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KINETIC STUDIES ON THE THERMAL DISSOCIATION OF β-CYCLODEXTRIN-CINNAMYL ALCOHOL INCLUSION COMPLEX

Shou-Zhi Yu, Xiao-Tao Li, Jing-Hua Li, Jin-Yun Wang[1] and Sheng-Jun Tian*

Department of Chemistry, Henan Normal University, Xinxiang 453002, P. R. China
[1]Department of Chemistry, University of Connecticut, Storrs, CT 06268, USA

Abstract

The stability of β-cyclodextrin-cinnamyl alcohol inclusion complex (β-CD·C_9H_{10}·$8H_2O$) was investigated using TG and DSC. The mass loss took place in three stages: the dehydration occurred between 50–120°C; the dissociation of β-CD·$C_9H_{10}O$ occurred in the range of 210–260°C; and the decomposition of β-CD began at 280°C. The dissociation of β-CD·$C_9H_{10}O$ was studied by means of thermogravimetry, and the results showed: the dissociation of β-CD·$C_9H_{10}O$ was dominated by a two-dimensional diffusion process (D_2). The activation energy E was 161.2 kJ mol^{-1}, the pre-exponential factor A was 4.5×10^{13} min^{-1}.

Cyclodextrin is able to form inclusion complexes with a great variety of guest molecules, and the interesting of studies focussed on the energy binding cyclodextrin and the guest molecule.

In this paper, β-cyclodextrin-cinnamyl alcohol inclusion complex was studied by fluorescence spectrophotometry and infrared absorption spectroscopy, and the results show: the stable energy of inclusion complexes of β-CD with weakly polar guest molecules consists mainly of Van der Waals interaction.

Keywords: β-cyclodextrin, cinnamyl alcohol, kinetics, thermal analysis

Introduction

β-cyclodextrin is an annular molecule composed of seven glucose units linked by 1,4-glucosidic bonds. Due to its annular structure, as a host molecule it is able to form inclusion complexes with a great variety of guest molecules [1]. The formation of inclusion complexes can change the state and the stability of the guest molecules, so the inclusion complexes of β-CD with many organic compounds have been successfully utilized in the pharmaceutical and food industries [2, 3]. Cinnamyl alcohol is usually utilized as a flavourant in cosmetics and toilet soap. However, when the cinnamyl alcohol is stored in air, it will gradually oxidize to cinnamic aldehyde. Once cinnamyl alcohol forms inclusion complexes with β-CD, its stability to air can

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* Author to whom all correspondence should be addressed.

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be greatly improved. In this paper, the kinetics of the dissociation of cinnamyl alcohol β-CD complex were investigated in solid state.

Experimental

Preparation of the sample

β-CD (purchased from Suzhou Gourmet Powder Factory) and cinnamyl alcohol (Analytical reagent) were dissolved in 1:2 molar ratio at 70°C in water. It was stirred for 1.5 h at 70°C and then filtered. The pale yellow crystals were dried for one week at room temperature in a desiccator, and sieved to less than 320 mesh. The composition of the inclusion complex formed was identified by TG analysis and elemental analysis as $\beta\text{-CD}\cdot C_9H_{10}O\cdot 8H_2O$.

Apparatus and measurements

Thermogravimetric analysis and differential scanning calorimetry were performed on a ZRY-1P multiple microbalance (Shanghai Balancing Instruments Factory). The experimental conditions were: sample mass, about 1.8 mg; atmosphere, dynamic dried nitrogen 40 cm^3 min^{-1}; sample holder, 5 mm×4 mm aluminium crucible.

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

Results and discussion

The stability of the inclusion complexes

Figure 1 shows the TG and DSC curves of $\beta\text{-CD}\cdot C_9H_{10}O\cdot 8H_2O$.

