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KINETIC STUDIES ON THE THERMAL DISSOCIATION OF β-CYCLODEXTRIN·ETHYL BENZOATE INCLUSION COMPLEXES

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Abstract

The stability of β-cyclodextrin·ethyl benzoate·$6H_2O$(β-CD·$C_6H_5COOC_2H_5$·$6H_2O$) was investigated by TG and DSC. The mass loss takes place in three stages: the dehydration occurs at 50–120°C; the dissociation of β-CD·$C_6H_5COOC_2H_5$ occurs at 200–260°C; the decomposition of β-CD begins at 280°C. The kinetics of the dissociation of β-CD·$C_6H_5COOC_2H_5$ in a dry nitrogen flow was studied by means of thermogravimetry both at constant temperature and linearly increasing temperature. The results show that the dissociation of β-CD·$C_6H_5COOC_2H_5$ is dominated by a three-dimensional diffusion process (D_3). The activation energy E is 116.19 kJ mol^{-1} and the pre-exponential factor A 6.5358·10^9 min^{-1}.

Cyclodextrin is able to form inclusion complexes with a great variety of guest molecules, and the studies focus on the energy of binding between cyclodextrin and the guest molecule. In this paper, the β-cyclodextrin·ethyl benzoate inclusion complex was studied by fluorescence spectrophotometry and infrared absorption spectroscopy, and the results show that the stable energy of inclusion complexes of β-CD with weakly polar guest molecules consists mainly of van der Waals interaction.

Keywords: β-cyclodextrin, ethyl benzoate, inclusion complex, kinetics, thermal decomposition

Introduction

β-cyclodextrin is an annular molecule composed of seven glucose units linked by 1,4-glucosidic bonds. The inside the cavity of β-CD is mainly constructed by oxygen atoms and hydrogen atoms of C(3) and C(5). The internal surface of β-CD is hydrophobic. The hydroxyl of the glucose unit is arranged at both ends of the β-CD cavity, so the whole molecule of β-CD is able to form inclusion

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complexes with a great variety of guest molecules [1, 2, 3]. Its inclusion function 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. Moreover, toxicity experiments show that β-CD can be absorbed as a carbohydrate by animal and human bodies [4]. Recent studies about β-CD have shown that there are vast vistas in many fields [5, 6]. Therefore, the stability and the mechanisms of the thermal decomposition of inclusion complexes are paid close attention. In this paper, the β-cyclodextrin·ethylbenzoate inclusion complex was prepared, and the kinetics of the dissociation of β-CD·ethyl benzoate was studied by thermogravimetry.

Experimental

Preparation of the sample

β-CD (purchased from Suzhou Gourmet Powder Factory) and ethyl benzoate (analytical reagent) were dissolved in a 1:2 molar ratio in 70°C water, stirred for 1.5 h at 70°C and then filtered. The white crystals were dried for five days at room temperature in a desiccator. The composition was identified by TG analysis and elemental analysis as β-CD·$C_6H_5COOC_2H_5$·$6H_2O$.

Apparatus and measurements

Thermogravimetric analysis was performed on a WRT-1 microbalance (Shanghai Balancing Instruments Factory). The analytical parameters were: sample mass, about 8 mg; atmosphere, dynamic dried nitrogen 30 ml min^{-1}; sample holder, 5×2.5 mm aluminium crucible.

Differential scanning calorimetry was carried out on a CDR-1 differential scanning calorimeter (Shanghai Balancing Instruments Factory). The experimental conditions were: sample mass, about 5 mg; heating rate, 5 K min^{-1}; atmosphere, static air; reference material, Al_2O_3.

Fluorescence spectrophotometry was carried out on a Model 930 fluorophotometer (Shanghai, China) and infrared spectroscopy on a RL260-50 infrared spectrophotometer (Japan).

All the thermogravimetric data (α, 0.1–0.9) were analyzed by an AT-386 computer.

Results and discussion

Stability of the inclusion complexes

Figure 1 shows the TG and DSC curves of β-CD·$C_6H_5COOC_2H_5$·$6H_2O$.

