

Pyrolysis characteristics and kinetics of β -cyclodextrin and its two derivatives

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β -cyclodextrin (β -CD) and its derivatives have been widely used to prepare inclusion complexes. However, systematic research on their thermal stabilities, pyrolysis characteristics and kinetics has rarely been reported. In this paper, thermogravimetric analysis was employed to investigate β -cyclodextrin and its two derivatives, 2-Hydroxypropyl- β -cyclodextrin (HP- β -CD) and monochlorotriazinyl- β -cyclodextrin (MCT- β -CD). The pyrolysis characteristics and kinetic parameters were obtained. The results show that three stages can be distinguished during the heating process of the above three samples. The temperature of initial decomposition of HP- β -CD (309.5°C) is higher than that of β -CD (297.8°C), while the temperature of initial decomposition of MCT- β -CD (231.4°C) is lower than that of β -CD. For the three cyclodextrins, the thermal stability in descending order is HP- β -CD, β -CD and MCT-HP- β -CD. The activation energy values are 350.6, 303.3 and 113.9 KJ/mol, and the pre-exponential factor values are 1.11×10^{31} , 1.37×10^{26} and 1.39×10^{10} for β -CD, HP- β -CD and MCT- β -CD respectively.

Keywords: Pyrolysis characteristics, Kinetics, β -cyclodextrin, Hydroxypropyl- β -cyclodextrin, Monochlorotriazinyl- β -cyclodextrin.

INTRODUCTION

Cyclodextrins (CDs) are cyclic carbohydrates derived from starch. CDs, sometimes called cycloamyloses, are a family of compounds made up of sugar molecules bound together in a ring (cyclic oligosaccharides). The parent CDs contain six, seven and eight glucopyranose units and are referred as alpha (α), beta (β) and gamma (γ)-CDs, respectively¹. In CDs, the secondary hydroxyl groups are located on the wider edge of the ring and the primary hydroxyl groups on the other edge, and that the apolar hydrogens and ether-like oxygens are at the inside of the torus-like molecules. This result in a molecule with a hydrophilic outside, which can dissolve in water and an apolar cavity which provides a hydrophobic matrix, described as a micro heterogeneous environment². Thus, CDs and their derivatives are suitable for a wide variety of possible uses e.g. for stabilization, masking or controlled release of hydrophobic substances³⁻⁵. Among the numerous CDs and their derivatives, β -CD (sometimes called β -Schardinger dextrin or cycloheptaamylose) and its derivatives are the favorite materials. In this paper, β -CD, HP- β -CD and MCT- β -CD were investigated. The structures of the three β -CDs are shown in Figure 1.

β -CD has been widely used to prepare inclusion complexes⁶⁻⁹. HP- β -CD, is a hydroxyalkylated cyclodextrin and is widely used to increase the solubility, stability, and bioavailability of drugs, because it is more water soluble and less toxic than β -CD^{10, 11}. Unlike β -CD, MCT- β -CD can form a direct covalent bond with textile materials.

MCT- β -CD possesses monochlorotriazinyl groups as reactive anchor and can form stable covalent bonds with nucleophilic groups. MCT- β -CD is the first reactive cyclodextrin derivative manufactured on an industrial scale. The optimized degree of substitution of DS = 0.4 per anhydroglucose ensures a good complexation capacity even when this derivative is fixed on the surface like textiles. MCT- β -CD can be used as building block for new CD derivatives, as a crosslinking agent or as excellent materials for surface modification¹².

Thermogravimetric analysis (TGA) is a method of thermal analysis, which can provide information about physical and chemical phenomena including vaporization, sublimation, adsorption, desorption, chemisorptions, desolvation, and decomposition. TGA is commonly used to determine selected characteristics of materials that exhibit either mass loss or gain due to decomposition, oxidation, or loss of volatiles¹³. Although the applications of β -CD and its derivatives have been extensively described in literatures, their thermal stabilities, pyrolysis characteristics and kinetics have rarely been reported. These basic data are very important for understanding the stability and further application of CDs. In this paper, TGA was employed to investigate β -CD, HP- β -CD and MCT- β -CD. The pyrolysis characteristics and kinetic parameters were obtained.

