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Thermochimica Acta 262 (1995) 165–173

thermochimica
acta

Kinetic studies on the thermal dissociation of β-cyclodextrin–anisaldehyde inclusion complex

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Received 5 January 1995; accepted 14 February 1995

Abstract

The stability of β-cyclodextrin–anisaldehyde (β-CDA) inclusion complex was investigated by TG and DSC. The weight loss of β-CDA·$9H_2O$ takes place in three stages: the dehydration occurs at 50–120°C; the dissociation of β-CDA occurs at 210–260°C; and the decomposition of β-CD begins at 280°C. The kinetics of the dissociation of β-CDA in flowing dry nitrogen was studied by means of thermogravimetry both at constant temperature and with linearly increasing temperature. The results show that the dissociation of β-CDA is dominated by a two-dimensional diffusion process (D_2). The activation energy E is 139.23 kJ mol^{-1}, the pre-exponential factor A is 1.0394×10^{12} min^{-1}.

Keywords: Anisaldehyde; β-cyclodextrin; Inclusion complex; Kinetics

1. Introduction

β-Cyclodextrin 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 with a great variety of guest molecules as a host molecule [1, 2]. β-CD inclusion complexes with many organic compounds have been successfully utilized in the pharmaceutical and food industries. Toxicity experiments show that β-CD can be absorbed as a carbohydrate by animal and human bodies [3]. The stability and kinetic mechanism of the thermal decomposition of inclusion complexes present interesting

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SSDI 0040-6031(95)02304-6

problems in industrial applications. In this paper, the β-CDA inclusion complex was prepared, and the kinetics of the dissociation of this complex was studied by thermogravimetry.

2. Experimental

2.1. Preparation of the sample

β-CD (Suzhou Gourmet Powder Factory) and anisaldehyde (Second Perfumery of Shanghai) were dissolved in water at 70°C in a 1:2 (β-CDA) molar ratio, stirred for 1.5 h at 70°C and then filtered. The white crystals were dried for 5 days at room temperature in a desiccator.

The composition of the crystals was identified by elemental analysis and TG as $\beta\text{-CD}\cdot C_8H_8O_2\cdot 9H_2O$.

2.2. 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 $\text{cm}^3\ \text{min}^{-1}$; sample holder, 5 mm × 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.

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

3. Results and discussion

3.1. The stability of the inclusion complex

Fig. 1 shows the TG and DSC curves of $\beta\text{-CD}\cdot C_8H_8O_2\cdot 9H_2O$. The TG curve shows an 11.61% weight loss at 50–120°C, a 10.34% weight loss at 210–260°C, and a large weight loss at 280°C. The three stages correspond respectively to the dehydration, dissociation of anisaldehyde, and the decomposition of β-CD. The DSC curve has three smaller endothermic peaks at 50–110°C. These indicate that the nine water molecules are distributed in different conditions, and the necessary energy for dehydration of the internal and external water molecules is different. In addition, the oxygen atoms whose electronegativities are larger in anisaldehyde molecules can probably form stronger hydrogen bonds with the adjacent water molecules, so the dehydration process of the external water molecules is also different. The smooth endothermic peak at 210–260°C is consistent with the weight loss at 210–260°C on the TG curve. This corresponds to the escape of anisaldehyde from the β-CD cavity. The low endothermic peak indicates