The TG curve of β-CD·$C_6H_5COOC_2H_5$·$6H_2O$ indicates a 7.59% mass loss at 50–120°C as well as a 10.71% mass loss at 200–260°C, and a large mass loss at

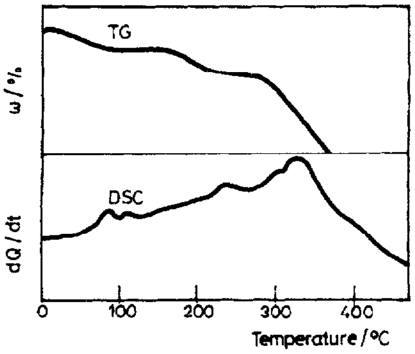

Fig. 1 TG and DSC curves of β-CD·$C_6H_5COOC_2H_5$·$6H_2O$. β=5°C min^{-1}

280°C. The three stages correspond respectively to dehydration, dissociation of ethyl benzoate and decomposition of β-CD. The DSC curve has two small endothermic peaks at 50–120°C. These indicate that the six water molecules are bound within different strengths. The endothermic peak at 210–260°C is accompanied by a mass loss at 200–260°C in the TG curve, and corresponds to the escape of ethyl benzoate from the β-CD cavity. A low endothermic peak indicates that the attraction between β-CD and ethyl benzoate is due to weak intermolecular forces.

Identification of the reaction mechanism

The results of thermal analysis indicate that the dissociation of β-CD·$C_6H_5COOC_2H_5$·$6H_2O$ takes place in three stages:

1. β-CD·$C_6H_5COOC_2H_5$·$6H_2O_{(s)} \rightarrow$ β-CD·$C_6H_5COOC_2H_{5(s)}+6H_2O_{(g)}$
2. β-CD·$C_6H_5COOC_2H_{5(s)} \rightarrow$ β-$CD_{(s)}+C_6H_5COOC_2H_{5(g)}$
3. decomposition of β-CD

We mainly identified the mechanism of the second stage. An isothermal method was adopted: the temperature was raised to 120°C at a heating rate of 5 K min^{-1}, and the constant temperature was maintained for 20 min in order to dehydrate the sample, then the temperature was rapidly raised to 180°C at a heating rate of 120 K min^{-1}. The isothermal TG curve at 180°C was recorded. Using similar methods, the isothermal TG curves were recorded at 190, 200 and 210°C. The non-isothermal method applied was as follows: the temperature was raised to 120°C at a heating rate of 5 K min^{-1}, and the constant temperature was maintained for 20 min, then the heating rate was adjusted and the non-isothermal TG curves were recorded at β=0.6, 1.2, 2.5, 5 K min^{-1}, respectively. A three-step judgement method was used in the identification of the mechanism, which combined the isothermal method and linear non-isothermal method with the kinetic compensation effect [7].

Isothermal method

The TG curves of isothermal mass loss of β-CD·$C_6H_5COOC_2H_5$ are shown in Fig. 2.

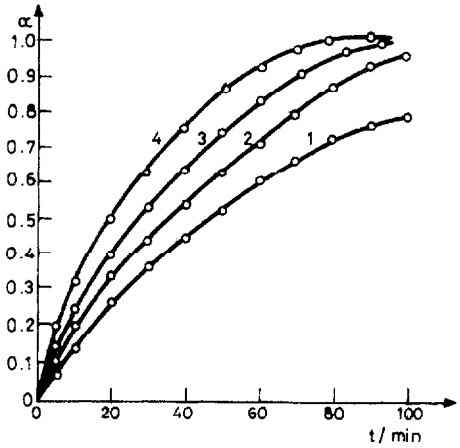

Fig. 2 Isothermal mass loss curves of β-CD·$C_6H_5COOC_2H_5$ 1 – 180°C; 2 – 190°C; 3 – 200°C; 4. 210°C

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

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

or

$$g(\alpha) = kt \qquad (2)$$

where α is the fractional mass loss at the reaction time t, k is the rate constant, $f(\alpha)$ and $g(\alpha)$ are functions describing the reaction mechanism. Typical theoretical model functions for solid-state reactions are shown in Table 1.

The mechanism of the mass loss process can be judged by the linearity of the $g(\alpha)$ *vs.* time t plot. Taking the dissociation of β-CD·$C_6H_5COOC_2H_5$ at 210°C as an example, Table 2 lists the linear regression results of $g(\alpha)$ *vs.* t. In the Table, k is the rate constant, r is the correlation coefficient and δ is the covariance. From the evaluation of r and δ, diffusion mechanisms were selected as possible $g(\alpha)$ models.