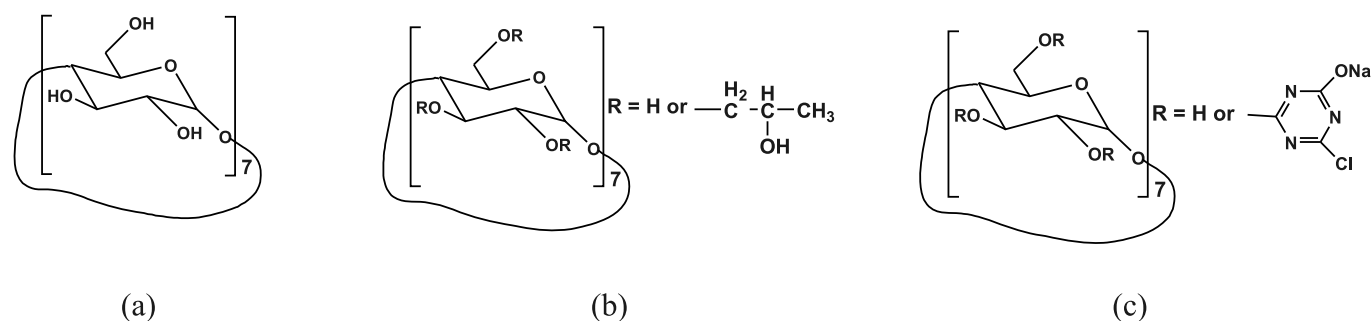


Figure 1. The structures of β -CD (a), HP- β -CD (b) and MCT- β -CD (c)

MATERIAL AND METHODS

Material

β -CD (white crystalline powder, content $\geq 98\%$, loss on drying $\leq 14\%$) was purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). HP- β -CD (white powder, content $\geq 98\%$, loss on drying $\leq 14\%$, degree of substitution 3.5–5.0) was purchased from Shandong Binzhou Zhiyuan Bio-Technology Co., Ltd. MCT- β -CD (with content 75% and average molecular weight 1560, loss on drying $\leq 12\%$, degree of substitution 3.0–5.0) was purchased from Yongtai Biotech Co., Ltd (Xi'an, China). All reagents were used without further purification.

Thermogravimetric analysis

The experiments were carried out in a TGA-Q5000IR thermogravimetric analyzer (TA Instruments, USA). In the experiment, approximately 5 mg of dried sample was spread uniformly on the bottom of the ceramic crucible of the thermal analyzer. The pyrolysis experiment was performed in a dynamic high purity nitrogen flow of 20 ml/min. The temperature of the furnace was programmed to rise from room temperature to 500°C.

RESULTS AND DISCUSSIONS

Pyrolysis characteristic comparison of β -CD, HP- β -CD and MCT- β -CD

TGA is an effective method to study changes in physical and chemical properties of material¹³. Figure 2 shows the weight loss and the rate of weight loss curve obtained during the pyrolysis of β -CD, HP- β -CD and MCT- β -CD samples under inert nitrogen atmosphere.

The thermogravimetry (TG) and derivative thermogravimetry (DTG) curves of β -CD, HP- β -CD and MCT- β -CD use solid lines, dash lines and dotted lines respectively. As shown in Figure 2, during thermal degradation of β -CDs, three stages can be distinguished during the heating process of the samples. The first stages go from room temperature to 297.8, 309.5 and 231.4°C for β -CD, HP- β -CD and MCT- β -CD respectively; slight weight losses in the TG curves are observed. This could be mainly due to the loss of water. The mass losses of the first stages are 8.5, 12.3 and 5.9% of total weight of β -CD, HP- β -CD and MCT- β -CD respectively. The slight weight loss was mainly attributed to desorption of moisture as bound water on the surface and the cavities of β -CDs¹³. The second stages go from 297.8 to 399.9°C, from 309.5 to 420°C and from 231.4 to 449.9°C for β -CD, HP- β -CD and MCT- β -CD respectively. The second stages were characterized by major weight losses, which corresponded to the main pyrolysis process. Most of β -CDs were decomposed in the second stages. The

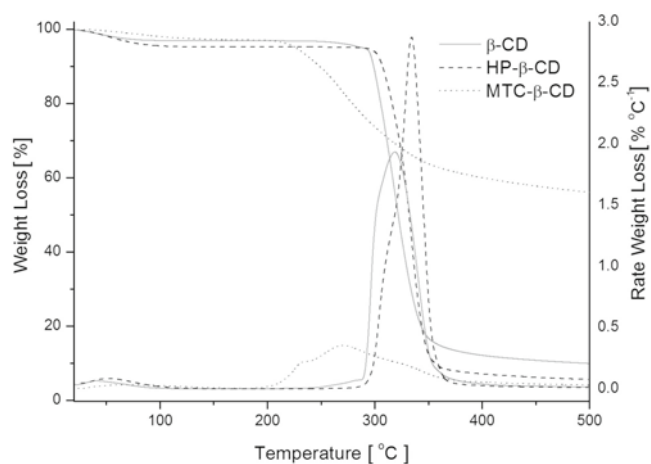


Figure 2. TG-DTG curves of β -CD, HP- β -CD and MCT- β -CD

third stages go from 399.9, 420 and 449.9°C for β -CD, HP- β -CD and MCT- β -CD respectively to the final temperature (500°C) of the experiment. The solid residuals of β -CDs continuously decomposed at a very slow rate in the third stages. Compared with residuals of β -CD and HP- β -CD, the residual of MCT- β -CD is relatively high. The content of MCT- β -CD is 75%. There are about 25% NaCl in the MCT- β -CD sample. Therefore, the content of the solid residuals is high as shown in Figure 2.