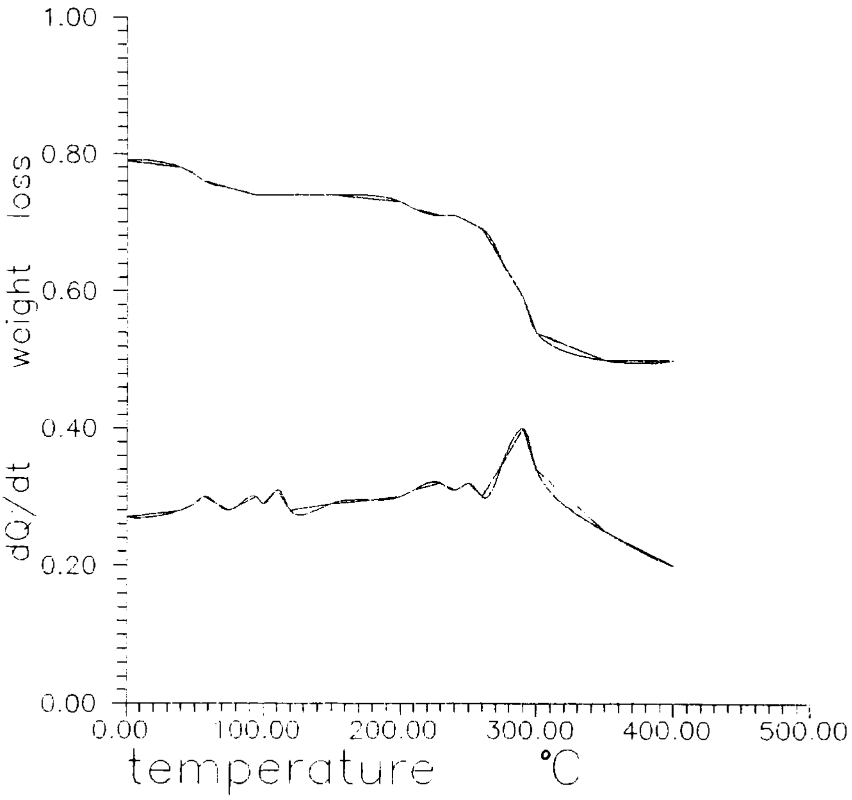

Fig. 1. TG and DSC curves of β-CD·$C_8H_8O_2$·$9H_2O$, β = 5 K min^{-1}.

that the attraction between β-CD and anisaldehyde results from a weak intermolecular force.

3.2. Identification of the kinetic mechanism

According to the thermal analysis results, the dissociation of β-CD·$C_8H_8O_2$·$9H_2O$ takes place in three stages:

1. $\beta\text{-CD}\cdot C_8H_8O_2\cdot 9H_2O \longrightarrow \beta\text{-CD}\cdot C_8H_8O_2(s) + 9H_2O(g)$
2. $\beta\text{-CD}\cdot C_8H_8O_2(s) \longrightarrow \beta\text{-CD}(s) + C_8H_8O_2(g)$
3. The decomposition of β-CD.

Our main purpose was to identify the kinetic mechanism of the second stage. First, the nine crystalline water molecules in the inclusion complex must be removed. To do this, the isothermal method was used as follows: the temperature was raised to 120°C at a heating rate of 5 K min^{-1}, and kept at this temperature for 20 min in order to dehydrate; the measurements were adjusted accordingly and then the temperature was rapidly raised to 210°C at a heating rate of 160 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. The non-isothermal method was used as follows: the temperature was raised to 120°C at a heating rate of 5 K min^{-1} and kept at constant temperature for 20 min; then the heating rate was adjusted, and the non-isothermal TG curves at $\beta = 0.6$, 1.2, 2.5 and 5 K min^{-1} were recorded respectively. The three-step judgement method [7] was used in the identification of the mechanism function, which combined an isothermal method and a linear non-isothermal method with the kinetic compensation effect.

3.3. *Isothermal method*

The TG curves for the isothermal weight loss of β-CD·$C_8H_8O_2$ are shown in Fig. 2. The kinetics of a solid-state decomposition reaction can be represented by the general equation

