (β-CD) is an annular molecule composed of seven glucose units linked by 1,4-glucosidic bonds. Due to its annular structure, it is able to form inclusion complexes by acting as host molecule to a great variety of guest molecules [1]. Cinnamic aldehyde is often utilized as a flavorant in the food industry. Because of its volatility, there are some difficulties in its use in certain processes, such as the manufacturing of sweets, since the temperature is above 150°C during the evaporating process. If the cinnamic aldehyde is added directly to the sugar, it will quickly evaporate. Additionally, the melted cinnamic aldehyde will float on the sugar and not mix [2]. In consequence of the thermal stability of the inclusion complex of β-CD with cinnamic aldehyde, the changes which take place above 150°C are of industrial interest [3]. Stability and kinetic studies on inclusion complexes of β-CD with guest molecules in water have been reported, but reports are rarer on stability

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and kinetic studies relating to the thermal dissociation of inclusion complexes in the solid state [4]. In this paper, the kinetics of dissociation of β-CD cinnamic aldehyde was studied by means of TG. Moreover, the dissociation processes of inclusion complexes in the crystal state were analysed.

These findings provide a theoretical basis for industrial applications of the β-cyclodextrin inclusion complexes.

Experimental

Preparation of the sample

β-CD (purchased from Suzhou Gourment Powder Factory, China) and cinnamic aldehyde (analytical reagent) were dissolved in a 1:1 molar ratio in water at 75°C and the mixture was then stirred for 1 h at constant temperature and subsequently filtered. The resulting pale-yellow crystals were dried for 24 h at 25°C and sieved to less than 190 mesh. The composition was identified by means of TG and elemental analysis as β-CD·C_9H_8O·$7H_2O$.

Apparatus and measurements

Thermogravimetric analysis was performed on a WRT-1 microbalance (Shanghai Balancing Instruments Factory). The analytical parameters were: sample mass, about 15 mg; heating rate, 5 K min^{-1}; chart speed, 4 mm min^{-1}; atmosphere, dynamic dried nitrogen, 20 cm^3 min^{-1}; sample holder, a 5×5 mm aluminum crucible.

Differential scanning calorimeter (DSC) (Shanghai Balancing Instruments Factory). The experimental conditions were: sample mass, about 5 mg; heating rate: 5 K min^{-1}; chart speed: 10 mm min^{-1}; atmosphere, static air; reference material, Al_2O_3. The structural changes in the thermal dissociation were observed on a Model 1000B scanning electron microscopy (Amray Co. USA).

All the thermogravimetric data were analysed on an AT-386 computer.

Results and discussion

Stability of the inclusion complexes

Figure 1 shows the TG and DSC curves of β-CD·$11H_2O$ and β-CD·C_9H_8O·$7H_2O$. The TG curve of β-CD·11 H_2O indicates that all of the constitutional water is released at 50–120°C, with a mass loss of 14.85%. At 270°C, a further mass loss indicates the decomposition of β-CD. The DSC curve of β-CD·$11H_2O$ exhibits two overlapping endothermic peaks in the interval 50–110°C. These show the volatilization of water in different steps, which is consistent with the X-ray diffraction results that six water molecules are internal and five are external [5]. Differently from β-CD·$11H_2O$, β-CD·C_9H_8O·$7H_2O$ gives an 8.72% mass loss at 50–120°C, a 10.23% mass loss at 200–260°C, and a large mass loss at 280°C. The three stages correspond, respectively, to dehydration, the dissociation of cinnamic aldehyde and the decomposition of β-CD. The DSC curve exhibits four smaller endothermic peaks in the range
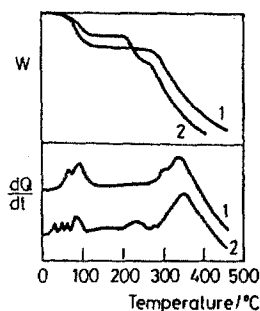
Fig. 1 TG and DSC curves of β-CD·11H$_2$O (1) and β-CD·C$_9$H$_8$O·7H$_2$O (2)

peaks in the range 50–120°C. These indicate that the energies for dehydration of the internal and external water molecules are different. Additionally, the oxygen atoms whose electronegativity is larger in the cinnamic aldehyde molecule will form stronger hydrogen-bonds with the adjacent water molecules, so the seven water molecules are distributed in four different conditions. Although there are no obvious breaks in the TG curve, the release of the seven water molecules occurs in different stages. The smooth endothermic peak at 200–260°C, corresponding to the loss of cinnamic aldehyde, shows that the interaction between β-CD and cinnamic aldehyde involves a weak intermolecular force.

