PYROLYSIS OF α-AMINO ACIDS

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Introduction

Amino acids are important constituents of most biomass. Pyrolysis of amino acids produces a complex slate of products. Of particular interest among the pyrolysis products are the polycyclic aromatic compounds (PAC) which include polycyclic aromatic hydrocarbons (PAH) and nitrogen containing polycyclic aromatic compounds (N-PAC). Patterson et al.1 pyrolyzed lysine, leucine and tryptophan and found that the total PAC yield was maximum at 850°C. Higman et al.2 pyrolyzed proline at 840°C and observed pyrrole, indole, pyridine, isoquinoline, quinoline and picoline as products. Smith et al.3 pyrolyzed valine, aminobutyric acid, and proline and observed nitriles, quinoline and isoquinoline at 850°C. Yoshida and Matsumoto4 observed the formation of amino-β-carbolines from tryptophan at 550°C. Recently, Chiavari and Galletti5 reported the main products from pyrolysis of amino acids in a CDS Pyroprobe 100 at 600°C for 5 s. Despite these studied, there is no detailed study on the effect of temperature and residence time on the product distribution. In this work, the formation of PAC from pyrolysis of asparagine, proline, and tryptophan was studied under various pyrolysis conditions. The results were analyzed to determine the major product components and the effect of pyrolysis conditions and the structure of amino acid on the PAC yields.

Experimental

Pyrolysis experiments were performed in a quartz reactor in two ways.5 In the first case, the amino acid was pyrolyzed in a single zone reactor at 300°C to collect LTT (low temperature tar) and LTC (char). A sample of 200 mg of amino acid was used and pyrolyzed for 60 minutes. The LTT was collected on a Cambridge pad. The pad was extracted with methanol. The LTC was then pyrolyzed further at 625°C for 60 min to collect HTT (high temperature tar) and HTC (char). In the second case, a two-zone reactor was used and the LTT and HTT leaving the first zone were pyrolyzed further in the second zone at 720-920°C. The final tars, LTFT (low temperature final tar) and HTFT (high temperature final tar) from LTT and HTT, respectively, were collected similarly. Only the runs with a residence time of 1370 ms in the second zone are discussed in this paper. Helium was used as carrier gas at 120 cm³/min. The LTT, HTT, LTFT, and HTFT were analyzed by chromatography/ mass spectrometry (GC/MS).

Results and discussion

Asparagine. The overall material balance from pyrolysis of asparagine showed that, at 300°C, the yield of LTT was negligible but the yield of LTC was 64%. The yields of HTT and HTC were 12% and 23% of initial weight of asparagine. The HTT consisted mainly of maleimide and succinimide with yields of ca. 8 and 48 mg/g of asparagine. Indole and a methylindoline were also observed in low yields. Chiavari and Galletti6 reported maleimide and succinimide from asparagine. Indole and a methylindole were also observed in low yields. No LTFT was obtained from asparagine. The yields of a few major PAC in HTFT are shown in Figure 1. At 700°C, succinimide was the major component of HTFT. Both maleimide and succinimide decreased at high temperature. The yield of maleimide passed through a maximum at 770°C. At 870°C and above, the yields of two- to four-ring N-PAC, such as a naphthalene carbonitrile, pyrrolocarbazole, a benzoquinoline, and azapyrene, were significant. Most other N-PAC, including fluorenecarbonitrile, and anthracencarbonitrile, were formed in relatively low yields. Among the PAH, the highest yield was of phenanthrene followed at high temperature by pyrene. The formation of PAH indicates a complete loss of nitrogen from the initial products of pyrolysis.

Proline. Proline was completely converted into volatile products at 300°C, with a LTT yield of ca. 80%. The LTT consisted mainly of 2,5-diketopiperazine. No HTT or HTFT was obtained. The yields of some of the major components of LTFT are presented in Figure 2. Above 820°C, both N-PAC and PAH were observed. Carbonitriles were the main components of the N-PAC fraction. The yield of acridine passed through a maximum at 870°C. The yields of fluorenecarbonitrile, anthracencarbonitrile, and azapyrene increased sharply with temperature above 820°C. At 920°C, methylbenzonitrile was absent from the products. Indole, quinoline, benzenecarbonitrile, phenylpyridine, naphthalencarbonitrile, benzoquinoline, fluoreminine, phenanthridine, carbazole, acenaphthopyridine, indenoisoquinoline, pyrrolocarbazole, and cyanopyrene were also observed. Among the PAH, phenanthrene was the major component at all the temperatures. Benzo[α]pyrene was observed only at 920°C. Other PAH, such as naphthalene, biphenyl, ethylanthracene, methylanthracene, phenylpyrrole, benzo[a]fluorene, methylpyrene, benzo[ghi]fluoranthene, and isochrysene were also observed. The yields of acenaphthylene, fluorene, and anthracene either decreased or leveled off at high temperatures. This could be due to their growth into larger PAH. The formation of PAH from proline has also been reported earlier in the literature.2,3 Smith et al.7 also reported the formation of butadiene at 650°C. Thus, the PAH in this study, may have formed via butadiene and related low molecular weight olefins.

