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MECHANISM AND KINETICS OF THERMAL DISSOCIATION OF INCLUSION COMPLEX OF BENZALDEHYDE WITH β-CYCLODEXTRIN

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Abstract

The inclusion complex of benzaldehyde (BA) with β-cyclodextrin (β-CD) was prepared and was studied by thermal analysis and X-ray diffractometry. The composition of the complex was identified by TG and elemental analysis as β-CD·BA·$9H_2O$. TG and DSC studies showed that the thermal dissociation of β-CD·BA·$9H_2O$ took place in three stages: dehydration in the range 70–120°C; dissociation of β-CD·BA in the range 235–270°C; and decomposition of β-CD above 280°C. The kinetics of dissociation of β-CD·BA in flowing dry nitrogen was studied by means of TG both at constant temperature and at linearly increasing temperature. The results showed that the dissociation of β-CD·BA was dominated by a one-dimensional random nucleation and subsequent growth process (A_2). The activation energy E was 124. 8 kJ mol^{-1}, and the pre-exponential factor A 5.04·10^{11} min^{-1}.

Keywords: benzaldehyde, β-cyclodextrin, inclusion complex, kinetics, mechanism, thermal dissociation

Introduction

As a host molecule, β-CD is able to form inclusion complexes with a great variety of guest molecules. After complexation, the guest molecules display additional stability against heat, light and oxygen. Their solubility and bioavailability may also be greatly improved. Accordingly, in recent years, β-CD has aroused great interest and has been successfully and widely utilized in the pharmaceutical and food industries [1–3]. Benzaldehyde (BA) is a widely-used perfume and pharmaceutical intermediate. However, its volatility and sensitivity to light and oxygen pose limits to its practical use. Nevertheless, after the formation of a BA

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inclusion complex with β-CD, the thermal and photochemical stabilities of BA can be improved considerably. The complex of BA with β-CD has therefore been studied by many researchers [4–8], but no detailed reports are to be found as to the mechanism and kinetics of thermal dissociation of the complex. The present paper describes the preparation of the inclusion complex of BA with β-CD and its investigation by thermal analysis, elemental analysis and X-ray diffractometry. The mechanism and the kinetics of the thermal dissociation of the complex were studied by using a three-step assessment method [9,10], which combined an isothermal method and a linear non-isothermal method with the kinetic compensation effect, to provide theoretical data for further applications.

Experimental

Preparation of the sample

A mixture of about 1.5 g β-CD (purchased from Suzhou Gourmet Powder Factory) and 50 ml double-distilled water was stirred vigorously and heated to 40°C, which resulted in a clear solution. At this temperature, BA was added in a 1:2 (β-CD:BA) molar ratio in one portion, which caused the solution to become cloudy. Within a few minutes, crystals began to form. The reaction mixture was stirred at 40°C for 2 h to allow crystallization to proceed. The reaction mixture was then filtered while hot, and the crystals were dried in vacuo. When dry, the crystals were washed thoroughly with diethyl ether and filtered, and the last traces of ether were removed in vacuo. This afforded the inclusion complex of β-CD and BA, which was white and odourless. The crystals of the complex were ground and sieved to less than 190 mesh.

Apparatus and measurements

TG analysis was performed on a WRT-1 microbalance (Shanghai Balancing Instruments Factory). The analytical parameters were: sample mass, about 10 mg; chart speed, 4 mm min^{-1}; atmosphere, dynamic dried nitrogen at 30 cm^3 min^{-1}; sample holder, 5×5 mm aluminium crucible. DSC experiments were carried out on a CDR-1 differential scanning calorimeter (Shanghai Balancing Instruments Factory). The experimental conditions were: sample mass, about 10 mg; heating rate, 5 K min^{-1}; chart speed 10 mm min^{-1}; atmosphere, static air; reference material, Al_2O_3.

Elemental analysis results were obtained with a PE-2400 CHN elemental analyzer (PE Co., U. S. A.).

The powder X-ray diffraction patterns were obtained with a D/MAX-3B X-ray diffractometer (Rigaku, Japan), with CuK_α radiation.

All TG data were analysed on an AT-386 computer, using self-compiled BASIC programs.

Results and discussion

Identification of formation of the complex

Figure 1 shows the TG and DSC curves of β-CD, BA and the complex of BA with β-CD.

