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Evaluate the pyrolysis pathway of glycine and glycylglycine by TG–FTIR

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Abstract

An online-coupled TG–FTIR evolved gas analysis (EGA) instruments has been used to identify and monitor the evolution of gaseous products during thermal decomposition of glycine and its dipeptide in flowing N_2 atmosphere up to 800 °C. The first gaseous products of glycine pyrolysis, evolved around 260 °C are NH_3, H_2O and CO_2. The max releasing rates of both NH_3 and H_2O are reached at 282 °C and that of CO_2 is reached at 308 °C. At 400 °C HNCO becomes the main product, accompanied by CO, HCN and some other species. HCN is the main gaseous species released around 700 °C. Compared with glycine, glycylglycine has lower thermal stability, which begins to decompose at 214 °C. However, that the evolution profiles of gaseous products from glycine and glycylglycine are similar, which suggests the decomposition of them may occur through similar pathways. Our results indicate that the primary decomposition steps include deamination and dehydration. CO_2 is mainly formed through the secondary reactions. And the crack of cyclic amide, 2,5-diketopiperazine (DKP), is suggested to be the main origin of HNCO and HCN at higher temperature.

Keywords: Pyrolysis; Glycine; Glycylglycine; TG–FTIR

1. Introduction

Most of biomass fuels, such as bagasse, straw, rapeseed and wood, contain nitrogen. Although the nitrogen content in biomass fuels is low, it is still important since the biomass nitrogen can be transformed into environmentally harmful gases under combustion and coking. It was found that most of the nitrogen in biomass fuels comes from proteins. The main pyrolysis gases from protein at high temperatures are HCN, NH_3 and HNCO. And their yields depend on temperature and also on the protein's amino acid composition [1]. Then the investigation of the pyrolysis of amino acid can bring us helpful information about the gaseous products release from protein and biomass fuels.

The pyrolysis of amino acid has also been extensively studied in last two decades [2–16]. The results show that the pyrolysis processes are complicated and involve many reactions such as decarboxylation, deamination, dehydration and a number of intermolecular condensation reactions [3]. The products consist of simple inorganic compounds (CO_2, H_2O, NH_3 and CO), a variety of volatile organic compounds (amines, nitriles, amides, hydrocarbons, etc.) and lots of less-volatile organic compounds (2,5-piperazinediones, lactams, hydantoins, etc.). However, the thermal decomposition pathways of the amino acids cannot be interpreted clearly yet, and many reaction mechanisms remain uncertain [2,3,9,10,12,15].

The former thermogravimetry research [9–11] of amino acids showed us an interesting phenomenon. The TG curves of many aliphatic α-amino acids present only one stage with weight loss of almost 100%, while that of the glycine presents multi weight loss stages. This indicates that their pyrolysis should obey different decomposition pathways. Recently, we have studied the solid-state decomposition processes of a typical aliphatic amino acid, leucine, in flowing N_2 atmosphere by TG–FTIR [17]. Our results showed that the 100% weigh loss

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of leucine is due to its sublimation. In this work we want to find out the pyrolysis pathways of glycine and interpret its TG curves. As the simplest amino acid, glycine was considered decomposing through a typical and simple pathway [18]. But in fact the pyrolysis process is complicated and different conclusions have been drawn by different researchers. Rodante and Biemam considered that the main primary process of fragmentation for glycine was decarboxylation [10,19], and Simmonds et al. thought that it maybe not [2].

In previous studies thermal decomposition mechanism of amino acids was often investigated based upon off-line products detecting methods such as Py-GC–MS and Py-LC–MS [2–16]. But by using these methods products from different reaction stages were mixed together, which brought many troubles to identify the reaction sequences. In present work, TG–FTIR technique, which can conduct simultaneous and continuous products analysis [20–24], was used. By this means, the sequence of decomposition reactions occurring can be observed directly.

This paper focused on determining the pathways of glycine pyrolysis in inert atmosphere. Since the dehydration reactions producing dipeptide and diketopiperazine have been suggested as crucial decomposition pathways [2], the glycylglycine was pyrolysed at the same condition as a reference.

2. Experimental

Commercially available glycine (Analytical Grade, purchased from Wako, Japan) was used without further purification. Glycylglycine (ultra-purity ≥99.5%) was purchased from Fluka, Switzerland.