The TG curve of $\beta\text{-CD}\cdot C_9H_{10}O\cdot 8H_2O$ has a 9.93% mass loss between 50–120°C as well as a 10.57% mas loss between 210–260°C, and a large mass loss over 280°C. The three stages correspond respectively to the dehydration, the escape of cinnamyl alcohol from the inclusion complex and the decomposition of β-CD. The DSC curve has two small endothermic peaks between 50–120°C. These indicate that eight water molecules exist with different binding force, and the energy required for dehydration of the internal and external water molecules is different. The endothermic peak in the range of 210–260°C is accompanied with the mass loss of the TG curve, and corresponds to the evaporation of cinnamyl alcohol from the β-

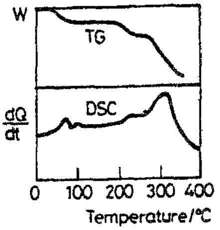

Fig. 1 TG and DSC curves of $\beta\text{-CD}\cdot C_9H_{10}O\cdot 8H_2O$

CD cavity. And this low endothermic peak indicates that the interaction between β-CD and cinnamyl alcohol is the weak intermolecule force.

The identification of the kinetic mechanism

According to the thermal analysis results, the dissociation of β-CD·$C_9H_{10}O$·$8H_2O$ takes place in three steps:

1. $\beta\text{-CD}\cdot C_9H_{10}O\cdot 8H_2O(s) \rightarrow \beta\text{-CD}\cdot C_9H_{10}O(s)+8H_2O(g)$
2. $\beta\text{-CD}\cdot C_9H_{10}O(s) \rightarrow \beta\text{-CD}(s)+C_9H_{10}O(g)$
3. the decomposition of β-CD

We have identified the kinetic mechanism of the second stage. An isothermal method was adopted: the temperature was raised to 120°C at 5 K $\min^{-1}$, and kept at a constant temperature for 20 min in order for the dehydration to be complete. Then the temperature was rapidly raised to 210°C at a heating rate of 80 K $\min^{-1}$. The isothermal TG curve at 210°C was recorded. Using similar methods, the isothermal TG curves at 220, 230 and 240°C were recorded respectively. Non-isothermal method was as follows: the temperature was raised to 120°C at a heating rate of 5 K $\min^{-1}$ and kept at a constant temperature for 20 min. The heating rate was adjusted to recorded the non-isothermal TG curves at 0.6, 1.2, 2.5, 5 K $\min^{-1}$. A three-step judgement method was used in the identification of the mechanism of the decomposition reaction, which combined the isothermal method, linear non-isothermal method with the kinetic compensation effect [4].

Isothermal method

The TG curves of isothermal mass loss of β-CD·$C_9H_{10}O$ are shown in Fig. 2.

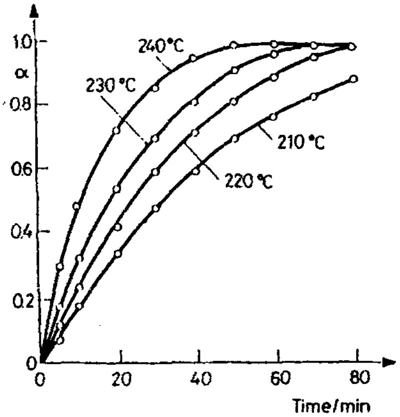

Fig. 2 Isothermal mass loss curves of β-CD·$C_9H_{10}O$; 1) 210; 2) 220; 3) 230; 4) 240°C

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

$$d\alpha/dt = kf(\alpha) \qquad (1)$$

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

where α is the fractional mass loss at the reaction time t (in this paper $\alpha = 0.1\sim0.9$), k is the rate constant, and $f(\alpha)$ and $g(\alpha)$ are functions describing the reaction mechanism.

The kinetic mechanism of the mas loss process can be judged by the linearity of the $g(\alpha)$ *vs.* time t plot. Taking the dissociation of β-CD·$C_9H_{10}O$ at 230°C as an example, Table 1 list the linear regression results of $g(\alpha)$ *vs.* t.