Figure 1. Effect of temperature on the yields of major N-PAC (a) and PAH (b) from the gas phase pyrolysis of HTT from asparagine at 700-920°C.

Figure 2. Above 820°C, both N-PAC and PAH were observed. Carbonitriles were the main components of the N-PAC fraction. The yield of acridine passed through a maximum at 870°C. The yields of fluorenecarbonitrile, anthracencarbonitrile, and azapyrene increased sharply with temperature above 820°C. At 920°C, methylbenzonitrile was absent from the products. Indole, quinoline, benzenecarbonitrile, phenylpyridine, naphthalencarbonitrile, benzoquinoline, fluoreminine, phenanthridine, carbazole, acenaphthopyridine, indenoisoquinoline, pyrrolocarbazole, and cyanopyrene were also observed. Among the PAH, phenanthrene was the major component at all the temperatures. Benzo[α]pyrene was observed only at 920°C. Other PAH, such as naphthalene, biphenyl, ethylanthracene, methylanthracene, phenylpyrrole, benzo[a]fluorene, methylpyrene, benzo[ghi]fluoranthene, and isochrysene were also observed. The yields of acenaphthylene, fluorene, and anthracene either decreased or leveled off at high temperatures. This could be due to their growth into larger PAH. The formation of PAH from proline has also been reported earlier in the literature.2,3 Smith et al.7 also reported the formation of butadiene at 650°C. Thus, the PAH in this study, may have formed via butadiene and related low molecular weight olefins.
Tryptophan. The yields of LTT and LTC from tryptophan were 15% and 56% whereas those of HTT and HTC were ca. 11% and 14%, respectively. The LTT contained indole, a methyl indole, norharman, harman and other indole derivatives, such as indoleethanamine and indoleacetonitrile. Ethylindole and dimethylindole were also observed in low yields. The HTT contained similar components but the yields of indole and substituted indoles were lower while those of the harmans were slightly higher. Other two- and three-ring PAC, such as quinoline and carbazole or azafluorene were also observed in small yields in the HTT. Some of these products have been reported earlier.5,7

Figure 2. Effect of temperature on the yields of major N-PAC (a) and PAH (b) from the gas phase pyrolysis of LTT from proline at 700-920 °C.

No PAH were observed in the LTFT and HTFT from tryptophan. The constituents of LTFT and HTFT ranged from N-heterocycles to three-ring N-PAC (benzo[a]carbazole and anthracenamine). For both LTFT and HTFT, the yields of indole and skatole decreased as the temperature was increased until they were completely destroyed above 850 °C (Figure 3). The temperature had only a small effect on the yields of norharman and harman, although above 820 °C the yields decreased. Whereas harman was completely absent in the product at 920 °C, the yield of norharman remained significantly high even at 920 °C. Essentially similar observations were made by Kleinbauer and Rabache.7 Harman and norharman were observed in the product even at 250 °C and the yield of norharman decreased slowly at high temperatures whereas the yield of harman decreased sharply. The nearly similar trends in the yields of norharman and harman in this study suggested that the norharman/harman ratio did not vary dramatically with temperature, except at high temperatures. The yield of quinoline remained relatively low at all temperatures. The yields of three-ring N-PAC, benzo[c]carbazole and anthracenamine, became significant only at 920 °C. In the case of HTFT, the yield of carbazole also became significant at high temperatures suggesting that it is one of the end products of the pyrolysis of tryptophan. In addition to the components shown in Figure 3, the product also contained cyanocarbazole, indenoisoquinoline, benzo[a]phenazinone, benzo[a]acridine and other products.

Conclusions

The results from the three amino acids showed that the amino acids pyrolyzed differently. The N-PAC from asparagine and proline were mainly aromatic carbonitriles and three- and four-ring azaarenes. Asparagine and proline also formed PAH, although the yields of PAH were low compared to the yields of N-PAC. In contrast, tryptophan did not form any PAH but it formed β-carbolines and indoles even at low temperatures. The pyrolysis mechanisms may be governed by the structure of the amino acid.

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References