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Mechanism and Kinetics of Thermal Dissociation of Inclusion Complex of β-Cyclodextrin and 1-Methylcyclopropene

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The inclusion-complex of CD-MCP (β-cyclodextrin (β-CD) including 1-methylcyclopropene (1-MCP)) was prepared and characterized. Basing on programmed-heating procedure and weight-temperature analysis, as well as the application of Satava-Sestak's, Ozawa's and Kissinger's methods, the mechanism and kinetics of thermal dissociation of this inclusion complex were studied. An additional mass loss is found at 170−180 °C. The mechanism of thermal dissociation of CD-MCP is dominated by a one-dimensional random nucleation and subsequent growth process ($A_{2/3}$). The activation energy E_S and the pre-exponential factor A_S for the process are 102.14 kJ/mol and 3.63×10^{10} s^{-1}, respectively. This E_S value shows that there is no strong chemical interactions between β-CD and 1-MCP.

Key words: 1-methylcyclopropene, β-cyclodextrin, Inclusion complex, Kinetics, Mechanism, Thermal dissociation

I. INTRODUCTION

Since Sisler and Pian reported that 2,5-norbornadiene counteracted the effectsof ethylene in plant tissues in 1973 [1], it has been found that many compounds can modulate ethylene responses. However, some known inhibitors have certain drawbacks [2]. The compound 1-methylcyclopropene (1-MCP) has been shown to compete with ethylene for the binding site on the ethylene receptor in plant tissue and to control its ethylene responses. Researchers have studied possible applications of 1-MCP to fruits and vegetables such as apples [3–5], lettuce [6], lichee [7], peach [8] and bananas [9–11]. But 1-MCP along is disadvantageous to use in agriculture products because of its resolvability (b.p. 10 °C) [12].

β-cyclodextrin (β-CD) is an ring molecule composed of seven glucose units linked by 1,4-glucosidic bonds. The internal cavity of β-CD mainly contains oxygen atoms and hydrogen atoms of C(3) and C(5). The internal surface of β-CD is hydrophobic. Because the hydroxyl groups of the glucose unit are arranged at both ends of the β-CD cavity, β-CD is able to form inclusion complexes with a great variety of guest molecules [13, 14]. After complexation, the guest molecules display additional stability against heat, light and oxygen [15]. Accordingly, in recent years, there has been great interests on β-CD, and it has been successfully and widely 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. Recently β-CD are studied in variety of fields [16–18]. However, even though its binding ability for 1:1 inclusion complexation with guest molecules was reported in many literatures [19], detailed report has not been found on the mechanism and kinetics of thermal dissociation of the complex. The present paper describes the preparation of the inclusion complex of 1-MCP with β-CD. This CD-MCP inclusion complex was then characterized with thermal analysis and X-ray diffractometry. The mechanism of the thermal decomposition kinetics of this CD-MCP inclusion complex was also investigated by thermogravimetry.

II. EXPERIMENTAL

A. Preparation of the inclusion complex

Under controlled stirring, a certain amount of β-CD (∼10 g; Shenyang Dongling fine chemicals Co.) was first added into 100 mL double-distilled water until the appearance of a cloudy solution, then it was followed by the addition of 1-MCP (prepared in lab). The reaction mixture was stirred at room temperature for several hours. The product mixture was then filtered, and the precipitate was dried in vacuo.

B. Apparatus and measurements

TG analysis was performed with a STA449C model thermo lance with Protous Analysis software (NETZSCH Co., Germany) under the following conditions: sample mass: about 14 mg; atmosphere: pure nitrogen at the flow rate of 25 mL/min; heating rate: ϕ=10, 20 and 30 K/min; temperature range: room temperature to 500 °C; reference material, Al_2O_3.

The powder X-ray diffraction patterns were obtained with a D/MAX-RB X-ray diffract meter (Rigaku, Japan), with Cu K radiation.

All TG data were analyzed on an AT-586 computer, using self-compiled C programs.

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III. RESULTS AND DISCUSSIONS

A. Identification of information of the inclusion complex

Figure 1 shows the thermal analysis curve of the CD-MCP complex. In comparison to the curve of CD, a sharp and high endothermic peak appeared at 91 °C in the curve of the complex. Even though 1-MCP is discommodious to use in agriculture products because of its resolvability (b.p. 10 °C), the thermal stability of 1-MCP is greatly improved after complexation. According to the TG curve of the complex, an additional mass loss is found at 170−180 °C. This may be due to the escape of 1-MCP from the β-CD cavity. That is to say, a true inclusion complex of 1-MCP with β-CD may exist [20–23]. At the same time, the prepared complex also increased the decomposition temperature of β-CD from 294 to 298 °C.