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

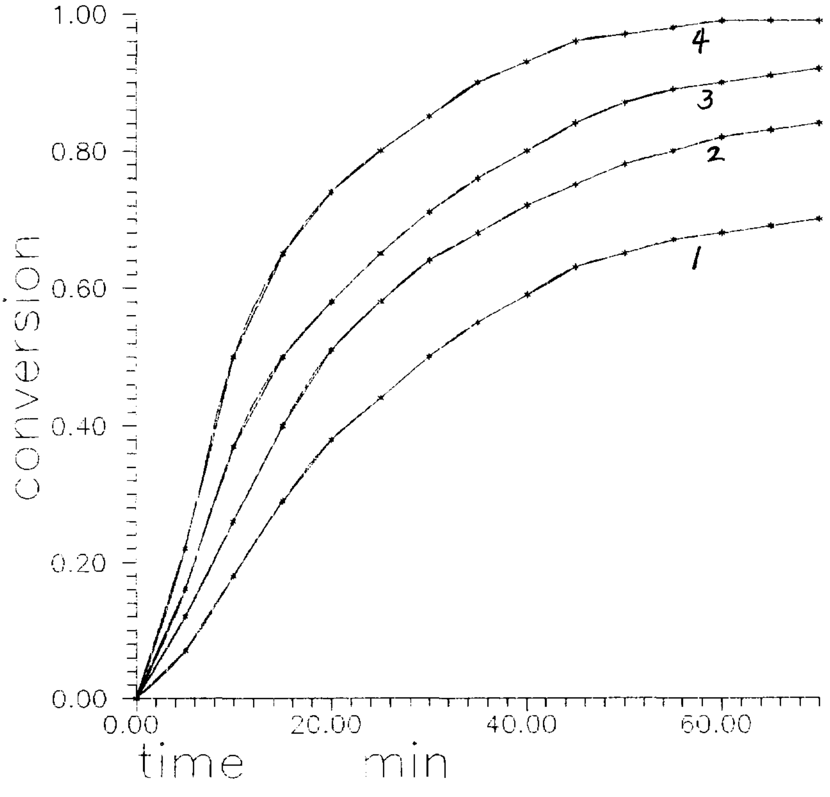

Fig. 2. Isothermal weight loss curves of β-CD·$C_8H_8O_2$: 1, 210°C; 2, 220°C; 3, 230°C; 4, 240°C.

or

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

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

The kinetic mechanism of the weight loss process can be judged by the linear plot of the $g(\alpha)$ against time t. Taking the dissociation of β-CD$\cdot$C$_8$H$_8$O$_2$ at 240°C as an example, Table 2 lists the linear regression results of $g(\alpha)$ versus t.

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

According to the Arrhenius equation

$$k = A\mathrm{e}^{-E/RT} \tag{3}$$

$$\ln k = \ln A - \frac{E}{R}\left(\frac{1}{T}\right) \tag{4}$$

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)
$1-(2/3)\alpha-(1-\alpha)^{2/3}$	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-dimensional)
$1-(1-\alpha)^{1/n}$	A_m	Random nucleation and subsequent growth (Avrami–Erofeyev function)

Table 2
The linear regression results of the dissociation of β-CD$\cdot$C$_8$H$_8$O$_2$ (240°C)

$g(\alpha)$	k/min^{-1}	r	δ	$g(\alpha)$	k/min^{-1}	r	δ
D_1	2.3081×10^{-2}	0.9912	3.6064	R_2	1.6604×10^{-2}	0.9861	2.5944
D_2	1.9686×10^{-2}	0.9993	3.0759	R_3	1.3448×10^{-2}	0.9926	2.1012
D_3	8.5414×10^{-3}	0.9934	1.3346	A_1	6.0949×10^{-2}	0.9981	9.5233
D_4	5.4605×10^{-3}	0.9993	0.8532	A_2	2.9292×10^{-2}	0.9838	4.5769
A_u	9.7376×10^{-2}	0.9750	15.2151	A_3	1.9579×10^{-2}	0.9726	3.0592
R_1	1.9344×10^{-2}	0.9538	3.0225	A_4	1.4750×10^{-2}	0.9656	2.3048

The related kinetic parameters of the dissociation of β-CD·$C_8H_8O_2$ can be obtained from a linear regression of log k versus $1/T$, based on the isothermal experimental data at 210, 220, 230 and 240°C. The related E, A and r values are listed in Table 3.

3.4. Non-isothermal method

The dynamic TG curves of the thermal dissociation of β-CD·$C_8H_8O_2$ at different heating rates are shown in Fig. 3.

