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Molecular Products from the Thermal Degradation of Glutamic Acid

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Supporting Information

ABSTRACT: The thermal behavior of glutamic acid was investigated in N_2 and 4% O_2 in N_2 under flow reactor conditions at a constant residence time of 0.2 s, within a total pyrolysis time of 3 min at 1 atm. The identification of the main pyrolysis products has been reported. Accordingly, the principal products for pyrolysis in order of decreasing abundance were succinimide, pyrrole, acetonitrile, and 2-pyrrolidone. For oxidative pyrolysis, the main products were succinimide, propiolactone, ethanol, and hydrogen cyanide. Whereas benzene, toluene, and a few low molecular weight hydrocarbons (propene, propane, 1-butene, and 2-butene) were detected during pyrolysis, no polycyclic aromatic hydrocarbons (PAHs) were detected. Oxidative pyrolysis yielded low molecular weight hydrocarbon products in trace amounts. The mechanistic channels describing the formation of the major product succinimide have been explored. The detection of succinimide (major product) and maleimide (minor product) from the thermal decomposition of glutamic acid has been reported for the first time in this study. Toxicological implications of some reaction products (HCN, acetonitrile, and acyrolnitrile), which are believed to form during heat treatment of food, tobacco burning, and drug processing, have been discussed in relation to the thermal degradation of glutamic acid.

KEYWORDS: *flow reactor, decarboxylation, pyroglutamic acid, succinimide, maleimide*

INTRODUCTION

Amino acids, from a nutritional standpoint, are perhaps the most important constituents of our daily diet.[1] They are the central building blocks of proteins and have applications in the food, agricultural, cosmetics, and pharmaceutical industries, where pyrolysis is commonly used.[2−4] The formation of mutagenics and carcinogenics in pyrolysates of proteinaceous foods is a health concern in the fields of food processing, preservation, and safety,[5] implying the existence of a correlation between mutagenic activity and proteins in food that have undergone thermal treatment during processing.[6−8] Glutamic acid is present in free form in many different foods such as wheat,[1,9] soybean,[10] almond,[10] cocoa beans,[11] and coffee.[12] It has been reported that pyrolysates of glutamic acid show more potent mutagenicities in the Ames test.[13,14] Accordingly, the presence of glutamic acid in a variety of heat-treated materials (food, wood, drugs, and tobacco) makes the investigation of the molecular products from the thermal degradation of glutamic acid necessary. Amino acid pyrolysis is also important in understanding hydrothermal systems and the origin of life.[15]

Most biomass materials contain nitrogen, which can be converted to environmentally harmful products such as HCN, furans, and aromatic compounds.[16,17] The health consequences resulting from consumption of tobacco products, for instance, has been blamed on the production of toxic molecular products such as acetonitrile, acrylonitrile, and HCN[18,19] as well as free radicals during tobacco burning.[20] Radicals produced during combustion of tobacco are very reactive and capable of causing oxidative stress, cancers, and reproductive health diseases.[7,8,21] For example, the principal nitrogenous precursors present in burley tobacco are amino acids such as glutamic acid and aspartic acid, whereas glutamine, asparagine, and proline are found in flue-cured tobacco.[18,22] Also, the thermal behavior of glutamic acid is considered interesting due to its wide spectrum of commercial applications including incorporation in drugs for the treatment of ulcers, epilepsy, and Parkinson's disease.[2,3,23−26] Hence, it is possible degradation may affect product quality and safety.[2,27]

The decomposition products of amino acids are mainly simple inorganic compounds (CO_2, H_2O, NH_3, and CO), with a variety of volatile organic compounds (amines, nitriles, amides, and hydrocarbons).[17,28,29] Simple amino acids undergo decarboxylation to produce CO_2 and alkylamine.[30] In addition to thermally induced loss of small, stable molecules, amino acids have been reported to undergo dehydration to form dipeptides as reactive intermediates.[31,32] Degradation of glutamic acid can proceed via intramolecular dehydration to form lactam.[32] This observation is consistent with this study, where it was noted glutamic acid sublimed completely at about 300 °C to form a waxy substance, suggesting possible formation of a lactam polymer or polyglutamic acid as the major intermediate product.[3] In the pyrolysis of amino acids, the thermal conditions provide sufficient energy to form intermediate peptides in the solid/liquid phase.[31] Generally, the mechanisms for amino acid pyrolysis are complicated and may include, in addition to decarboxylation, deamination, dehydration, and condensation, random bond cleavage, thermal cracking of cylic amides, addition, substitution, recombination, rearrangement, and hydrogenation reactions.[28,33,34]