Table 1 Linear regression results for the dissociation of β–CD·$C_9H_{10}O$ at 230°C

$g(\alpha)$	k/min^{-1}	r	σ	$g(\alpha)$	k/min^{-1}	r	σ
D_1	1.2548×10^{-2}	0.9973	3.6762	R_2	8.9693×10^{-3}	0.9885	2.7955
D_2	1.4029×10^{-2}	0.9986	2.5538	R_3	7.1881×10^{-3}	0.9914	2.0812
D_3	4.3558×10^{-3}	0.9967	0.8180	A_1	3.1793×10^{-2}	0.9956	7.8131
D_4	2.8560×10^{-3}	0.9984	0.6412	A_2	1.5696×10^{-2}	0.9893	4.9850
A_u	5.2041×10^{-2}	0.9669	17.6075	A_3	1.0567×10^{-2}	0.9719	3.6371
R_1	1.9743×10^{-2}	0.9773	4.0542	A_4	7.9857×10^{-3}	0.9671	2.8583

In the Table, k is the rate constant, r is the correlation coefficient and σ is the covariance. From the evaluation of r and σ, D_1, D_2, D_3, D_4, R_3 and A_1 were selected as possible $g(\alpha)$ models.

According to Arrhenius equation:

$$k = Ae^{-E/RT} \qquad (3)$$

$$\ln k = \ln A - E/RT \qquad (4)$$

where k is the rate constant, A is the pre-exponential factor.

The related kinetic parameters of the dissociation of β-CD·$C_9H_{10}O$ can be obtained from a linear regression of $\lg k$ *vs.* $1/T$, based on the isothermal experimental data at 210, 220, 230 and 240°C. The values of E, A, and r are listed in Table 2.

Table 2 Kinetic parameter of isothermal dissociation of β–CD·$C_9H_{10}O$

$g(\alpha)$	E_a/kJ mol^{-1}	r	$\lg A$	$g(\alpha)$	E_a/kJ mol^{-1}	r	$\lg A$
D_1	154.28	0.9948	12.4034	R_2	156.91	0.9928	13.1654
D_2	161.23	0.9957	13.6570	R_3	158.64	0.9931	13.6928
D_3	168.55	0.9968	14.0434	R_1	163.96	0.9940	13.7274
D_4	163.21	0.9964	13.3517	A_2	157.29	0.9917	13.3154
A_u	158.94	0.9905	13.0554	A_3	156.83	0.9910	12.8909
R_1	155.84	0.9915	12.7176	A_4	155.17	0.9906	12.3533

Non-isothermal method

Non-isothermal TG curves of the thermal dissociation of β-CD·$C_9H_{10}O$ at different heating rates are shown in Fig. 3.

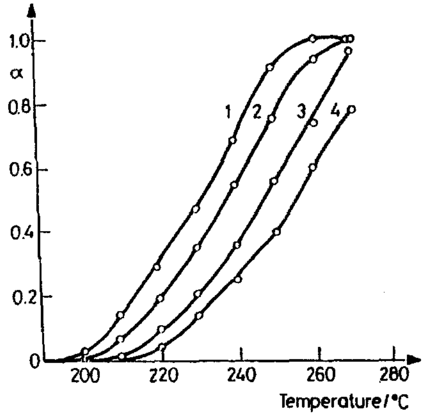

Fig. 3 Non-isothermal TG curves of β-CD·$C_9H_{10}O$ heating rate β (°C min^{-1}); 1) 0.6; 2) 1.2; 3) 2.5; 4) 5

At a constant heating rate:

$$d\alpha/dt = A/\beta e^{-E/RT} f(\alpha) \tag{5}$$

$$\int d\alpha/f(\alpha) = A/\beta \int e^{-E/RT} dT \tag{6}$$

$$g(\alpha) = AE/\beta P(x) \tag{7}$$

where $P(x)=e^{-x}/x(1-2!/x+3!/x^2-4!/x^3+\ldots)$, $x=E/RT$, $\beta=dT/dt$.

Usually $x=E/R \gg 1$, and taking the first two approximate values

$$g(\alpha) \approx ART^2/\beta E(1-2RT/E)e^{-E/RT} \tag{8}$$

$$\log(g(\alpha)/T^2) = \log[AR/\beta E(1-2RT/E)]-E/2.303RT \tag{9}$$

From Eq. (9), it is clear that a straight line of slope $-E/2.303R$ should result when plotting $\log(g(\alpha)/T^2)$ *vs.* $1/T$; the frequency factor A can be obtained from the intercept.

