Available online at www.sciencedirect.com

ScienceDirect

Thermochimica Acta 469 (2008) 36–42

thermochimica acta

www.elsevier.com/locate/tca

Study on thermal decomposition behavior of survived β-cyclodextrin in its inclusion complex of clove oil by nonisothermal thermogravimetry and gas chromatography coupled to time-of-flight mass spectrometry analyses

Peng Xu, Le Xin Song [*], Hai Ming Wang

Department of Chemistry, University of Science and Technology of China, Hefei 230026, China

Received 9 September 2007; received in revised form 16 December 2007; accepted 26 December 2007
Available online 15 January 2008

Abstract

The thermal decomposition behavior of survived β-cyclodextrin in its inclusion complex of clove oil is investigated by nonisothermal thermogravimetry (TG) analysis at the heating rates of 5.0, 10.0, 15.0, 20.0 and 25.0 K min^{-1}. The TG profiles based on mass loss as a function of temperature show a clear trend of increased thermal decomposition temperature with increased heating rate. Gas chromatography coupled to time-of-flight mass spectrometry (GC-TOF-MS) with a programmed temperature heating treatment is performed to experimentally investigate the relationship between procedural decomposition temperature and fragment composition of the sample. The results on the basis of fragment analysis explain the different mass loss of the sample corresponding to different temperatures on the gradient hot stage.

© 2008 Elsevier B.V. All rights reserved.

Keywords: Cyclodextrin; Clove oil; Supermolecule; Inclusion complex; GC-TOF-MS

1. Introduction

β-Cyclodextrin (β-CD, Fig. 1) is a cyclic oligomer of seven α-D-glucose units jointed by 1,4-glycosidic bonds. It has the shape of a hollow truncate cone [1,2]. The hydrophilic outer surface and relatively hydrophobic inner cavity make it possible to form supramolecular inclusion complexes with many organic compounds [3–6].

Clove oil (Clo) is a clear yellow liquid with a characteristic aromatic odor and has been extensively used as flavoring agent by the food industry. It is a seminatural mixture mainly comprising 4-allyl-2-methoxyphenol (AMP, >85%, Fig. 1).

The characterizations of the solid inclusion complexes of β-CD with organic guests have been extensively investigated by using X-ray powder diffraction, infrared spectra, nuclear magnetic resonance spectroscopy, mass spectra, thermal analysis, and so on [7–9]. Although many efforts have been concentrated on the thermal decomposition behaviors of β-CD and its inclusion complexes [10], most of them investigated the percentage mass loss of solid samples in the range from 30 to 70% by thermal degradation, and designated the loss process as the thermal decomposition process of host–guest inclusion complexes [11,12]. As a matter of fact, in many studies the molecular mass of the selected organic guest is usually below 400, the percent of total mass for the guest in its inclusion complex of β-CD would be less than 30%. Additionally, the boiling points of the organic guests are often lower than the melting/decomposition temperature of free β-CD. Therefore, after the mass loss of the inclusion complex exceeds 30%, only β-CD can remain in the residue in a specified state. Clearly, the residue should no longer be regarded as an inclusion complex of β-CD because there is no guest molecule in it. Furthermore, the residue, even though consisting of only β-CD, could be different from free β-CD between their respective three-dimensional molecular stacks. The residue is named as survived β-CD. According to this view, many reported results about thermal decomposition behaviors of so-called inclusion complexes should be those of survived β-CD molecules [13–15]. It is also worth noting that the thermal decomposition behaviors of the survived β-CD molecules depend to some extent upon the nature of guests [14,15].

---

[*] Corresponding author.
E-mail address: solexin@ustc.edu.cn (L.X. Song).

0040-6031/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2007.12.009

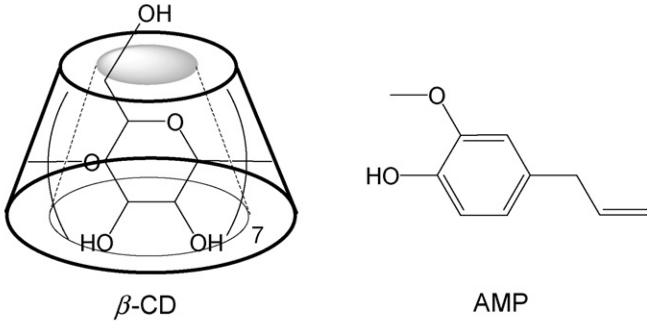

Fig. 1. Structural features of β-CD and AMP.

This study aims to distinguish the different thermal decomposition behaviors of free β-CD, survived β-CD and the inclusion complex of β-CD with Clo, Clo–β-CD. It should be noted that mass spectrometry (MS) is usually employed to characterize the formation of inclusion complexes, but here we take advantage of gas chromatography coupled to time-of-flight mass spectrometry (GC-TOF-MS) with a programmed temperature to investigate the thermal decomposition behavior of Clo–β-CD, with the objective of trying to find details regarding the decomposition process of the sample.