Despite the efforts made on the pyrolysis of amino acids, there is considerable variation in the amount and type of products reported by various investigators.[35] This discrepancy has been attributed to adsorption of extremely polar fragments either in the chromatographic column or on other parts of the analytical system.[35] In this work, the System for Thermal

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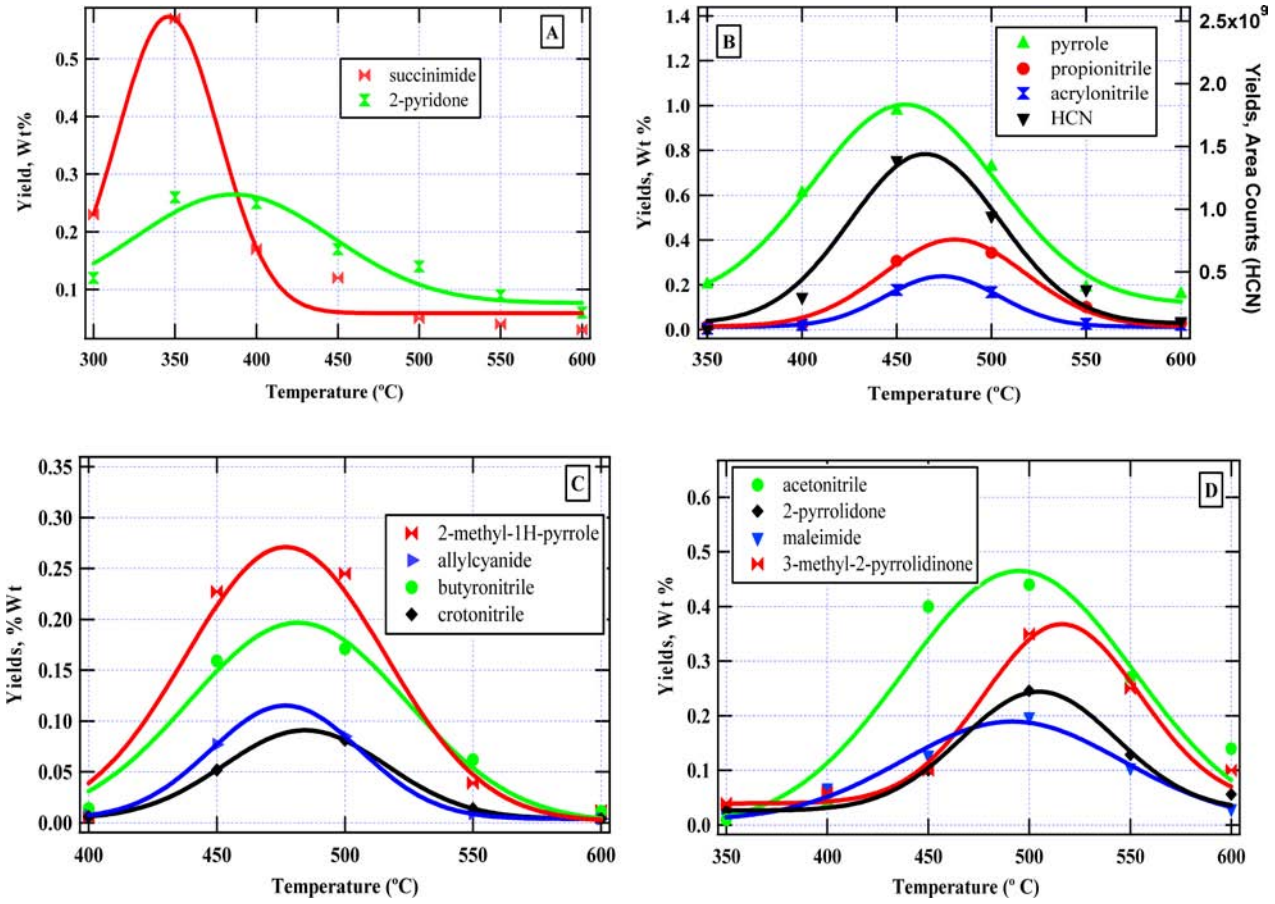