The analysis of the rate of weight loss curves shows that only one strong peak for each of β -CDs was observed during the main pyrolysis process. The three strong peaks were due to the degradation of β -CD, HP- β -CD and MCT- β -CD respectively. The degradation characteristics of the three β -CDs were given in Table 1.

From Table 1, it can be seen that HP- β -CD excels β -CD in thermal stability, and the decomposition temperature of HP- β -CD is enhanced. However, MCT- β -CD is unstable compared with β -CD and the decomposition temperature of MCT- β -CD decreased. Introducing the hydroxypropyl group and monochlorotriazinyl group resulted in stability change of β -CD. The temperature of initial decomposition of HP- β -CD is higher than that of β -CD, while the temperature of initial decomposition of MCT- β -CD is lower than that of β -CD. The monochlorotriazinyl group is reactive. This may cause the thermal stability decrease of MCT- β -CD.

Pyrolysis kinetic parameters of β -CD, HP- β -CD and MCT- β -CD

Kinetic analysis of thermal decomposition processes has been the subject interest along the modern history of thermal decomposition. On the one hand, kinetic data are essential for designing any kind of device; on the other hand, kinetics is intrinsically related with the decomposition mechanisms. TGA is a simple method and has been widely used for studies of degradation kinetics^{14–16}. The apparent activation energy of decompo-

Table 1. Characteristic devolatilization temperatures and total volatile matter content for β -CD, HP- β -CD and MCT- β -CD

Samples	T_s [°C] ^a	T_{max} [°C] ^b	$[dw/dT]_{max}$ [% °C ⁻¹]	VM [%] ^c
β -CD	297.8	319	1.935	79.4
HP- β -CD	309.5	334	2.873	81.2
MCT- β -CD	231.4	270	0.3538	36.3

^a T_s is the temperature of initial decomposition.

^b T_{max} was determined from the respective DTG curve peaks.

^c VM is the total volatile matter evolved in the second stage.

sition reaction can be obtained by TGA. DTG measures the overall weight loss rate. Therefore, it provides general information on the overall kinetics^{15, 16}. It is clear that the selection of correct model is a critical point in kinetic analysis. There are different methods to study the kinetics of non-isothermal processes. Coats-Redfern method gives more reliable results. It has become one of the most widely used methods in non-isothermal kinetic analysis^{17, 18}. Therefore, Coats-Redfern method was selected for pyrolysis kinetic analysis in this paper. Coats-Redfern method is an integral method, and it involves the thermal degradation mechanism¹⁹. According to Coats-Redfern method, the relationship among pre-exponential factor, activation energy, temperature, and the fraction of substrate decomposed can be expressed by two equations as follows:

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \quad (\text{for } n \neq 1) \quad (1)$$

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \quad (\text{for } n=1) \quad (2)$$

where E is the activation energy, R is the gas constant, T is the absolute temperature, n is reaction order, A is the pre-exponential factor, β is the heating rate and α is the converted rate of reaction.

Thus a plot of either in $\ln[(1-(1-\alpha)^{1-n})/(T^2(1-n))]$ against $1/T$ or, where $n = 1$, $\ln[-\ln(1-\alpha)/T^2]$ against $1/T$ should result in a straight line of slope $-E/R$ for correct value of n .

In the experiments, different n were adopted for β -CD, HP- β -CD and MCT- β -CD to fit straight lines. All the values of linear correlation coefficients (R^2) calculated from Eq(1) and Eq(2) by fitting the experiment data are shown in Table 2.

The closer are the values of linear correlation coefficients to 1, the better the linear relationship between $\ln[(1-(1-\alpha)^{1-n})/(T^2(1-n))]$ or $\ln[-\ln(1-\alpha)/T^2]$ and $1/T$ should be. When the values of n are 2.5, 1.5 and 3 for β -CD, HP- β -CD and MCT- β -CD respectively, the values of linear correlation coefficients are relatively closer to 1. Therefore, the pyrolysis reaction orders adopted as 2.5, 1.5 and 3 for β -CD, HP- β -CD and MCT- β -CD respectively.

The plots of $\ln[(1-(1-\alpha)^{1-n})/(T^2(1-n))]$ against $1/T$ are shown in Figure 3.

As shown in Figure 3, when the values of reaction order are 2.5, 1.5 and 3 for β -CD, HP- β -CD and MCT- β -CD respectively, there are good linear relationships between $\ln[(1-(1-\alpha)^{1-n})/(T^2(1-n))]$ and $1/T$. All the plots has a high linear correlation coefficients (R^2) greater than 0.99.