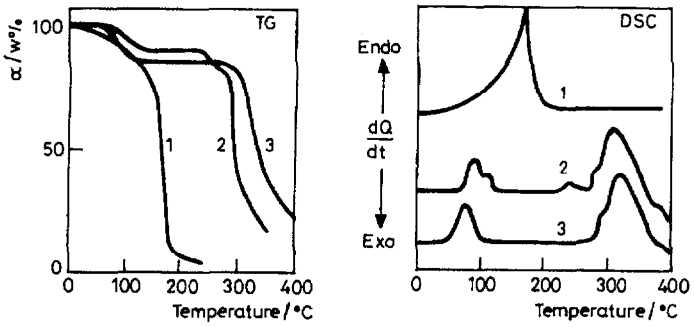

Fig. 1 TG and DSC curves of BA, β-CD and the complex of BA with β-CD (heating rate β=5 K min^{-1}), (1) BA; (2) the complex; (3) β-CD

Owing to its volatility, pure BA undergoes a small mass loss from the beginning of heating. When the temperature reaches the boiling point (about 179°C), a large and rapid mass loss is reflected in the TG curve, corresponding to a sharp and high endothermic peak in the DSC curve. However, after BA is complexed, this endothermic peak and also the large mass loss are not observed in this temperature range. When the TG curve of the complex is compared with that of β-CD, an additional mass loss is found at 230–270°C in the curve of the complex. The DSC curve of the complex also has an additional low endothermic peak in this temperature range. This extra mass loss (or endothermic peak) can only be due to the escape of BA from the β-CD cavity. That is to say, a true inclusion complex of BA with β-CD exists. The thermal stability of BA is greatly improved after complexation.

In order to confirm the complexation of BA with β-CD, the complex and β-CD were examined by powder X-ray diffractometry (XRD). Figure 2 shows the XRD patterns of the complex and β-CD. The diffraction pattern of the complex is clearly different from that of β-CD, suggesting the existence of a true inclusion complex.

Composition of the complex

The TG curve of the complex of BA with β-CD (Fig. 1) reveals an 11.58% mass loss between 70–120°C, corresponding to the release of the constitutional water; a 7.56% mass loss in the range 235–270°C, corresponding to the dissociation of β-CD·BA; and a large mass loss above 280°C, indicating the decomposi-

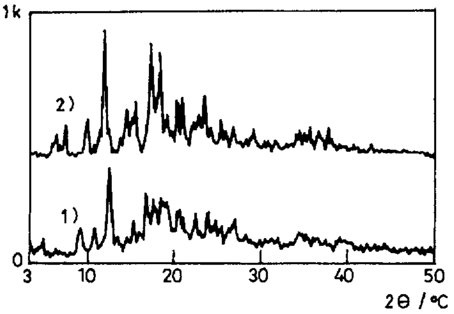

Fig. 2 XRD patterns of β-CD and the complex (1) β-CD; (2) the complex

tion of β-CD. These data indicated that we obtained the complex β-CD·BA·9H_2O, i. e. the complex with molar ratio 1:1 (BA : β-CD), and not 3:2, as reported by Uekama [5]. This difference may be due to the different method of preparation of the complex or the different method of calculation whereby the molar ratio was obtained. The results of elemental analysis coincide quite well with those of theoretical calculations on β-CD·BA·9H_2O (Table 1), which confirms that the composition of the complex is β-CD·BA·9H_2O.

Table 1 Comparison of results of elemental analysis and those of theoretical calculation on β-CD·BA·9H_2O

Element	Elemental analysis	Theoretical calculation
C	41.87%	41.94%
H	6.67%	6.70%
N	0.00%	0.00%

Mechanism and kinetics of thermal dissociation of the complex

The dissociation of β-CD·BA·9H_2O can be expressed by the following three steps:

$\beta\text{-CD}\cdot\text{BA}\cdot 9\text{H}_2\text{O}_{(s)} \rightarrow \beta\text{-CD}\cdot\text{BA}_{(s)} + 9\text{H}_2\text{O}_{(g)}$

$\beta\text{-CD}\cdot\text{BA}_{(s)} \rightarrow \beta\text{-CD}_{(s)} + \text{BA}_{(g)}$

decomposition of β-CD.

Our main aim was to identify the kinetic mechanism of the second step, so the nine crystalline water molecules in the inclusion complex had to be removed first. To do this, the isothermal method was used as follows: the temperature was raised to 125°C at a heating rate of 5 K min^{-1}, and this temperature was maintained for half an hour in order to achieve dehydration; the measurements were adjusted accordingly and the temperature was then rapidly raised to 245.5°C at a heating rate of 80 K min^{-1}, and the isothermal TG curve at 245.5°C was recorded. Using similar methods, the isothermal TG curves at 250, 258.5 and 264°C were also recorded.

The non-isothermal method was used as follows: the temperature was raised to 125°C at a heating rate of 5 K min^{-1} and maintained costant for half an hour; the heating rate was then adjusted, and the non-isothermal TG curves were recorded at $\beta = 0.6$, 1.2, 2.5 and 5 K min^{-1}.