2. Experimental

2.1. Materials

β-CD is purchased from Shanghai Chemical Reagent Company and recrystallized twice from deionized distilled water. Clo, a seminatural and semisynthetic product, is purchased from Shanghai Feixiang Chemical Company and used without further purification. All chemicals are of general purpose reagent grade unless otherwise stated.

2.2. Preparation of Clo–β-CD

Clo–β-CD is prepared by mixing Clo with β-CD and stirring for 48 h at 298.2 K. The initial molar ratio of Clo to β-CD is 10:1 in deionized water. The separated crude product is washed using small amounts of deionized water (3 mL × 5 mL) and alcohol (95%, 3 mL × 3 mL) to remove the unreacted Clo. The obtained sample is dried for 24 h at 383.2 K *in vacuo*, and then stored in a vacuum desiccator over silica gel.

The studies on UV–visible spectroscopy and high performance liquid chromatography of the prepared sample in aqueous solution, and on nuclear magnetic resonance, powder X-ray diffraction and infrared spectroscopy of the sample in solid state are described in a paper entitled "Inclusion phenomena of clove oil with α-, β-, γ- and heptakis(2,6-di-*O*-methyl)-β-cyclodextrin" which has been submitted to Natural Product Research.

2.3. Instrument and method

Thermogravimetric (TG) curves are recorded on Shimadzu TGA-50 thermogravimetric analyzer at the heating rates of 5.0 (ζ_1), 10.0 (ζ_2), 15.0 (ζ_3), 20.0 (ζ_4), 25.0 (ζ_5) K min^{-1} under a nitrogen gas flow of 25 mL min^{-1}.

The sample is analyzed by GC-TOF-MS (Micromass GCT-MS). It is introduced by a direct insertion probe and heated with an increasing temperature. Firstly, it is kept 3 min at 303.2 K. When the temperature is increased to 553.2 K at a 100.0 K min^{-1} rate, it is allowed to stabilize for 5 min at 553.2 K. Subsequently, continue to raise the temperature until 653.2 K at a 5.0 K min^{-1} rate and stabilize it for 5 min at 653.2 K. Finally, the temperature is enhanced to 723.2 K at a rate of 100.0 K min^{-1}. Two types of diagrams are analyzed: total ionic current (TIC, expressed in intensity according to the time) and mass spectrum at accurate time during temperature increase. Computer analysis allows extraction of specific fragments abundance.

3. Results and discussion

3.1. TG profiles of β-CD at a 5.0 K min^{-1} rate and Clo–β-CD at five different heating rates

The thermal decomposition of β-CD or Clo–β-CD is a heterogeneous reaction process, in which TG analysis is an important method to examine the changes in the solid samples when heated. The typical TG curves of β-CD at a 5.0 K min^{-1} rate (ζ_1) and

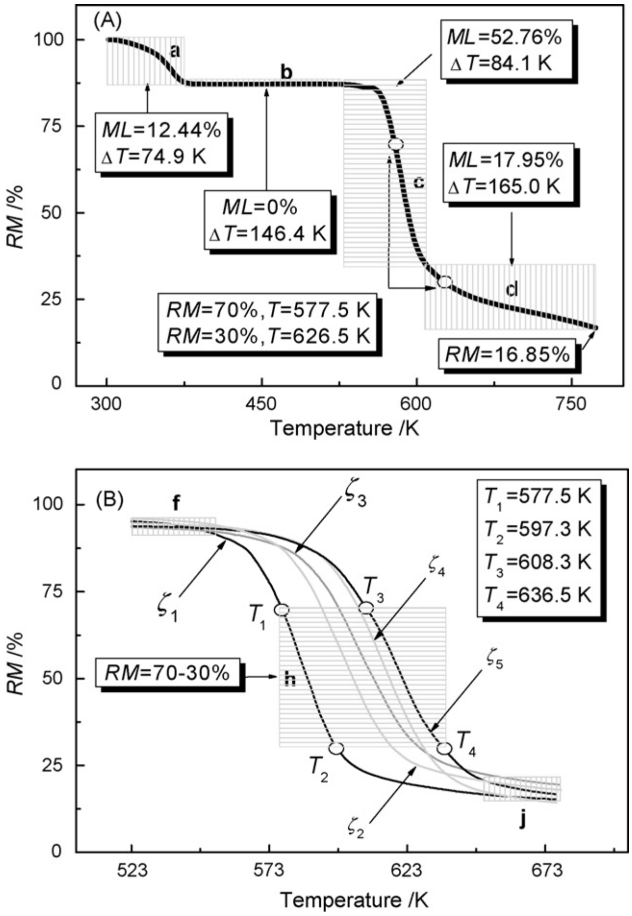

Fig. 2. TG profiles of (A) β-CD at a 5.0 K min^{-1} rate (ζ_1) and (B) Clo–β-CD at different heating rates (ζ_1–ζ_5).