According to the Arrhenius equation

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

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

where A is the pre-exponential factor.

Table 1 Kinetic models of the decomposition of solids

$g(\alpha)$	Symbol	Rate-controlling process
α^2	D_1	one-dimensional diffusion
$\alpha+(1-\alpha)\ln(1-\alpha)$	D_2	two-dimensional diffusion
$[1-(1-\alpha)^{1/3}]^2$	D_3	three-dimensional diffusion (Jander function)
$1-2\alpha/3-(1-\alpha)^{2/3}$	D_4	three-dimensional diffusion (G-B function)
$\ln[\alpha/(1-\alpha)]$	A_u	autocatalytic reaction (P-T function)
$1-(1-\alpha)^{1/n}$	R_n	phase boundary reaction n=1, 2, 3 (one-, two,- three-dimensionas, respectively)
$[-\ln(1-\alpha)]^{1/m}$	A_m	random nucleation and subsequent growth, m=1, 2, 3, 4 (Avrami-Erofeev function)

Table 2 Linear regression results of the dissociation of β–CD·$C_6H_5COOC_2H_5$ (210°C)

$g(\alpha)$	k/min^{-1}	r	δ	$g(\alpha)$	k/min^{-1}	r	δ
D_1	$1.0267\cdot10^{-2}$	0.9863	0.8741	R_2	$7.6150\cdot10^{-3}$	0.9811	0.5830
D_2	$7.5739\cdot10^{-3}$	0.9904	0.5799	R_3	$5.7246\cdot10^{-3}$	0.9832	0.4382
D_3	$2.4367\cdot10^{-3}$	0.9941	0.1866	A_1	$2.1857\cdot10^{-2}$	0.9866	1.6738
D_4	$1.9064\cdot10^{-3}$	0.9919	1.4596	A_2	$1.2967\cdot10^{-2}$	0.9785	0.9928
A_u	$4.3248\cdot10^{-2}$	0.9749	3.3112	A_3	$9.1722\cdot10^{-3}$	0.9754	0.7023
R_1	$1.0653\cdot10^{-2}$	0.9747	0.8156	A_4	$7.0830\cdot10^{-3}$	0.9738	0.5423

Table 3 Kinetic parameters of the isothermal dissociation of β–CD·$C_6H_5COOC_2H_5$

$g(\alpha)$	E/kJ mol^{-1}	r	lg$A$	$g(\alpha)$	E/kJ mol^{-1}	r	lg$A$
D_1	102.19	0.9994	9.0660	R_2	100.08	0.9999	8.7032
D_2	109.59	0.9992	9.7353	R_3	101.55	0.9999	8.7384
D_3	114.86	0.9982	9.8153	A_1	104.76	0.9998	9.6693
D_4	111.65	0.9987	9.3601	A_2	97.63	0.9999	8.6675
A_u	94.80	0.9997	8.8823	A_3	95.33	0.9998	8.2667
R_1	95.41	0.9998	8.3408	A_4	94.17	0.9997	8.0286

The related kinetic parameters of the dissociation of β-CD·$C_6H_5COOC_2H_5$ can be obtained from a linear regression of lg$k$ *vs.* $1/T$, based on the isothermal experimental data at 180, 190, 200 and 210°C. The values of E, A and r are listed in Table 3.

Non-isothermal method

Non-isothermal TG curves of the thermal dissociation of β-CD·$C_6H_5COOC_2H_5$ at different heating rates are shown in Fig. 3.

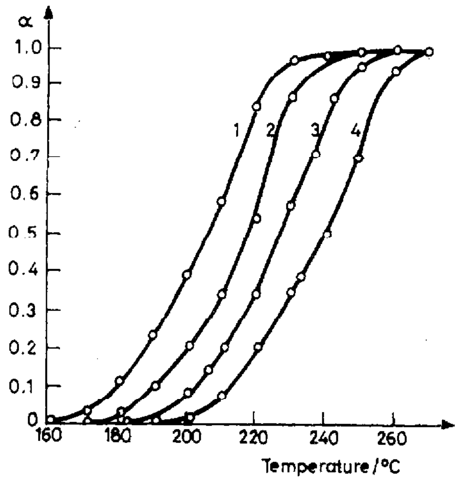

Fig. 3 Non-isothermal TG curves of β-CD·$C_6H_5COOC_2H_5$ heating rate β(°C min^{-1}): 1 – 0.6; 2 – 1.2; 3 – 2.5; 4 – 5