The three-step assessment method was used in the identification of the mechanism function.

Isothermal method

The TG curves for the isothermal mass loss from β-CD·BA are shown in Fig. 3.

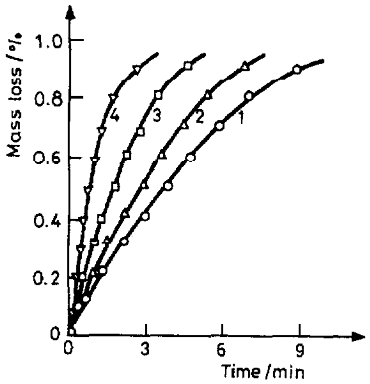

Fig. 3 Isothermal mass loss curves of β-CD·BA. 1. 245.5°C; 2. 250°C; 3. 258.5°C; 4. 264°C

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

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

or

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

where α is the fraction of mass lost at reaction time t, k is the rate constant, and $f(\alpha)$ and $g(\alpha)$ are functions describing the reaction mechanisms.

The kinetic mechanism of the mass loss process can be assessed via the linear plot of $g(\alpha)$ *vs.* time t. Taking the dissociation of β-CD·BA at 245.5°C as an example, Table 2 lists the linear regression results of $g(\alpha)$ *vs.* t.

According to the Arrhenius equation:

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

$$\ln k = \ln A - E/RT \tag{4}$$

The related kinetic parameters of the dissociation of β-CD·BA can be obtained from a linear regression of log*k* *vs.* 1/*T*, based on the isothermal experimental data at 245.5, 250, 258.5 and 264°C. The related values of *E* and *A* are listed in Table 3.

Table 2 Linear regression results of dissociation of β-CD·BA (245.5°C)

$g(\alpha)$	k/min^{-1}	r	$g(\alpha)$	k/min^{-1}	r
D_1	$1.08\cdot10^{-1}$	0.9953	R_2	$7.83\cdot10^{-2}$	0.9996
D_2	$8.17\cdot10^{-2}$	0.9955	R_3	$6.02\cdot10^{-2}$	0.9981
D_3	$2.95\cdot10^{-2}$	0.9963	A_1	$2.42\cdot10^{-1}$	0.9917
D_4	$2.13\cdot10^{-2}$	0.9797	A_2	$1.17\cdot10^{-1}$	0.9993
Au	$6.96\cdot10^{-1}$	0.9983	A_3	$9.60\cdot10^{-2}$	0.9985
R_1	$10.4\cdot10^{-1}$	0.9976	A_4	$7.41\cdot10^{-2}$	0.9970

* *k* is the rate constant, *r* is the correlation coefficient

Table 3 Kinetic parameters of isothermal dissociation of β-CD·BA

$g(\alpha)$	E/kJ mol^{-1}	A/min^{-1}	$g(\alpha)$	E/kJ mol^{-1}	A/min^{-1}
D_1	124.5	$3.78\cdot10^{11}$	R_2	124.6	$2.78\cdot10^{11}$
D_2	125.3	$3.38\cdot10^{11}$	R_3	124.8	$2.26\cdot10^{11}$
D_3	126.4	$1.58\cdot10^{11}$	A_1	125.5	$1.05\cdot10^{12}$
D_4	125.6	$9.60\cdot10^{10}$	A_2	124.8	$5.04\cdot10^{11}$
Au	124.4	$2.01\cdot10^{11}$	A_3	124.6	$3.43\cdot10^{11}$
R_1	124.0	$3.20\cdot10^{11}$	A_4	124.6	$2.61\cdot10^{11}$

Non-isothermal method

The dynamic TG curves of the thermal dissociation of β-CD·BA at different heating rates are shown in Fig. 4.

At constant heating rate:

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

In the Coats and Redfern method [11], the integral form is

$$g(\alpha)=\frac{ART^2}{\beta E}\left[1-\frac{2RT}{E}\right]e^{-E/RT} \tag{6}$$

Taking logarithms of both sides:

$$\log\frac{g(\alpha)}{T^2}=\log\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)-\frac{E}{2.303RT} \tag{7}$$

Usually, $E/RT \gg 1$, so the plot of $\log\frac{g(\alpha)}{T^2}$ *vs.* $1/T$ will give a straight line of slope $-\frac{E}{2.303R}$, and the frequency factor A can be obtained from the intercept.