At a constant heating rate

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

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

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

where

$$P(x)=\frac{\mathrm{e}^{-x}}{x}\left(1-\frac{2!}{x}+\frac{3!}{x^2}-\frac{4!}{x^3}+\dots\right),\ x=\frac{E}{RT}\quad \beta=\frac{\mathrm{d}T}{\mathrm{d}t}$$

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

$$g(\alpha)=\frac{ART^2}{\beta E}\left(1-\frac{2RT}{E}\right)\mathrm{e}^{-E/RT} \tag{8}$$

Taking logarithms of both sides

$$\log\frac{g(\alpha)}{T^2}=\log\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)-\frac{E}{2.303R}\frac{1}{T} \tag{9}$$

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

Table 3
Kinetic parameters of isothermal dissociation of β-CD·$C_8H_8O_2$

$g(\alpha)$	E_a/(kJ mol^{-1})	r	A	$g(\alpha)$	E_a/(kJ mol^{-1})	r	A
D_1	130.82	0.9920	1.2042×10^{11}	R_2	132.19	0.9754	4.7555×10^{11}
D_2	136.37	0.9914	1.0394×10^{12}	R_3	134.46	0.9815	6.5539×10^{11}
D_3	144.55	0.9975	4.4330×10^{12}	A_1	139.69	0.9903	1.0134×10^{13}
D_4	139.12	0.9941	3.9774×10^{12}	A_2	133.92	0.9724	1.2593×10^{12}
A_u	134.49	0.9852	4.7808×10^{12}	A_3	132.38	0.9621	5.8627×10^{11}
R_1	131.48	0.9439	1.5463×10^{11}	A_4	131.71	0.9557	3.7731×10^{11}

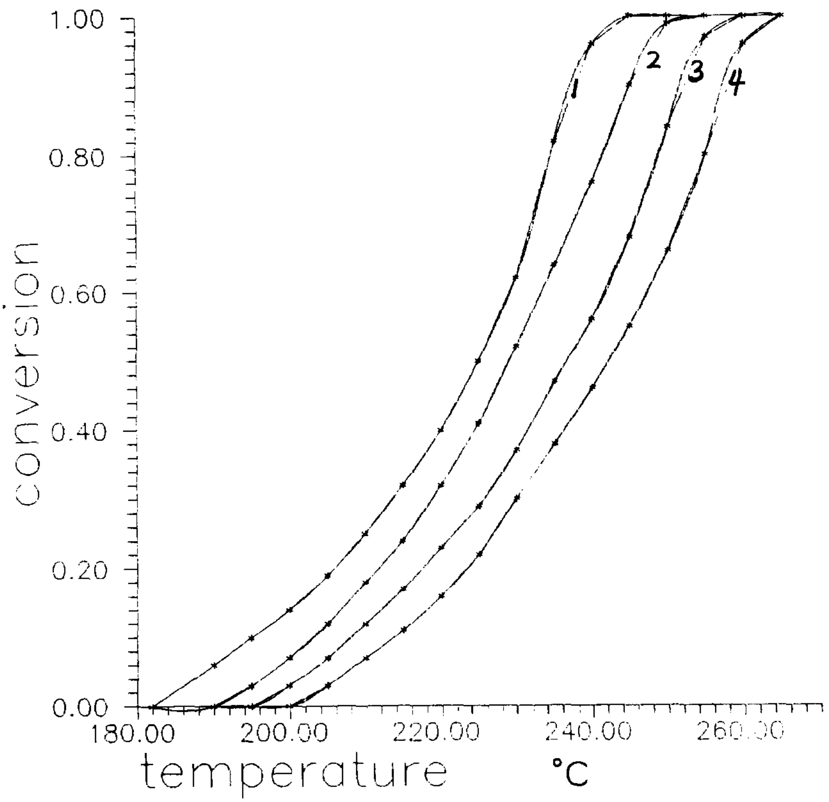

Fig. 3. Non-isothermal TG curves of β-CD · $C_8H_8O_2$ at a heating rate of: 1, 0.6; 2, 1.2; 3, 2.5; 4, 5 K min^{-1}.

Treating the experimental data at different heating rates by this method, it was found that the E and A values decreased with increasing heating rate. This is mainly because the sample temperature could not keep pace with the procedural temperature and the temperature range of weight loss moved to the higher region. Only when the heating rate is very low, can the recording temperature catch up with the sample temperature. Therefore, 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 different mechanism functions.