At a constant heating rate

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

$$g(\alpha) = (AE/\beta R)P(x) \tag{6}$$

where $P(x)=e^{-x}/x(1-2!/x+3!/x^2-4!/x^3+...)$, $x=E/RT$, $\beta=dT/dt$. Usually $x=E/R\gg 1$, and taking the first two approximate values

$$g(\alpha) \approx (ART^2/\beta E)(1 - 2RT/E)e^{-E/RT} \tag{7}$$

and

$$\log(g(\alpha)/T^2) = \log[(AR/\beta E)(1 - 2RT/E)] - E/2.303RT \tag{8}$$

From Eq. (8) 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.

Treating the experimental data at different heating rates by this method, the E and A values decreased with increasing heating rate. This is so mainly because the sample temperature could not keep pace with the procedural temperature, and caused the temperature range of mass loss to move to higher region. The record temperature can catch up with the sample temperature only when the heating rate is very low. We extrapolated β to 0 K min^{-1}. Table 4 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 functions.

Table 4 Kinetic parameters of the thermal dissociation of β–CD·$C_6H_5COOC_2H_5$ when extrapolating β to 0 K min^{-1}

$g(\alpha)$	E/kJ mol^{-1}	lg$A$	$g(\alpha)$	E/kJ mol^{-1}	lg$A$
D_1	114.38	13.7400	R_2	62.46	0.3040
D_2	115.66	13.8869	R_3	62.58	–0.0159
D_3	116.19	13.7707	A_1	62.71	1.2152
D_4	115.86	13.5469	A_2	35.86	–6.2892
A_u	–	–	A_3	26.91	–8.7913
R_1	61.69	6.4403	A_4	22.44	–10.0421

For the correction mechanism functions, the kinetic parameters should be identical whether they are obtained by isothermal method or by non-isothermal method. Comparing Table 3 with Table 4, and considering the appropriate E and A values, it is obvious that only D_2, D_3 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 [8]. Table 5 lists the compensation constants a and b for different mechanisms, and also the correlation coefficient of the linear regression.

The kinetic compensation formulas are

$$\log A = aE + b \tag{9}$$

$$E = (\log A - b)/a \tag{10}$$

$$k = Ae^{-(\log A - b)/aRT} \tag{11}$$

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 210°C as an example, Table 6 lists the k values.

Table 5 Kinetic composition constants

$g(\alpha)$	a	b	r	$g(\alpha)$	a	b	r
D_1	0.2639	–12.4846	0.9948	R_2	0.3473	–16.1774	0.9928
D_2	0.2818	–14.4850	0.9957	R_3	0.3560	–16.9569	0.9931
D_3	0.2894	–23.6008	0.9968	A_1	0.3823	–17.0221	0.9940
D_4	0.3273	–22.4798	0.9964	A_2	0.3714	–14.0368	0.9917
A_u	–	–	–	A_3	0.3628	–13.1113	0.9910
R_1	0.3318	–14.8453	0.9915	A_4	0.3553	–12.6841	0.9906

Table 6 k values obtained according to the compensation law (210°C)

$g(\alpha)$	k/min^{-1}	$g(\alpha)$	k/min^{-1}	$g(\alpha)$	k/min^{-1}
D_1	1.7257	R_1	6.1049	A_2	$1.1433 \cdot 10^2$
D_2	2.7721	R_2	9.0717	A_3	$7.8692 \cdot 10$
D_3	$2.1469 \cdot 10^{-3}$	R_3	8.6080	A4	$5.3182 \cdot 10$
D_4	$6.9574 \cdot 10^{-2}$	A_1	$2.2954 \cdot 10^3$		

Comparing Table 2 with Table 6, it is clear that only the two k values from the D_3 mechanism are equal. This confirms that the thermal dissociation process of β-CD·$C_6H_5COOC_2H_5$ follows a D_3 mechanism.

Fluorescence analysis

β-cyclodextrin has very strong fluorescent properties. The spectra of β-CD, β-CD·ethyl benzoate and ethyl benzoate are shown in Fig. 4.