Using the experimental data at different heating rates by this method, the E and A values decreased with increasing heating rate. These mainly because the sample temperature could not reach with the procedural temperature, and caused the temperature range of mass loss moved to higher region. Only when heating rate is very low the record temperature can catch up with the sample temperature. So we extrapolated β to 0 K min^{-1}. Table 3 shows the results of the linear regression for the related data when extrapolating β to 0 K min^{-1}. The Table also lists the *E* and *A* values obtained with the different mechanism function.

Table 3 Kinetic parameters of the β–CD·$C_9H_{10}O$ thermal dissociation when $\beta \to 0$ K min^{-1}

$g(\alpha)$	E_a/kJ mol^{-1}	lg*A*	$g(\alpha)$	E_a/kJ mol^{-1}	lg*A*
D_1	143.76	17.3075	R_2	91.69	4.3989
D_2	162.28	21.7922	R_3	97.01	5.1327
D_3	180.81	25.1702	R_1	101.57	8.9846
D_4	159.12	19.4784	A_2	61.73	–1.1122
A_u	–	–	A_3	44.18	–5.6215
R_1	78.43	2.9211	A_4	36.58	–7.7515

For the correct mechanism function, the kinetic parameters should be identical either obtained by isothermal method or by non-isothermal method. Comparing Table 2 with Table 3, and considering the appropriate *E* and *A* value, it is obvious that only D_2 and D_4 mechanisms satisfy such requirements.

Kinetic compensation effect

In the non-isothermal thermogravimetric experiments, the *E* and *A* values will decrease with increasing heating rate. This tendency can be shown by the kinetic compensation effect [3]. Table 4 list the compensation constants *a* and *b* for different mechanisms, and also the correlation of the linear regression.

Table 4 The kinetic compensation constans

$g(\alpha)$	*a*	*b*	*r*	$g(\alpha)$	*a*	*b*	*r*
D_1	0.2589	–24.2307	0.9990	R_3	0.2516	–16.4872	0.9975
D_2	0.2587	–24.9981	0.9991	A_1	0.2509	–15.7897	0.9936
D_3	0.2505	–26.8752	0.9966	A_2	0.2549	–14.0605	0.9959
D_4	0.2507	–26.8045	0.9912	A_3	0.2539	–13.8158	0.9913
R_1	0.2599	–15.7392	0.9950	A_4	0.2564	–13.8007	0.9972
R_2	0.2566	–15.6487	0.9989				

The kinetic compensation formulas are

$$\log A = aE + b \tag{10}$$

$$E = (\log A - b)/a \tag{11}$$

$$k = Ae^{-(\log A - b)/aRT} \tag{12}$$

where *a*, *b* are the compensation constants.

According to the compensation law, the *k* values can be obtained for the eleven $g(\alpha)$ models at constant temperature. Taking data at 230°C as an example, Table 5 list the *k* values.

Table 5 The *k* values obtained according to the compensation law (230°C)

$g(\alpha)$	k/min^{-1}	$g(\alpha)$	k/min^{-1}	$g(\alpha)$	k/min^{-1}
D_1	5.1654×10^{-3}	R_1	2.2404×10^{1}	A_2	1.4635×10^{2}
D_2	1.3941×10^{-2}	R_2	3.2190×10^{1}	A_3	9.3456×10^{1}
D_3	1.2162×10^{-3}	R_3	3.2511	A4	5.7980×10^{1}
D_4	5.2766×10^{-4}	A_1	3.2631×10^{1}		

Comparing Table 1 with Table 5, it is clear that only the two *k* values from the D_2 mechanism are equal. It confirms that the β-CD·$C_9H_{10}O$ thermal dissociation process follows a D_2 mechanism.

Fluorescence analysis

β-cyclodextrin has very strong fluorescent property. The fluorescent spectra of β-CD, β-CD·cinnamyl alcohol and cinnamyl alcohol are shown are shown in Fig. 4.