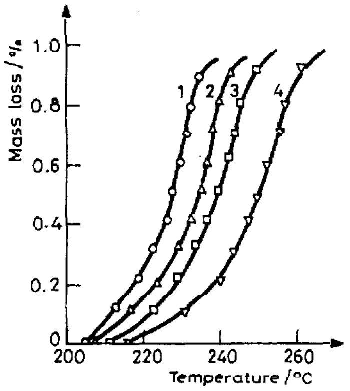

Fig. 4 Non-isothermal TG curves of β-CD·BA at different heating rates (K min^{-1}); 1. 0.6; 2. 1.2; 3. 2.5; 4. 5.0

When the experimental data at different heating rates were treated by this method, it was found that the values of E and A decreased with increasing heating rate. This is due to the thermal lag phenomenon: the temperature of the sample cannot catch up with the programmed temperature. In order to eliminate this temperature deviation, we calculated the E and A values at different heating

Table 4 Kinetic parameters of thermal dissociation of β-CD·BA for $\beta \rightarrow 0$ K min^{-1}

$g(\alpha)$	E/kJ mol^{-1}	log$A$	$g(\alpha)$	E/kJ mol^{-1}	log$A$
D_1	407.3	41.0	R_2	239.1	23.2
D_2	456.1	45.9	R_3	253.8	24.6
D_3	515.9	51.7	A_1	285.6	28.6
D_4	475.8	47.4	A_2	128.7	11.9
Au	–	–	A_3	89.7	7.6
R_1	199.5	19.2	A_4	65.2	4.9

rates, $\beta = 0.6, 1.2, 2.5$ and 5 K min^{-1}, and then extrapolated β to zero. In this way, the values of E and A at $\beta \rightarrow 0$ were obtained (Table 4).

For the correct mechanism functions, the kinetic parameters obtained by the isothermal method or the non-isothermal method should be identical. From a comparison of the data in Tables 3 and 4, and considering the proper values of E and A, it is obvious that only mechanism A_2 satisfies the requirements. Thus, the dissociation of β-CD·BA is dominated by mechanism A_2.

To confirm this conclusion, the kinetic compensation effect was considered.

Kinetic compensation effect

In non-isothermal thermogravimetric experiments, E and A decrease with increasing heating rate. This tendency can be shown by the kinetic compensation effect [12].

The kinetic compensation formulae are

$$\log A = aE + b \tag{8}$$

$$k = Ae^{-E/RT} = Ae^{-(\log A - b)/aRT} \tag{9}$$

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 the data at 245.5°C as an example, Table 5 lists the compensation constants a and b for different mechanisms and the corresponding k values calculated from the compensation law.

Table 5 Kinetic compensation constants for different mechanisms and k values calculated from the compensation law (245.5°C)

$g(\alpha)$	a	b	k	$g(\alpha)$	a	b	k
D_1	0.1096	–3.6657	$3.7432 \cdot 10^{-3}$	R_3	0.1042	–1.8018	$4.3657 \cdot 10^{-2}$
D_2	0.1108	–4.5901	$7.5582 \cdot 10^{-4}$	A_1	0.1060	–1.7082	$9.4715 \cdot 10^{-2}$
D_3	0.1119	–5.9827	$5.3699 \cdot 10^{-5}$	A_2	0.0924	0.1233	$1.1692 \cdot 10^{-1}$
D_4	0.1112	–5.4978	$1.1416 \cdot 10^{-4}$	A_3	0.0794	0.5189	$3.6769 \cdot 10^{-3}$
R_1	0.1005	–0.8222	$1.4051 \cdot 10^{-1}$	A_4	0.0661	0.6355	$9.9505 \cdot 10^{-3}$
R_2	0.1033	–1.4849	$6.9716 \cdot 10^{-2}$				

On comparison of the data in Table 2 with those in Table 5, it is clear that only the two k values from mechanism A_2 are equal. This confirms that the thermal dissociation process of β-CD·BA is dominated by mechanism A_2. The value of E for the process is 124.8 kJ mol^{-1}, and the value of A is $5.04 \cdot 10^{11}$ min^{-1}. The small value of E shows that there are no strong chemical interactions between β-CD and BA. This is consistent with the reports that the stable energy of inclusion complexes of β-CD with weakly polar guest molecules is mainly Van der Waals energy [13, 14].

Conclusions

β-CD can form a stable inclusion complex with BA. The composition of the complex is β-CD·BA·$9H_2O$. The thermal stability of BA is greatly improved after its complexation by β-CD. The mechanism of thermal dissociation of β-CD·BA is dominated by a one-dimensional random nucleation and subsequent growth process (A_2). The activation energy E and the pre-exponential factor A for the process are 124.8 kJ mol^{-1} and $5.04 \cdot 10^{11}$ min^{-1}, respectively.

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