Table 1
The RM values (%) of β-CD and Clo–β-CD at different temperatures

Compound	T (K)	RM (%)				
		ζ_1	ζ_2	ζ_3	ζ_4	ζ_5
β-CD	393.2	87.56	89.43	92.02	90.35	91.63
	636.5	18.14	22.58	25.76	23.22	30.05
Clo–β-CD	393.2	97.16	97.52	95.92	97.21	96.51
Survived β-CD	597.3	30.32	61.44	71.81	80.74	82.18
	636.5	18.13	22.87	23.16	25.60	29.92

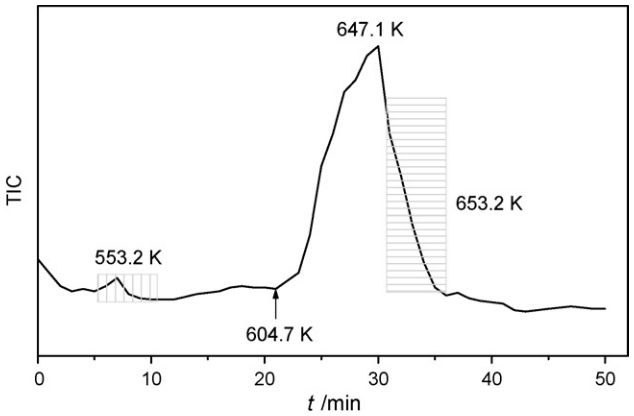

Fig. 3. A sketch depicting measured TIC throughout the heating time.

Clo–β-CD at five different heating rates (ζ_1–ζ_5) are depicted in Fig. 2A and B, respectively.

As shown in Fig. 2A, the mass loss (ML, %) of free β-CD at the heating rate of $5.0\,\mathrm{K\,min^{-1}}$ can be divided into four consecutive processes (a–d). The sample in Process a is in the temperature range from 302.8 to 377.7 K with a ML of 12.44%, which is due to the release of water molecules from the outside or/and inside of β-CD cavity. Subsequently, the sample in Process b is kept in a very wide temperature range from 377.7 to 524.1 K ($\Delta T = 146.4$ K). Then the sample in Process c undergoes a rapid melting/decomposition (ML = 52.76%, $\Delta T = 84.1$ K). During continuous heating, the sample in Process d is carbonized and incinerated (ML = 17.95%, $\Delta T = 165.0$ K). Finally, the residue mass (RM) of the remains at 773.2 K is 16.85%. It should be noted that the temperatures corresponding to the RM values of 70 and 30% are 577.5 and 626.5 K, respectively. The temperature difference (ΔT) between them is 49.0 K at ζ_1.

The TG data of Clo–β-CD at five different heating rates are shown in Table 1. The RM values of the samples at 393.2 K are 97.16%, 97.52%, 95.92%, 97.21% and 96.51% from ζ_1 to ζ_5, respectively. However, at the same temperature, the RM value of free β-CD is 87.56%, 89.43%, 92.02%, 90.35% and 91.63% from ζ_1 to ζ_5, respectively. This difference can be explained as a result of the formation of the inclusion complex of β-CD with AMP, the main component of Clo. AMP as a guest molecule substitutes for the original water molecules in the cavity of β-CD. Then a continuous volatilization of AMP in Clo occurs in a wide temperature range from 393.2 to about 564.7 K (the boiling point of AMP is 526.4 K). Since the total content of water and guest is less than 30%, it is the thermal decomposition process of the survived β-CD when the RM value is below 70%.

No significant difference in two narrow areas (f and j) among these curves is found in Fig. 2B. However, each differed from one another to a considerable degree in area h, in which the ML values of the sample at different heating rates are kept in the range from 30 to 70%. On the whole, the temperature difference (ΔT) between the ML values of 30 and 70% increases with increasing heating rates. For example, $\Delta T = 19.8$ K at ζ_1 ($T_1 = 577.5$ K, $T_2 = 597.3$ K) and $\Delta T = 28.3$ K at ζ_5 ($T_3 = 608.3$ K, $T_4 = 636.5$ K). The values of ΔT of survived β-CD are all below 30.0 K, and obviously lower than that (49.0 K) of free β-CD in the same range of ML at ζ_1.

According to the data in Table 1, an obvious difference in the RM values under the same heating rate at 636.5 K (T_4) between free β-CD and survived β-CD is observed. This finding should be ascribed to the fact that a guest molecule can change the type of β-CD molecular stack when it formed an inclusion complex with β-CD [16].