In Fig. 4, by the comparison of the fluorescent spectra of β-CD and β-CD·cinnamyl alcohol, it is clear that the peaks of β-CD at 500 nm and 630 nm disappear when β-CD forms inclusion complex with cinnamyl alcohol. It shows that the fluorescent properties of β-CD has changed greatly after forming inclusion complex with cinnamyl alcohol. These probably because that the cinnamyl alcohol molecule

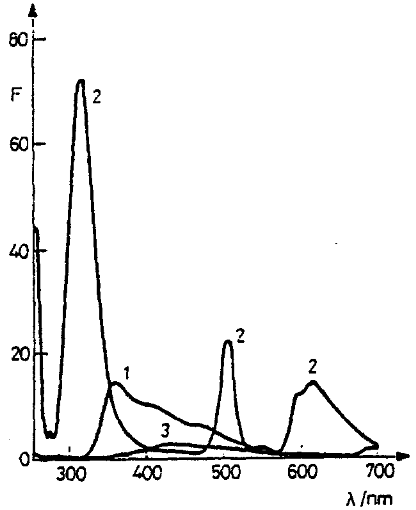

Fig. 4 Fluorescent spectrums; 1) β-CD·cinnamyl, 2) β-CD, 3) cinnamyl alcohol

influences the structure of the glucose unit or because that new bonds have formed between β-CD and cinnamyl alcohol, as confirmed by IR spectra.

Infrared absorption method

The infrared spectrograms of β-CD and β-CD·cinnamyl alcohol are shown in Figs 5 and 6.

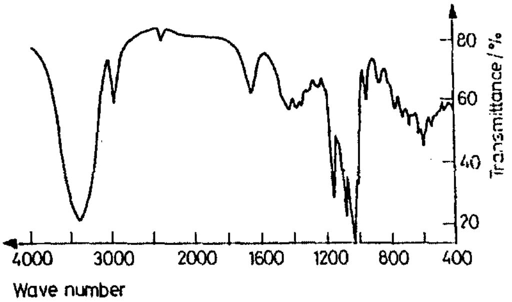

Fig. 5 The infrared spectrogram of β-CD

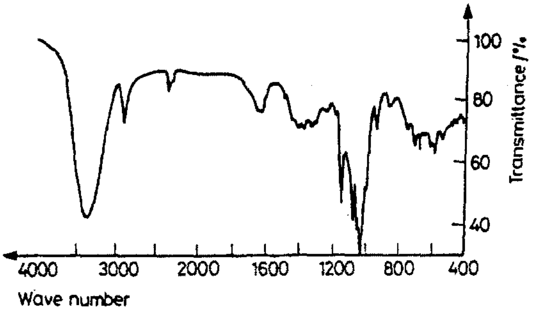

Fig. 6 The infrared spectrogram of β-CD·cinnamyl alcohol

Comparing Figs 5 and 6, it is clear that the several strong absorption peaks of β-CD·cinnamyl alcohol don't move to lower wavelength. It means that, after being complexed by β-CD, new bonds do not form between cinnamyl alcohol and β-CD. This is consistent with the interior of β-CD cavity being non-polar. The inside of β-CD cavity is mainly constructed by hydrogen atoms of C(3) and C(4), so the activation energy of inclusion complexes of β-CD with weakly polar guest molecules (cinnamyl alcohol) consists mainly of Van der Waals energy.

The results of TG and DSC show that the escape of the cinnamyl alcohol molecules from the β-CD cavity is dominated by diffusion mechanism, in other words, no chemical reaction occurs during the complex process or the dissociation process. These are consistent with the results of fluorescence spectrophotometry and infrared absorption spectroscopy.

Conclusions

β-CD can form a stable inclusion complex with cinnamyl alcohol, and the composition is $\beta\text{-CD}\cdot C_9H_{10}O\cdot 8H_2O$. The stability of $C_9H_{10}O$ improved greatly after being complexed by β-CD. The activation energy of inclusion complex of β-CD with cinnamyl alcohol consists mainly of Van der Waals energy. The thermal dissociation mechanism of $\beta\text{-CD}\cdot C_9H_{10}O$ is dominated by a two-dimensioned diffusion process (D_2). The activation energy (E) is 161.23 kJ mol^{-1}, and the pre-exponential factor (A) is 4.5394×10^{13} min^{-1}.

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