For the correct mechanism functions, the kinetic parameters obtained by the isothermal method or the non-isothermal method should be identical. Comparing the data in Table 3 with those in Table 4, and considering the proper E and A values, it is obvious that only the diffusion mechanism satisfies the requirements.

3.5. *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

Table 4
Kinetic parameters of the β-CD·$C_8H_8O_2$ thermal dissociation when $\beta \to 0$ K min^{-1}

$g(\alpha)$	$E_a/(kJ\ mol^{-1})$	$\log A$	$g(\alpha)$	$E_a/(kJ\ mol^{-1})$	$\log A$
D_1	122.66	16.5703	R_2	70.96	3.9893
D_2	139.23	20.2297	R_3	76.10	4.7231
D_3	160.18	24.2071	A_1	80.75	7.6489
D_4	138.21	18.4874	A_2	40.37	−2.2211
A_u	–	–	A_3	23.81	−6.5126
R_1	57.34	1.1129	A_4	15.85	−8.5157

Table 5
The kinetic compensation constants

$g(\alpha)$	a	b	r	$g(\alpha)$	a	b	r
D_1	0.2698	−23.7032	0.9997	R_3	0.2661	−15.2784	0.9999
D_2	0.2678	−23.9267	0.9998	A_1	0.2690	−14.7987	0.9943
D_3	0.2657	−25.2573	0.9996	A_2	0.2694	−13.5060	0.9999
D_4	0.2670	−25.5401	0.9999	A_3	0.2693	−12.8518	0.9998
R_1	0.2699	−14.2937	0.9997	A_4	0.2646	−12.7008	0.9997
R_2	0.2666	−14.8746	0.9999				

compensation effect [8]. Table 5 lists the compensation constants a and b for different mechanisms, together with the correlation of the linear regression.

The kinetic compensation formulae are

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

$$E = \frac{\log A - b}{a} \tag{11}$$

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

where a and 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 240°C as an example, Table 6 list the k values.

Table 6
The k values obtained according to the compensation law (240°C)

$g(\alpha)$	k/min^{-1}	$g(\alpha)$	k/min^{-1}	$g(\alpha)$	k/min^{-1}
D_1	8.6012×10^{-3}	R_1	3.6465×10^{1}	A_2	2.5601×10^{2}
D_2	2.1426×10^{-2}	R_2	3.3253×10^{1}	A_3	2.7980×10^{2}
D_3	1.2598×10^{-2}	R_3	2.7160×10^{1}	A_4	1.6634×10^{2}
D_4	1.0815×10^{-2}	A_1	2.9253×10^{2}		

Comparing data in Table 2 with those in Table 6, it is clear that only the two *k* values from the D_2 mechanism are equal. This confirms that the β-CD·$C_8H_8O_2$ thermal dissociation process is dominated by a D_2 mechanism.

4. Conclusions

β-CD can form a stable inclusion complex with anisaldehyde, β-CD·$C_8H_8O_2$·$9H_2O$, and the stability of $C_8H_8O_2$ changes on being complexed by β-CD. The identification of procedural mechanism functions is one of the most difficult subjects in the study of solid thermal decompositions. The results of this study, using the three-step judgement method, show that the thermal dissociation mechanism of β-CD·$C_8H_8O_2$ is dominated by a two-dimensional diffusion process (D_2).

It has been confirmed that the stable energy of inclusion complexes of β-CD with weakly polar guest molecules is mainly Van der Waals energy [9, 10]. The escape of the guest molecules from the β-CD cavity is easy. The dissociation temperature far exceeds the temperature of the evaporation of anisaldehyde, and the desorption is fast. Because of the large volume of the anisaldehyde molecule, diffusion is difficult compared with that of water. Therefore the diffusion step is rate-controlling for the dissociation of β-CD·$C_8H_8O_2$, and the activation energy *E* and pre-exponential factor *A* are 139.23 kJ mol^{-1} and 1.0394×10^{12} min^{-1} respectively.

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