Furthermore, in area h, it is found that, with increasing heating rate, the thermal decomposition temperature of survived β-CD at the same value of RM increases gradually. This phenomenon may be because the thermal decomposition of the survived β-CD is an endothermic process [17], that is, the real temperature of the solid sample failed to catch up with the programmed temperature.

Area h in Fig. 2B clearly depicts the main mass loss in the TG curves of Clo–β-CD system. As described in introduction, the ML range from 30% to 70% should approximately reflect the melting-decomposition process of survived β-CD after the completely release of the main component in Clo.

3.2. MS analysis on the thermal decomposition process of the survived β–CD in Clo–β-CD system

Thermoanalytical techniques are frequently used in the investigation of the thermal properties of CDs and their inclusion complexes, but they do not provide any information on the chemical composition of the split fragments from heated samples [9,18,19].

MS measurements in this study are carried out under vacuum. Hence, the mass loss range of measured sample under vacuum may be different from those described above under the atmosphere of nitrogen gas. Here, both a direct sample injection method and a temperature-programmed heating treatment are carried out. A set of MS spectra under various temperatures are obtained.

Fig. 3 is the measured values of TIC as a function of *t* (min). The program for the temperature-controller is given in the section of “Instrument and method”. The shaded areas with the same pattern have identical temperature behavior in the figure. In the two peaks in Fig. 3, one (small peak at 553.2 K) indicates a release of AMP (boiling point, 526.4 K) as main component of Clo from its inclusion complex of β-CD; the other one implies a rapid increase of fragments of the survived β-CD (large peak at 647.1 K). The intensity difference between the two peaks is quite

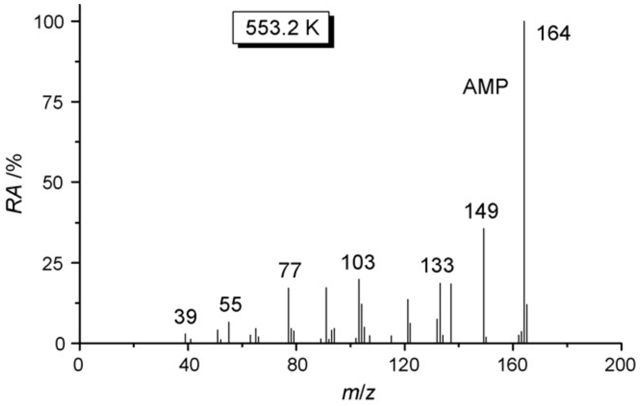

Fig. 4. Mass spectrum of the sample at 553.2 K.

obvious, which is closely related to the relative mass content of host and guest in Clo–β-CD. Furthermore, a swift increase in TIC occurred in a narrow temperature range from 604.7 to 647.1 K, which is in accordance with the fast mass loss of the sample in its TG profiles.

Although the appearance of many unexpected fragment peaks in MS spectra makes it complicated to analyze all of the molecular ions with structural models of host and guest, the differences among the spectra with increasing temperature are rather obvious. These differences in MS spectra are just what we need in such experiments.

When the temperature stays at 553.2 K for 5 min, a prominent molecular ion peak at *m/z* 164.0846 ($C_{10}H_{12}O_2$) with a relative abundance (RA) 100% appears in the mass spectrum (see Fig. 4), which is attributed to the molecular fragment of AMP in Clo.

In such temperature environment, no other fragment peak is particularly intense. Moreover, the corresponding peaks of β-CD are not found in Fig. 4, suggesting that it does not start to decompose at least at 553.2 K.

As the temperature increases to 626.7 K in Fig. 5, the RA values of the top three intense fragment peaks are *m/z* 60.0214 (RA of 100%, $C_2H_4O_2$), *m/z* 73.0293 (RA of 58.77%, $C_3H_4O_2$) and *m/z* 57.0344 (RA of 51.55%, C_3H_5O). Clearly, they are all due to the thermal decomposition products of the survived β-CD after rupture of 1,4-glycosidic bonds. Compared with the fragment peak at *m/z* 60.0214 (RA, 100%) resulting from β-CD, the first strongest peak at *m/z* 164.0846 in 553.2 K (see Fig. 4) has become to be the fifth strongest peak with a value of RA of 43.49%.

It is well known that the relative mass content of an organic guest is usually much lower than that of β-CD in its inclusion complex. Therefore, the fragment peaks resulting from the organic guest will be very weak relative to those of β-CD if a great number of β-CD molecules have already decomposed into radicals. But here the difference (ΔRA, 56.51%) in the two RA values between *m/z* at 164.0846 and *m/z* at 60.0214 is not extremely large so that it can deduce that the survived β-CD in Clo–β-CD system is just at the beginning of its thermal decomposition reaction.