From the slope of the line, apparent activation energy can be estimated. If $2RT/E \ll 1$, the pre-exponential factor can be calculated from the intercept of the line. The values of activation energy and pre-exponential factor obtained from the slope and intercept of the lines by Coats-Redfern method are given in Table 3.

As shown in Table 3, the activation energy and pre-exponential factor values of MCT- β -CD are the lowest compared with those of β -CD and HP- β -CD. The low activation energy may result in the instability of MCT- β -CD, the temperature of initial decomposition of which is 231.4°C. The activation energy of HP- β -CD is close to that of β -CD. The difference of them is relatively little. The activation energy and pre-exponential factor of β -CD are relatively higher than those of HP- β -CD respectively.

It is known that the chemical mechanisms which are sufficiently similar have calculated values of E and pre-exponential factor (A) almost the same or very close to each other. In Table 3, the activation energy (E) of the third sample (MCT- β -CD) calculated with Coats-Redfern method is quite far from the E values of β -CD and HP- β -CD. This may be caused by introducing the monochlorotriazinyl group to β -CD. Unlike hydroxypropyl group, monochlorotriazinyl group is reactive and relatively unstable. During the pyrolysis process of MCT- β -CD, the monochlorotriazinyl group decomposed firstly, and then the skeleton of β -CD decomposed. This was different from β -CD and HP- β -CD. The different pyrolysis mechanisms cause E of MCT- β -CD far from the values of β -CD and HP- β -CD.

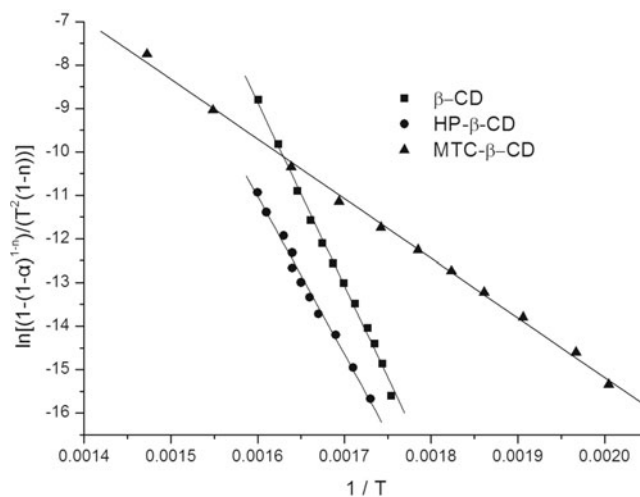


Figure 3. The plots of $\ln[(1-(1-\alpha)^{1-n})/(T^2(1-n))]$ against $1/T$ (β -CD, $n = 2.5$; HP- β -CD, $n = 1.5$; MCT- β -CD, $n = 3$)

Table 2. The values of linear correlation coefficients (R^2) calculated according to Coats-Redfern method at various reaction orders by fitting the experiment data

	$n = 0.5$	$n = 1$	$n = 1.5$	$n = 2$	$n = 2.5$	$n = 3$
β -CD	0.8906	0.9404	0.9748	0.9918	0.9959	0.9930
HP- β -CD	0.9640	0.9893	0.9974	0.9900	0.9736	0.9548
MCT- β -CD	0.8157	0.8967	0.9540	0.9849	0.9965	0.9976

Table 3. Pyrolysis kinetic results of β -CD, HP- β -CD and MCT- β -CD with Coats-Redfern method

Samples	n	T [°C]	α [%]	E [KJ/mol]	A
β -CD	2.5	300.4–351.5	10–95	350.6	1.11×10^{31}
HP- β -CD	1.5	311.1–352.6	10–95	303.3	1.37×10^{26}
MCT- β -CD	3	235.2–406.1	10–95	113.9	1.39×10^{10}

CONCLUSIONS

This paper concentrated on the pyrolysis characteristics and kinetics of β -CD, HP- β -CD and MCT- β -CD. The pyrolysis characteristics and kinetic parameters were obtained. The temperatures of initial decomposition of β -CD, HP- β -CD and MCT- β -CD are 287.8, 309.5 and 231.4°C respectively. The pyrolysis activation energy values are 350.6, 303.3 and 113.9 KJ/mol, and the pre-exponential factor values are 1.11×10^{31} , 1.37×10^{26} and 1.39×10^{10} for β -CD, HP- β -CD and MCT- β -CD respectively. Introducing the hydroxypropyl group and monochlorotriazinyl group resulted in stability change of β -CD. HP- β -CD excels β -CD in thermal stability. MCT- β -CD possesses monochlorotriazinyl groups as reactive anchor and is relatively instable compared with HP- β -CD and β -CD. For the three β -CDs, the thermal stability in descending order is HP- β -CD, β -CD and MCT-HP- β -CD. These results are crucial to research on further application of cyclodextrins.

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