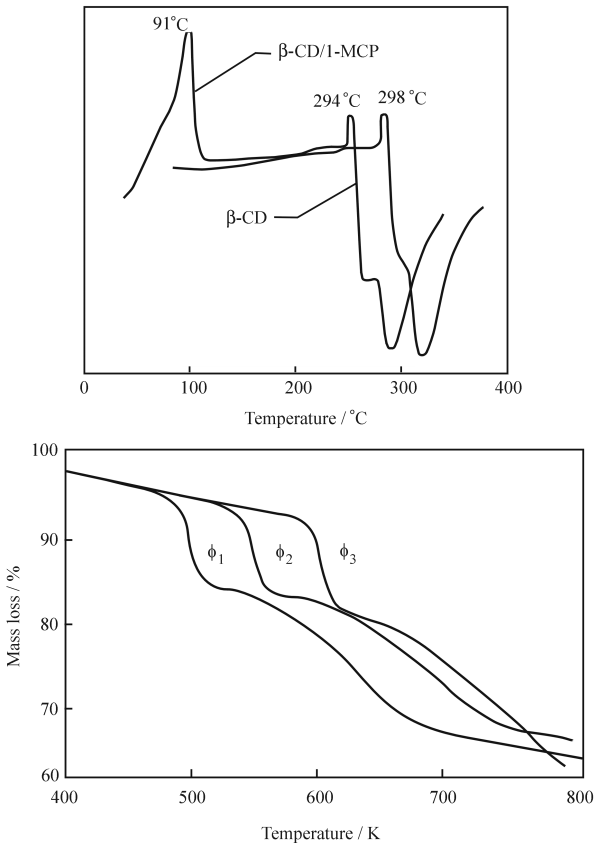

FIG. 1 Thermal analysis curve of the inclusion complex of 1-MCP with β-CD and the curves on vary heating rate (ϕ_1= 10 K/min, ϕ_2= 20 K/min, ϕ_3= 30 K/min)

In order to confirm the form of complexation of 1-MCP with β-CD, the complex and β-CD were examined by powder X-ray diffraction (XRD).

Figure 2 shows the XRD patterns of the complex and β-CD. It was found that β-CD has latent peaks at 2θ=10.62°(93%), 12.38°(100%), 17.66°(62%), 18.84°(51%), 19.40°(63%) and 20.86°(59%), whereas the complex has latent peaks at 2θ=15.98°(29%), 17.16°(42%), 28.56°(29%), 31.82°(26%) and 34.92°(33%). These differences suggest the formation of a true inclusion complex.

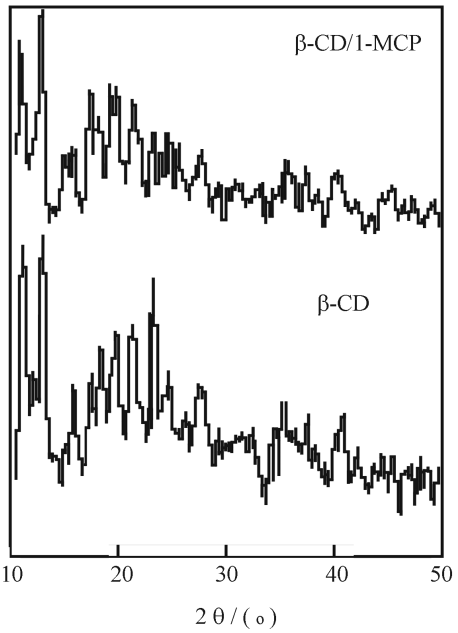

FIG. 2 XRD patterns of the inclusion complex of 1-MCP with β-CD

TABLE I Basic data for thermal decomposition process of complex by TG ($\phi_1 = 10$ K/min)

No.	α	T/K	$1/T\times10^3$
1	0.10	442.12	2.262
2	0.15	447.12	2.237
3	0.20	459.62	2.176
4	0.25	509.62	1.962
5	0.30	537.12	1.862
6	0.35	562.12	1.779
7	0.40	579.62	1.725
8	0.45	604.62	1.654
9	0.50	689.62	1.450

B. Mechanism and kinetics of thermal dissociation of the complex

The dissociation of β-CD·1-MCP complex can be described by the following two major steps:

Step 1: β-CD•1-MCP$_{(s)} \longrightarrow \beta$-CD$_{(s)}$ + 1-MCP$_{(g)}$

Step 2: Decomposition of β-CD$_{(s)}$

In order to identify the kinetic mechanism of the first step, from the TG curve of the prepared complex, the data (α, T) were obtained and as listed in Table I.

To process the data, Ozawa method (Eq.(1)) and Kissinger method (Eq.(2)) were used. The equations are shown below:

$$\log\phi = \log\frac{AE}{R_g(\alpha)} - 2.315 - 0.4567\frac{E}{RT} \quad (1)$$

$$\ln\frac{\phi}{T_m^2} = -\frac{E}{RT_m} + \ln\frac{AR}{E} \quad (2)$$

TABLE II The activate energy E_O in different α by Ozawa method

α	E_O/(kJ/mol)	r
0.10	99.3	0.9964
0.15	80.1	0.9958
0.25	78.4	0.9993
0.30	101.9	0.9978
0.35	135.0	0.9999
0.40	118	0.9975

With the Ozawa method, it is advantageous that with the increase of heating rate, thermo gravimetric measurements shift to higher temperature. For the same relative mass losses, α, the plot of the logarithm of the heating rate, $\log\phi$, as a function of $1/T$, is a straight line. Its slope is proportional to the activation energy. Since the second term on the right side of Eq.(1) is a constant and the first term is small as compared with the last term, the slope of the resulting line should be $-0.4567E/R$.

