Study on the mechanisms of hydrocyanic acid formation during glycine pyrolysis

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1. Introduction

Hydrogen cyanide is one of the major ciliatoxic components in cigarette smoke. It is formed from pyrolysis of various nitrogenous compounds such as amino acids and nitrates in tobacco. Several experimental studies have been carried out on pyrolysis of amino acids in order to establish the formation mechanisms of HCN. However, in previous studies, the thermal decomposition pathways of amino acids were often investigated based upon pyrolysis only at fixed temperatures that did not reveal the precise temperatures for HCN formation. Consequently, the formation mechanisms of HCN have not yet been clearly elucidated. In the present work, thermal degradation of glycine was studied by TG-FTIR, Py-heart-cutting two-dimensional GC-MS and LC-MS/MS. The objectives of this study were to reveal the HCN formation mechanisms during glycine pyrolysis.

2.Experimental

2.1 TG-FTIR analysis

Thermogravimetric analyses (TGA) were performed using a Netzsch STA 449 F3 TG/DSC connected to BRUKER TENSOR 27 Fourier Transform Infrared Spectrometer by a heated transfer line. Samples of 10 mg were heated at a constant rate of 20 ℃/min from 30 ℃ to 900 ℃. Helium (99.999% purity) was used as carrier gas at a flow rate of 35 ml/min. The IR spectra were collected at 4 cm^{-1} resolution. In this work, the concentration of each gas species was determined based on the integral value of the release curves under specific IR absorption.

2.2 Online pyrolysis-heart-cutting two-dimensional GC-MS analysis

A CDS 5200 pyrolyser was coupled to Agilent 7890 gas chromatograph. A 1 mg sample of glycine was pyrolyzed during each test. The pyroprobe was heated at 30 ℃/s to a preset temperature and then maintained for 10 s. The helium carrier gas continuously passed through the interface at a flow rate of 20 ml/min to transport the pyrolysate from the quartz tube into the heated GC injection port. The interface was maintained at 280 ℃ to condensation of pyrolysis products during pyrolysis.

2.3 LC-MS/MS analysis of water extracts from pyrolysis residues

Offline pyrolysis was carried out in an infrared image furnace with a quartz tube. The experimental conditions during offline pyrolysis were chosen to match the conditions of the online pyrolysis. After offline pyrolysis, the residues were shaken with 20 ml deionized water for 20 min and filtered through 0.45 μm filters. The water extracts were analyzed by LC-MS/MS using the molecular ion [M+H]+ (m/z 115) and daughter Ion (m/z 87) for the qualitative analysis of DKP.

3. Results and discussion

3.1 TG-FTIR analysis

The main gaseous pyrolysis products of glycine in the first heating stage (200-300 ℃) were NH_3, H_2O and CO_2. The maximum release rates for both NH_3 and H_2O were reached simultaneously at 273 ℃. Also in this heating stage, HCN exhibits a weak absorbance. Between 300-440 ℃ production of HNCO predominates and an increase in the release of HCN and CO was observed. Starting at 440 ℃ up to 900 ℃, where the TG detects a modest weight loss, a marked production of HCN was observed, which reached its maximum release at 763 ℃. From Fig.1(c) the IR absorbance peak temperatures of HCN are 273 ℃, 422 ℃ and 763 ℃.

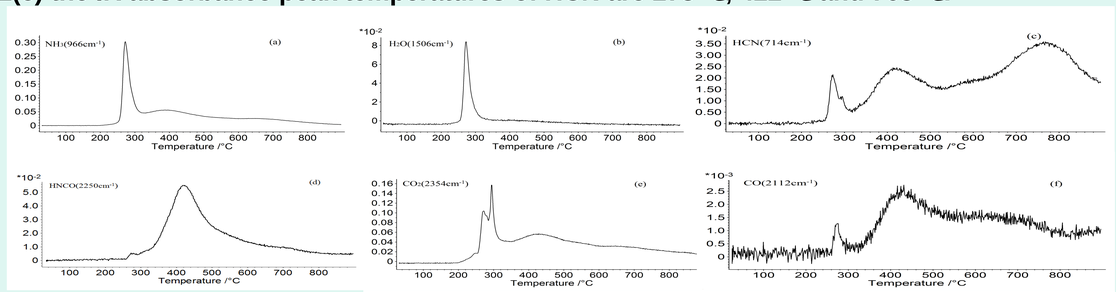
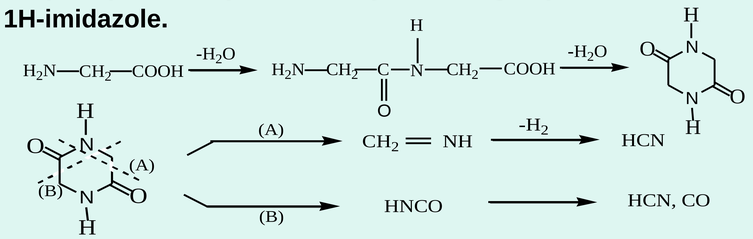


Fig.1 IR absorbance vs. temperature curves for (a) NH_3, (b) H_2O, (c) HCN, (d) HNCO, (e) CO_2, (f) CO evolved from glycine pyrolysis

3.2 Online pyrolysis-heart-cutting two-dimensional GC-MS analysis

During 200-273 ℃, the most significant product formed from the pyrolysis of glycine was water (61.94%) along with N-.alpha.-acetylglycinamide (2.75%), acetamide (1.97%), acetic acid (0.95%) and methylamine (0.79%). The second heating stage was characterized by the appearance of DKP (4.1%). A variety of heterocyclic nitrogen products formed in the third stage such as pyrrole, 1H-imidazole.



3.3 Qualitative analysis of DKP from pyrolysis residues

The water extracts from the 273 ℃ and 422 ℃ residues of glycine exhibited pronounced mass signals (m/z) 115 and (m/z) 87, which coincided with the standard solution of DKP. These results suggested that there was a proportion of DKP in the solid residues of glycine after pyrolysis at 273 ℃and 422 ℃.

4. Conclusions

At 200-273 ℃, glycine undergoes a decarboxylation reaction to produce methylamine that subsequently yields HCN via dehydrogenation. Upon further heating at 273-422 ℃ and 422-763 ℃, glycine gives relatively large amounts of HCN, presumably via 2,5-diketopiperazine and subsequent HNCO and/or methylenimine formation.

References

1. R.K. Sharma, W.G. Chan, J. Wang, B.E. Waymack, J.B. Wooten, J.I. Seeman, and M.R. Hajaligol. Journal of Analytical and Applied Pyrolysis 72 (2004) 153-163.