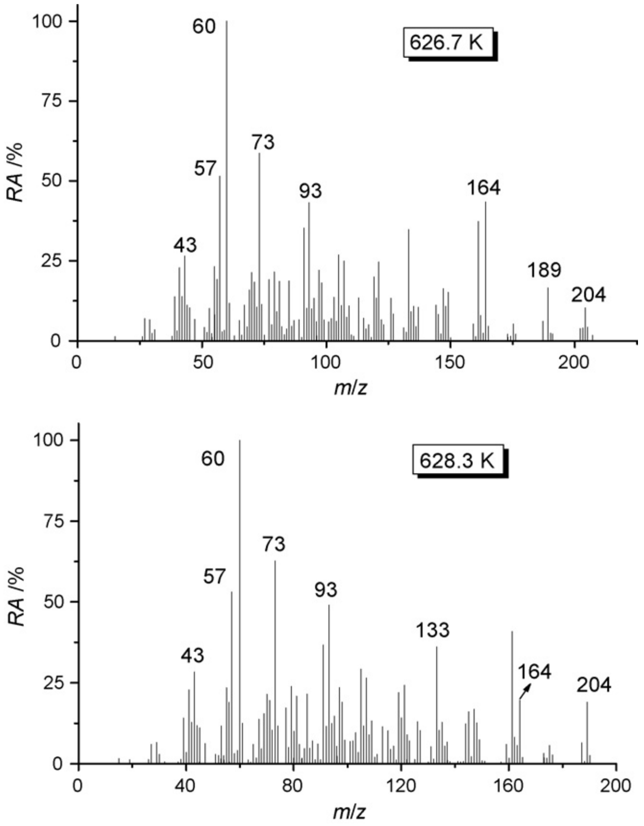

Fig. 5. Mass spectra of the sample at 626.7 and 628.3 K.

While at 628.3 K, the RA value of the peak at *m/z* of 164.0846 has declined to 19.08%. An astonishing change happens in an extremely narrow temperature range of less than 2.0 K. The observation reveals that once β-CD begins to decompose, its thermal decomposition reaction will be very violent. It is worthy of note that the molecular ion peaks concerning mono-, di- and poly-glucose units of β-CD has not been yet found, even in Fig. 5.

When it reaches 647.1 K, the MS spectrum in Fig. 6 is considerably different from that in Fig. 5, in particular, from that under 626.7 K. The peak at *m/z* 60.0214 (RA, 100%) in Fig. 5 is still the first strongest. However, in Fig. 6, the intensity of the peaks at *m/z* 73.0293 (RA, 79.78%) and *m/z* 57.0344 (RA, 55.77%) increase to a certain extent in comparison with those

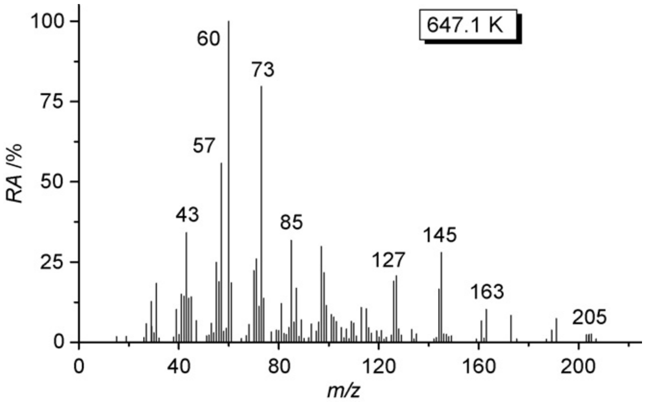

Fig. 6. Mass spectrum of the sample at 647.1 K.

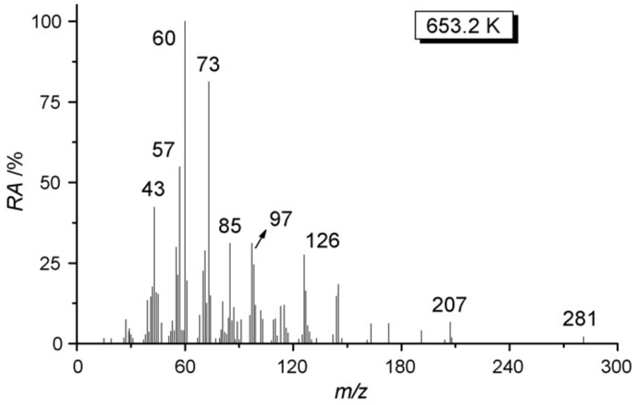

Fig. 7. Mass spectrum of the sample at 653.2 K.

in Fig. 5. The peak at *m*/*z* 163.0608 (RA of 11.09%, $C_6H_{11}O_5$), which is due to mono-glucose unit of β-CD, appears. In addition, a few fragments with *m*/*z* value between those of mono- and di-glucose are also found, but they have quite low values of RA.