From Fig. 4, by comparing the fluorescence spectra of β-CD and β-CD·ethyl benzoate, it is clear that the relative intensity of peaks at 500 and 630 nm has changed significantly. This shows that the fluorescent properties of β-CD have changed after forming inclusion complex with ethyl benzoate. This is probably because the ethyl benzoate molecule influences the structure of the glucose unit or because new bonds are formed between β-CD and ethyl benzoate, as can be confirmed by the IR spectrum.

Infrared absorption method

The infrared spectra of β-CD and β-CD·ethyl benzoate are shown in Figs 5 and 6, respectively.

Comparing Figs 5 and 6, it is clear that the several stronger absorption peaks of β-CD·ethyl benzoate do not move to lower wavelengths. This suggests that after being complexed by β-CD, no new bonds are formed between ethyl benzoate

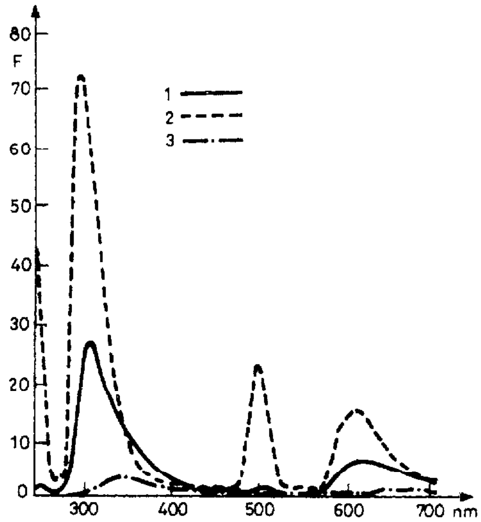

Fig. 4 Fluorescence spectra 1 – β-CD·$C_6H_5COOC_2H_5$·$6H_2O$; 2 – β-CD; 3 – $C_6H_5COOC_2H_5$

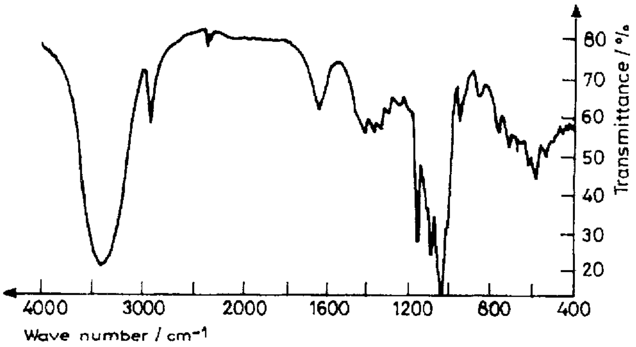

Fig. 5 Infrared spectrum of β-CD

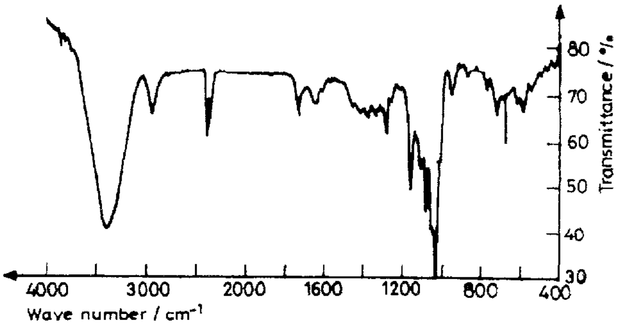

Fig. 6 Infrared spectrum of β-CD·$C_6H_5COOC_2H_5$·$6H_2O$

and β-CD. This is consistent with the fact that the interior of the β-CD cavity is non-polar. So the stable energy of inclusion complexes of β-CD with ethyl benzoate consists mainly of van der Waals interactions.

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

Conclusions

β-CD can form a stable inclusion complex with ethyl benzoate, and the composition is $\beta\text{-CD}\cdot C_6H_5COOC_2H_5\cdot 6H_2O$. The stable energy of inclusion complexes of β-CD with ethyl benzoate consists mainly of van der Waals interactions. The thermal dissociation mechanism of $\beta\text{-CD}\cdot C_6H_5COOC_2H_5$ is dominated by a three-dimensional diffusion process (D_3). The activation energy E is 116.19 kJ mol^{-1}, and the pre-exponential factor A 6.5358×10^9 min^{-1}.

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