Similarly, with the Kissinger method, for different heating rates, ϕ, plot of the logarithm of the $(\phi/{T_m}^2)$, $\ln(\phi/{T_m}^2)$, as a function of $1/T$, is a straight line, whose slope and intercept are proportional to the activation energy and pre-exponential factor, respectively. According to equation (2), the slope of the resulting line is described by $-E/R$, the intercept of the resulting line is described by $\ln(AR/E)$.

Satava-Sestak method equation (3) was also used here:

$$\log g(\alpha) = \log\frac{AE}{R\phi} - 2.315 - 0.4567\frac{E}{RT} \qquad (3)$$

In the equations, α is the fraction of decomposition at temperature T; Tm is the corresponding temperature of maximum peak in the thermal analysis curve for different heating rates ϕ; R is the gas constant; E is the activation energy and A is the pre-exponential factor, and $g(\alpha)$ is differential and integral expression of kinetic function. When plotting $\log\phi$ *vs* $1/T$, E_O can be obtained and the results are shown in Table II. Kinetic parameter E_O was 78.4−135.0 kJ/mol as obtained with the Ozawa method.

When plotting $\ln(\phi/{T_m}^2)$ *vs* $1/T_m$, the following linear regression equation can be obtained as $\ln(\phi/{T_m}^2) = -12.234/T_m + 17.316$ with the linear correlation coefficient r=0.9973. Compared with equation (2), Kinetic parameter A_K was 4.05×10^{11} s^{-1} as obtained by Kissinger method.

Thirty types of kinetic model functions [24] were used in Eq.(3). The E_S and A_S and linear correlation coefficients r of different model functions were calculated from a plot of $\log g(\alpha)$ *vs* $1/T$. The results are listed in Table III.

Comparing the kinetic parameters from different models with kinetic parameter E_O obtained by Ozawa method and A_K obtained by Kissinger method, the E_S and corresponding A_S were kept down if they satisfy $|(E_O - E_S)/E_O| \le 0.1$ and $|(\log A_S - \log A_K)/\log A_K| \le 0.2$. Thus, the probable kinetic model function No.10 was selected whose values of correlation coefficient r was bigger than 0.99 with values of E_S and AS satisfy $|(E_O - E_S)/E_O| \le 0.1$ and $|(\log A_S - \log A_K)/\log A_K| \le 0.2$. It is concluded that the kinetic equation of the thermal decomposition of β-CD•1-MCP for the first step is $d\alpha/dT = [(A/\phi)\exp(-E/RT)][3(1-\alpha)[-\ln(1-\alpha)]^{1/3}]/2$, and $g(\alpha) = [-\ln(1-\alpha)]^{2/3}$. It showed that the first step of decomposition for β-CD•1-MCP is controlled by simple (2/3)th order reaction mechanism, whose activity energy, E_S, was 102.14 kJ/mol, and pre-exponential factor, A_S, was 3.63×10^{10} s^{-1}. The value of E_S shows that there is no strong chemical interactions between β-CD and 1-MCP.

TABLE III Results of kinetic analysis for β-CD and 1-MCP

No.	E/(kJ/mol)	log A_S	r
1	28.72	4.63	0.9538
2	30.34	4.53	0.9572
3	30.92	3.94	0.9583
4	32.10	4.09	0.9605
5	80.23	5.72	0.9605
6	78.05	6.32	0.9589
7	26.66	3.42	0.9501
8	24.69	3.17	0.9463
9	169.51	14.76	0.9635
10	102.14	10.56	0.9935
11	84.76	8.69	0.9635
12	56.50	6.74	0.9634
13	67.81	7.51	0.9635
14	42.38	5.80	0.9636
15	33.90	5.26	0.9635
16	50.86	6.36	0.9635
17	156.13	9.99	0.9590
18	113.02	10.69	0.9273
19	121.23	11.38	0.9417
20	86.04	9.60	0.9110
21	160.49	8.81	0.9605
22	162.71	7.85	0.9613
23	143.62	11.35	0.9538
24	215.42	15.81	0.9538
25	71.81	7.02	0.9538
26	47.87	5.65	0.9538
27	35.90	5.00	0.9538
28	55.38	9.90	0.9842
29	199.00	18.62	0.9708
30	27.69	6.50	0.9842

IV. CONCLUSIONS

Thermal analysis and X-ray diffractometry studies showed that β-CD can form a stable inclusion complex with 1-MCP . The thermal stability of 1-MCP is greatly improved after its complexation with β-CD. The mechanism of thermal dissociation of β-CD·1-MCP is dominated by a one-dimensional random nucleation and subsequent growth process ($A_{2/3}$). The activation

energy E_S and the pre-exponential factor AS for the process are 102.14 kJ/mol and 3.63×10^{10} s^{-1}, respectively. The value of E_S shows that there are no strong chemical interactions between β-CD and 1-MCP.

V. ACKNOWLEDGMENT

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