When the temperature arrives at 653.2 K, the sample is kept for 5 min, and the fragment peak at *m*/*z* of 164.0846 disappears (see Fig. 7). Although the peaks at *m*/*z* of 207.0328 (RA of 6.65%, $C_{10}H_7O_5$) and *m*/*z* value of 281.0501 (RA of 2.17%, $C_{16}H_9O_6$) increase to a certain degree, the intensities of many fragment peaks all decrease, such as *m*/*z* of 163.0608 decreases to 6.19%, *m*/*z* of 191.0556 ($C_7H_{11}O_6$) decreases to 4.02%. Some fragment peaks shown in Fig. 6, such as one at *m*/*z* of 235.0809 and the other at *m*/*z* 255.1233, have disappeared in Fig. 7.

It is surprised that at a higher temperature of 720.1 K, as shown in Fig. 8, the RA value of fragment peak at *m*/*z* of 207.0347 increases to 100% from 6.75% in Fig. 7. It should be noted that the peak becomes the maximum only in a rather short time interval ($\Delta T = 66.9$ K, $\Delta t = 0.669$ min). We know from general knowledge that the higher the temperature the rapider the rupture of a covalent bond, and the smaller the fraction component. In this paper, we attempt to explain the abnormal phenomenon as a result of the effective collision and mutual combination among smaller fragments when the temperature increases to a certain degree.

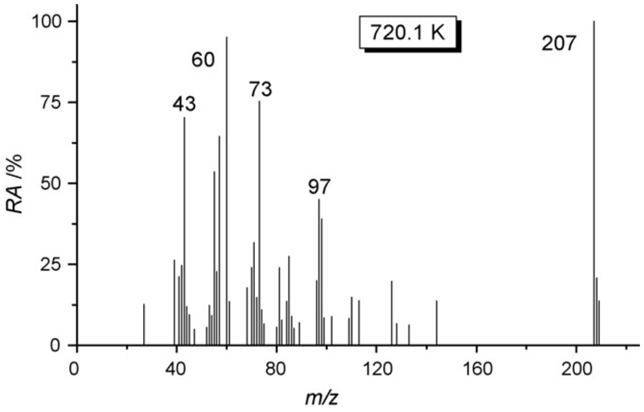

Fig. 8. Mass spectrum of the sample at 720.1 K.

Table 2
Some major fragments related to the decomposition of Clo–β-CD

m/*z*	Composition	RA (%)	*T* (K)	Ascription
57.0344	C_3H_5O	51.55 55.77 54.87	626.7 647.1 653.2	β-CD
60.0214	$C_2H_4O_2$	100 95.15 58.77	626.7 720.1 626.7	β-CD
73.0293	$C_3H_5O_2$	79.78 81.23	647.1 653.2	β-CD
163.0608	$C_6H_{11}O_5$	10.35 6.19 100	647.1 653.2 553.2	Glucose unit
164.0841	$C_{10}H_{12}O_2$	43.49 0 1.77	626.7 647.1 626.7	AMP
207.0328	$C_3H_{11}O_{10}$	0 100	647.1 720.1	β-CD

The properties of several major fragments described above are summarized in Table 2. The measured *m*/*z* for the fragment ions is in good accordance with the calculated results according to accurate atom mass.

When the main component of Clo is partly or entirely releases from its inclusion complex at 553.2 K or below, which is defined as the thermal decomposition of the inclusion complex Clo–β-CD, the survived β-CD does not start to decompose. In view of the TIC, MS spectrum at 626.7 K and TG curves in area h (577.5–636.5 K), it can be sure that a rapid, large mass loss process in TG profiles is indeed due to the thermal decomposition of the survived β-CD in Clo–β-CD system (system denotes the inclusion system consisting of β-CD and Clo, but Clo has been released), which is confirmed by the following experimental result.

The peak of *m*/*z* at 164.0846, which represents the AMP in Clo, suddenly decreases from RA 43.49% to almost RA 0% in a narrow temperature range of 626.7 to 647.1 K. Although the relative mass content of AMP is rather low relative to that of β-CD, the RA of 0% at 647.1 K gives a strong impression that the survived β-CD molecules decompose quickly in a temperature range of about 20.4 K and the signal of the fragment ($C_2H_4O_2$) with RA 100% is so strong that the signals from the guest fragments seems to be negligible. Therefore, this experimental result proves that the thermal decomposition curves of area h in Fig. 2, with sharp slopes in TG profiles, are ascribed to the survived β-CD, not the β-CD complex of Clo, which is to dispel a conceptual confusion about the thermal decomposition of guest–CD complexes.