Identification of the kinetic mechanism

The thermal analysis results reveal that the dissociation of β-CD·C$_9$H$_8$O·7H$_2$O takes place in three stages:

1) β-CD·C$_9$H$_8$O·7H$_2$O → β-CD·C$_9$H$_8$O(s)+7H$_2$O(g)
2) β-CD·C$_9$H$_8$O(s) → β-CD(s)+C$_9$H$_8$O(g)
3) decomposition of β-CD

The kinetics of the second stage, after the seven molecules of crystal water had been lost, was also analysed. The isothermal method was performed as follows: the temperature was raised to 120°C at a heating rate of 5 K min^{-1}, and then kept constant for 20 min in order to dehydrate the sample; the temperature was then rapidly raised to 200°C at a rate of 160 K min^{-1}. The isothermal TG curve at 200°C was recorded. With similar methods, the isothermal TG curves at 200, 210, 220 and 230°C were recorded.

The kinetics of a solid-state decomposition reaction can be represented by the general equation:

$$d\alpha/dt = kf(\alpha) \tag{1}$$

$$\text{or } g(\alpha) = kt \tag{2}$$

where α is the fractional extent of reaction at reaction time t, k is the rate constant, and $f(\alpha)$ and $g(\alpha)$ are functions describing the reaction mechanism.
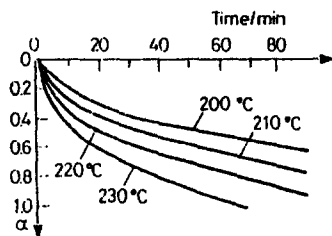
Fig. 2 Isothermal mass loss curves of β-CD·C_9H_8O

Isothermal studies

The TG curves of isothermal mass loss of β-CD·C_9H_8O are shown in Fig. 2. The kinetics of the mass loss process can be judged from the linearity of the $g(\alpha)$ vs. time (t) plot. With data at 210°C as an example, Table 1 lists analytical results on the linear regression between $g(\alpha)$ and t.

Table 1 Linear regression results for the dissociation of β-CD·C_9H_8O (210°C)

$g(\alpha)$	k/min^{-1}	r	$g(\alpha)$	k/min^{-1}	r
D_1	3.100×10^{-3}	0.9988	R_2	2.335×10^{-3}	0.9868
D_2	2.312×10^{-3}	0.9990	R_3	1.761×10^{-3}	0.9900
D_3	7.655×10^{-4}	0.9980	A_1	6.780×10^{-3}	0.9949
D_4	5.872×10^{-4}	0.9984	A_2	4.047×10^{-3}	0.9799
A_u	1.345×10^{-2}	0.9570	A_3	2.874×10^{-3}	0.9722
R_1	3.254×10^{-3}	0.9737	A_4	2.222×10^{-3}	0.9670

In the Table, k is the rate constant and r is the correlation coefficient. The correct mechanism should give a good linearity of $g(\alpha)$ vs. t. Table 1 shows that the diffusion mechanisms have almost equally good linearity, and therefore all other mechanisms should be abandoned. Thus, D_1, D_2, D_3 and D_4 (Table 1) were selected as possible mechanisms.

Non-isothermal studies

For a non-isothermal process, the general equation can be given as

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-E/RT} f(\alpha) \tag{3}$$

where A is the pre-exponential factor, E is the apparent activation energy, and β is the heating rate. From Eq. (3), Criado [6] advanced a simple and high-speed analytical method, such that

$$\left(\frac{T}{T_{0.5}}\right)^2 \frac{d\alpha/dt}{(d\alpha/dt)_{0.5}} = \frac{f(\alpha)g(\alpha)}{f(0.5)g(0.5)} \tag{4}$$

where $T_{0.5}$ is the temperature at $\alpha=0.5$, $(d\alpha/dt)_{0.5}$ is the rate of mass loss at $\alpha=0.5$ and $f(0.5)$ and $g(0.5)$ are the values of the corresponding functions at $\alpha=0.5$.

The right-hand side of Eq. (4) only relates to the mechanism function. A plot of $\dfrac{f(\alpha)g(\alpha)}{f(0.5)g(0.5)}$ vs. α will give a series of standard curves, as shown in Fig. 3. The left-hand side of Eq. (4) can be obtained from the DTG curve. A plot of $\left(\dfrac{T}{T_{0.5}}\right)^2 \dfrac{d\alpha/dt}{(d\alpha/dt)_{0.5}}$ vs. α will give an experimental curve. The suitable mechanism function can be defined by comparing the experimental and standard curves. The TG and DTG curves of β-CD·C_9H_8O dissociation at $\beta=0.5$ K min^{-1} were recorded. The values of $\left(\dfrac{T}{T_{0.5}}\right)^2 \dfrac{d\alpha/dt}{(d\alpha/dt)_{0.5}}$ relating to various α were calculated from the DTG curve, and a series of experimental points were obtained in Fig. 3. The results show that at $\alpha<0.8$ these points almost always fell on the R_1 and D_1 curves. The deviations at $\alpha=0.8$ were probably caused by the different size of the sample, because when $\alpha>0.8$ the reactions of the smaller particles were completed and the reaction rate was reduced. From a combination of the isothermal experiment results, it was concluded that the dissociation of β-CD·C_9H_8O is dominated by a D_1 mechanism.
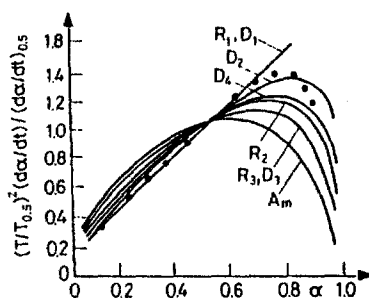