The TG–FTIR system composed of the Setaram Setsys 16 TG–DTA/DSC Instrument and a Thermo Nicolet Nexus 670 Fourier Transform Infrared Spectrometer. For TG–FTIR measuring, about 10 mg sample was weighted into an open alumina crucible. The heating rate of the TG furnace was 20 K min^{-1}, and nitrogen gas of high purity (≥99.999%) with a flow rate of 100 ml min^{-1} was used as carrier gas. The sample was heated from ambient temperature to 600 °C. The transfer line used to connect TG and FTIR was a 1 m long stainless steel tube with an internal diameter of 2 mm, of which the temperature is maintained at 200 °C. The TGA accessory of the IR spectrometer was used, which has a 45 ml gas cell with a 200 mm path length. It was also heated at the constant temperature of 200 °C. The IR spectra were collected at 8 cm^{-1} resolution, co-adding 8 scans per spectrum. This resulted in a temporal resolution of 4.32 s. Lag time that the gas products went from furnace to gas cell was about 7 s. The FTIR spectra have been identified based on the FTIR reference spectra available on the World Wide Web in the public spectrum libraries of NIST [25] and SADTLER Standard Infrared Spectra [26].

3. Results and discussion

Fig. 1 presents the weight loss (TG), the associated derivative thermogram (DTG) and the total infrared absorbance

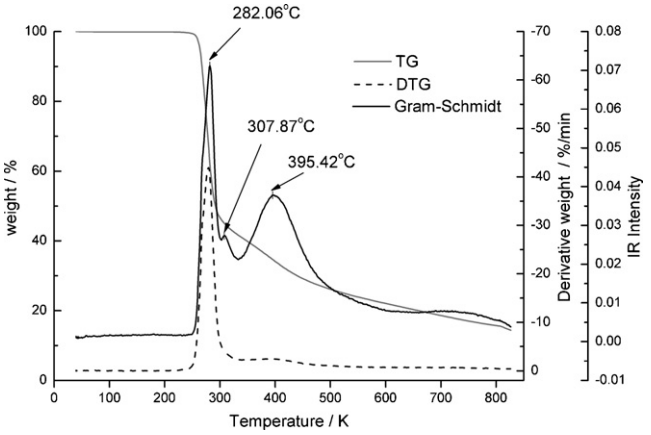

Fig. 1. The curves of TG, DTG and the total FTIR absorbance intensity of evolved gases, gotten during the glycine pyrolysis process by TG–FTIR (heating rate 20 K/min; N_2 flow rate 100 ml/min).

(Gram–Schmidt curve) profile of glycine as a function of temperature at a heating rate of 20 °C/min. In this figure, the lag time of the evolved gases passing through the IR cell has been deducted. The TG curve shows three weight loss stages. The first stage with a sharp weight loss of 53.8% takes place in the temperature range of 238–313 °C, which is followed by two slow weight losing stages in 313–456 °C and 456–800 °C. The overall weight loss measured at 800 °C is 85.4%. Comparison of Gram–Schmidt curve with DTG curve indicates that the temperature of the IR absorbance peaks coincide with that of the DTG peaks, although the Gram–Schmidt curve has one more peak than the DTG curve. The DTG curve shows only two peaks at 282.06 °C and 395.42 °C, while the Gram–Schmidt curve shows three peaks existing at 282.06 °C, 307.87 °C and 395.42 °C. This indicates that the thermolysis process of glycine really includes four stages.

The 3D FTIR spectrum of the evolved gases of glycine pyrolysis is shown in Fig. 2. In this figure FTIR spectrum of all the volatile pyrolysis products evolved at different time are shown. And the characteristic spectra obtained at 282.06 °C, 307.87 °C, 395.42 °C and 725.52 °C are shown in Fig. 3. From

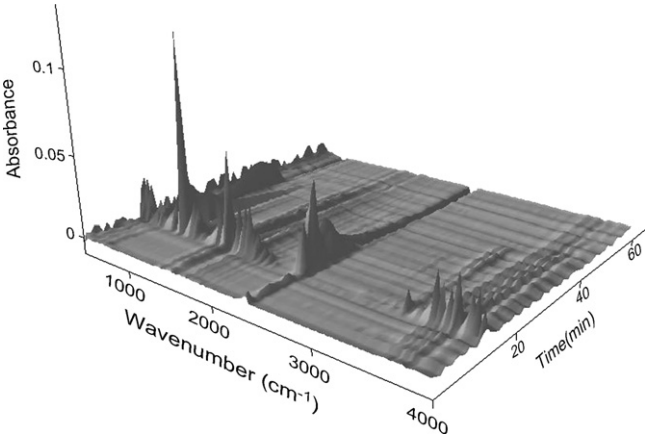

Fig. 2. The 3D surface graph for the FTIR spectra of the evolved gases produced by glycine pyrolysis (heating rate 20 K/min; N_2 flow rate 100 ml/min).