The changes of characteristic fragment signal intensities can enlighten us on what the decomposition process of the survived β-CD is. It is found that the infrared absorption band in the region of C–O–C stretching vibration due to the glucose ring in β-CD disappears faster than the other bands with increasing temperature [20]. Combined with the changing of MS fragment signals, it reminds us that the dissociation of any two contiguous

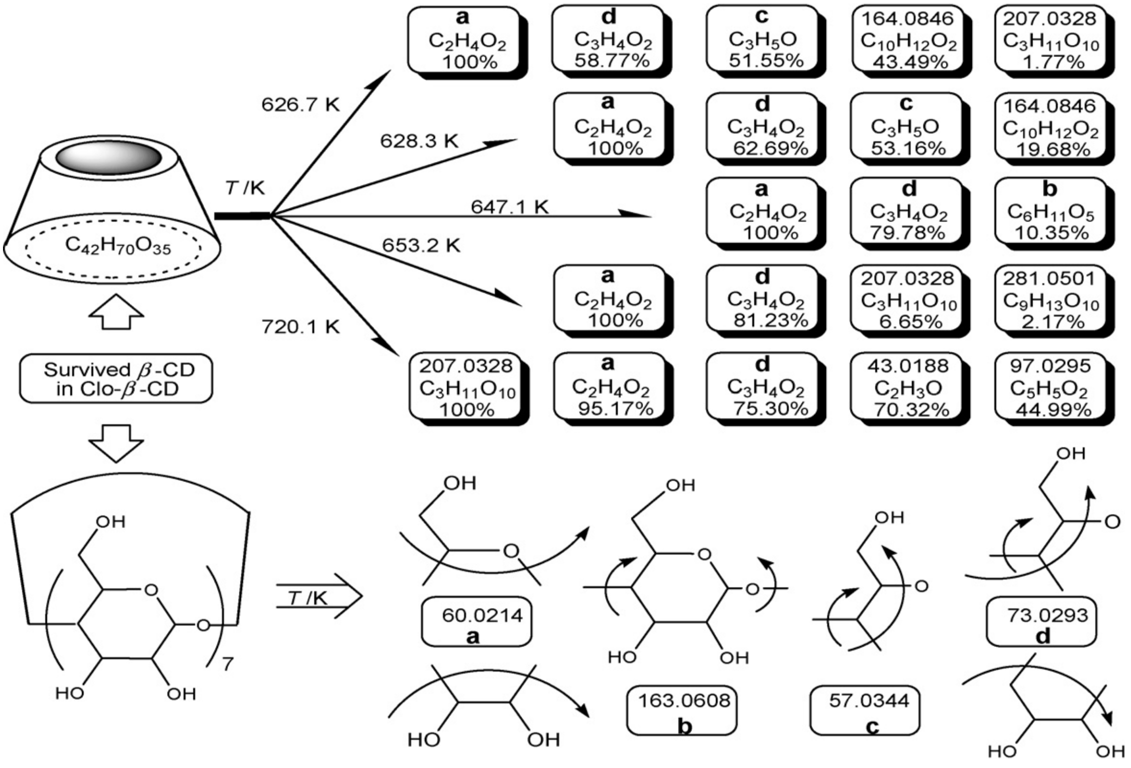

Fig. 9. A schematic sketch describing the formation and properties of the main fragments resulting from the thermal decomposition of the survived β-CD in Clo–β-CD system under different temperatures.

glucose units in β-CD is more advantageous than the rupture of covalent bonds in a glucose unit.

Fig. 9 summarizes the thermal decomposition behaviors of the survived β-CD in Clo–β-CD system at different temperatures. Since there is the existence of the strain among the glucose units of β-CD, we consider that 1,4-glycosidic bonds will first be destroyed by the enhanced temperature to release the strain. Simultaneously, some covalent bonds such as C–C especially C–O bonds in the glucose units will also start to rupture.

Vacuum environment allows us to simplify the analysis of thermal decomposition process by avoiding the disturbance of oxygen. The loop backbone of β-CD is divided into many parts, and then each part will be further cracked into small fragments with the increasing temperature. Only the fragments with a higher stability and suitable molecular mass at a corresponding temperature are able to transfer into gas phase so as to be detected by ion detector. The largest fragment appeared in the gas phase is the one with a peak at m/z of 281.0501. We consider it as a residue with a loss of some small groups from a di-glucose unit because no molecular ion peaks at m/z of 324 (corresponding to a di-glucose unit) or above are observed. Moreover, the number and intensity of the peaks larger than m/z of 163.0608 (fragment b, corresponding to a glucose unit) are all decreased with increasing temperature on the whole, except for the incineration temperatures of the sample, such as 720.1 K and above.