Fig. 3 Criado standard curves, "·" experiment points

From the Arrhenius equation $\log k=\log A - E/(2.303RT)$, the related kinetic parameters of the dissociation of β-CD·C_9H_8O can be obtained from a linear regression of $\log k$ vs. $1/T$, based on the isothermal D_1 mechanism function at 200, 210, 220 and 230°C. The kinetic parameters are $E=159.62$ kJ mol^{-1} and $A=5.765\times10^{14}$ min^{-1}.

Crystal structure analysis

Scanning electronmicroscopic observations on the samples and the products show that the side and the prism structure do not change markedly during the dissociation process. This indicates that the crystals do not break into pieces during the dissociation process. Figure 4 shows the crystal structure of β-CD·C_9H_8O at about 50% mass loss.
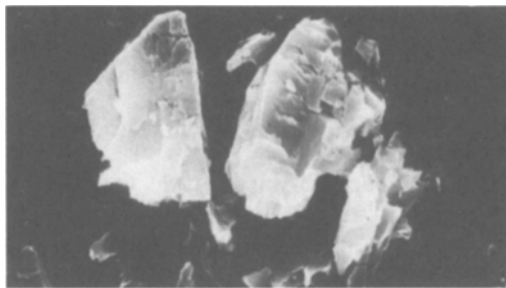
Fig. 4 Scanning electron micrograph of β-CD·C$_9$H$_8$O (×2000)

The inclusion complexes of β-CD with guest molecules generally form a tubu-lar-type structure (Fig. 5). Due to the crystal anisotropy, the rate of reaction is different in the different directions. For cinnamic aldehyde, it is difficult to move along the direction perpendicular to the stacking axis, because of the impediment due to the β-CD structure and the restrain caused by hydrogen bonds between adja-cent β-CDs. However, a cinnamic aldehyde molecule escaping from a β-CD cage can easily pass into another β-CD cavity. In the dissociation process, the cinnamic aldehyde molecules first escape from β-CD on the crystal surface which is perpen-dicular to the axis. As the reaction advances, a phase interface between the product (β-CD) and the reactant (β-CD·C$_9$H$_8$O) forms and moves towards the interior of the particles. In the dissociation of β-CD·C$_9$H$_8$O, the cinnamic aldehyde molecules es-cape from the β-CD cages, diffuse towards the crystal surface along the axis, and finally desorb from the surface. This process is similar to the successive reaction. The cinnamic aldehyde molecule escapes from one β-CD cage, enters the adjacent β-CD cavity, and then gradually diffuses towards the surface according to the hole theory. The desorption on the crystal surface is fast, so the reaction rate depends on the diffusion step. This result is consistent with the D$_1$ mechanism, as identified by the TG and DTG analyses.
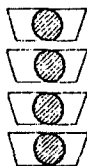

Fig. 5 The stacking diagram of β-CD·C$_9$H$_8$O

It has been reported that the complexing process between cyclodextrins and guest molecules occurs at approximately the diffusion rate in solution [7]. The dis-sociation of β-CD·C$_9$H$_8$O is dominated by a diffusion mechanism. This is consis-tent with the findings of other methods. All these results confirm that the stabilizing energy of inclusion complexes of β-CD with guest molecules is provided by the Van der Waals forces. In other words, there is no chemical interaction between cinnamic aldehyde and β-CD.

Conclusions

The thermal dissociation of β-CD·C_9H_8O is dominated by a one-dimensional diffusion mechanism. The diffusion process takes place according to the hole theory. The apparent activity energy E is 160 kJ mol^{-1}, and the pre-exponential factor A is 5.8×10^{14} min^{-1}.

β-CD can form a stable inclusion complex with cinnamic aldehyde at temperatures below 150°C, and the cinnamic aldehyde molecules are unable to escape from the β-CD complex. After forming an inclusion complex with β-CD, cinnamec aldehyde can be evenly mixed as a flavorant of sweets. Such inclusion complexes may be used as confectionary flavors in industrial processes which involve elevated temperatures without significant loss of cinnamic aldehyde, so its utilization ratio is improved.

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