The peaks due to fragments a, d and c in Fig. 9 appeared in MS spectra of the sample corresponding to the top three peaks almost throughout the whole process of rapid thermal decomposition (626.7–653.2 K) of the survived β-CD. The algorithm is used to assign the most probable composition to each of these fragments using the mass spectra data. The structural information and the formation manners of the fragment structures are also illustrated in Fig. 9. In general, there are two possible decomposition patterns: single (c) and double (a and d). They are represented using an arrow notation indicating the direction in which the covalent bonds are expected to rupture. The latter (double pattern) could produce a higher abundance than the former (single pattern).

The applications of β-CD and its inclusion complexes play an important role in many fields as food, cosmetics, agriculture and pharmaceutical technology [1,21]. Thermal analysis is one of the most important methods to characterize the formation and stability of solid guest–β-CD inclusion complexes [10]. Clearly, the investigation on the thermal decomposition process of β-CD complexes can be helpful to predict and control the release of an included guest. Several significant problems are needed to be considered when β-CD inclusion complexes are applied in practice: (1) whether and when the guest is released alone (2), whether the thermal decomposition reaction of an inclusion complex produces harmful radicals. The present work, based on the combined technique (TG-GC-TOF-MS), reveals the diversity of the decomposition products of the solid inclusion complex of Clo with β-CD. Many small radical fragments from the covalent bond rupture instead of the retention of glucose units that compose the backbone of β-CD structure have been detected. The detected fragment structures create an impression that there should be a limitation on the applications of β-CD and its inclusion complexes at higher temperature.

References

[1] J. Szejtli, Chem. Rev. 98 (1998) 1743–1753.

[2] G. Wenz, Angew. Chem. Int. Ed. Engl. 33 (1994) 803–822.

[3] L.X. Song, H.M. Wang, Y. Yang, Acta Chim. Sinica 65 (2007) 1593–1599.

[4] H.M. Wang, L.X. Song, Chem. Lett. 36 (2007) 596–597.

[5] Y.J. Cao, X.H. Xiao, R.H. Lu, Q.X. Guo, J. Incl. Phenom. Mol. Recogn. Chem. 46 (2003) 195–200.

[6] Y. Yang, L.X. Song, J. Incl. Phenom. Macrocycl. Chem. 53 (2005) 27–33.

[7] L.X. Song, C.F. Teng, Y. Yang, J. Incl. Phenom. Macrocycl. Chem. 54 (2006) 221–232.

[8] M.M. Meier, M.T.B. Luiz, B. Szpoganicz, V. Soldi, Thermochim. Acta 375 (2001) 153–160.

[9] Z. Éhen, F. Giordano, J. Sztatisz, L. Jicsinszky, C. Novák, J. Therm. Anal. Cal. 80 (2005) 419–424.

[10] F. Giordano, C. Novak, J.R. Moyano, Thermochim. Acta 380 (2001) 123–151.

[11] Y. He, J. Sun, Chin. J. Chem. Phys. 19 (2006) 89–92.

[12] J.H. Li, N. Zhang, X.T. Li, J.Y. Wang, S.J. Tian, J. Therm. Anal. 49 (1997) 1527–1533.

[13] G.Z. Feng, X. Huang, K. Lu, J. Zhengzhou Inst. Technol. 25 (2004) 44–48.

[14] Y. Zheng, J.B. Weng, R.Y. Chen, J. Fujian, Teachers' Univ. (Nat. Sci.) 13 (1997) 55–59.

[15] P.F. Chen, J. Fujian, Teachers' Univ. (Nat. Sci.) 14 (1998) 47–50.

[16] C.C.L. Pereira, S.S. Braga, F.A.A. Paz, M. Pillinger, J. Klinowski, I.S. Gonçalves, Eur. J. Inorg. Chem. (2006) 4278–4288.

[17] V.T. Yilmaz, A. Karadag, H. Icbudak, Thermochim. Acta 261 (1995) 107–118.

[18] M. Lahiani-Skiba, A. Coquard, F. Bounoure, P. Verite, P. Arnaud, M. Skiba, J. Incl. Phenom. Macrocycl. Chem. 57 (2007) 197–201.

[19] H. Aki, T. Niiya, Y. lwase, Y. Kawasaki, K. Kumai, T. Kimura, Thermochim. Acta 416 (2004) 87–92.

[20] M. Wei, J. Wang, J. He, D.G. Evans, X. Duan, Micropor. Mesopor. Mat. 78 (2005) 53–61.

[21] L.P. Fernandes, Zs. Éhen, T.F. Moura, Cs. Novάk, J. Sztatisz, J. Therm. Anal. Cal. 78 (2004) 557–573.