Figure 1. Weight percent yields of the major products (A–D) and yields of HCN (based on GC area counts) (B) from the pyrolysis of glutamic acid in N_2 at 1 atm.

Diagnostic Studies (STDS) was used to analyze the gas-phase reaction products from the thermal degradation of glutamic acid.[36] This technique has proven credible over the years for analysis of gas-phase products that would be difficult to analyze using routine methods.[37,38] For this reason, reaction products (succinimide and maleimide) that have not been detected before are reported during the thermal degradation of glutamic acid. Accordingly, this investigation will focus in detail on the formation mechanism of succinimide while describing briefly the mechanistic pathways for other major products, pyrrole, acetonitrile, 2-pyridone, maleimide, and HCN. The toxicity implications of some of the reaction products from the pyrolysis of glutamic acid such as hydrogen cyanide, acetonitrile, acrylonitrile, and pyrrole will be discussed briefly.

EXPERIMENTAL PROCEDURES

Materials. The L-glutamic acid (≥99.5%, purity) used in this study was purchased from Sigma-Aldrich (St. Louis, MO, USA) and used without further treatment.

System for Thermal Diagnostic Studies. To avoid many experimental pitfalls associated with the analysis of amino acid pyrolysis,[17] the STDS[36] was used in this work. The STDS is a continuous flow reactor system, with collection of the reactor effluent with an in-line GC-MS at the head of the GC column at −60 °C. It is a well-established technique for the analysis of a wide range of organic materials including biomass components.[36] STDS contains various units: the reactor compartment, which houses the electrical heater and the reactor; the temperature control console, which controls the pyrolysis temperature within a temperature gradient of ±5 °C; the injection port, the cryogenic trap, and the in-line detection system. The experimental details for STDS are reported elsewhere.[37,38]

Reactor and Sample Loading. A straight quartz tubular reactor of dimensions 0.3 cm i.d. × 17.7 cm was used for the pyrolysis of glutamic acid. Glutamic acid (30 ± 0.2 mg) was placed inside the quartz tube and held in place by quartz wool. A residence time of 0.2 s was chosen for all temperature runs. Tubular reactors have been in use for many years and are generally acceptable because in addition to withstanding high temperatures (about 1400 K), they have very small coefficients of thermal expansion.[38,39] All of the connections to the quartz tubular flow reactor were made of silica to maintain an inert atmosphere.[39] Nitrogen was the carrier gas for the pyrolytic condition, whereas 4% O_2 in N_2 was the carrier gas for the reactive (oxidative) condition. The flow of the carrier gas was controlled by a digital mass flow controller (Siera, model 810-DR-2), which has the capacity to deliver up to 700 mL/min of gas into the reactor system.

The flow reactor effluent is transported through a transfer line heated at 275 °C to prevent condensation along the transfer line. The transfer line is coated with deactivated silica lined with a steel tube. In addition, there is a splitter in the transfer line to deliver only a small amount of sample to the GC-MS system without damage to the detector. The splitter also helps to maintain a constant pressure of 1 atm in the reactor. This splitter is controlled by a pressure gauge, where the excess effluent flows through a charcoal trap and out to a fume hood.

Fractional Pyrolysis and Fractional Oxidative Pyrolysis. The fractional pyrolysis technique applied in this study is an experimental procedure in which the same sample is continuously pyrolyzed at each pyrolysis temperature.[4] It is defined as a selective in situ conversion of biomass materials to desired products.[4,40,41] The fractional pyrolysis technique offers some advantages in comparison with conventional pyrolysis because only one loading of sample is used and it can be

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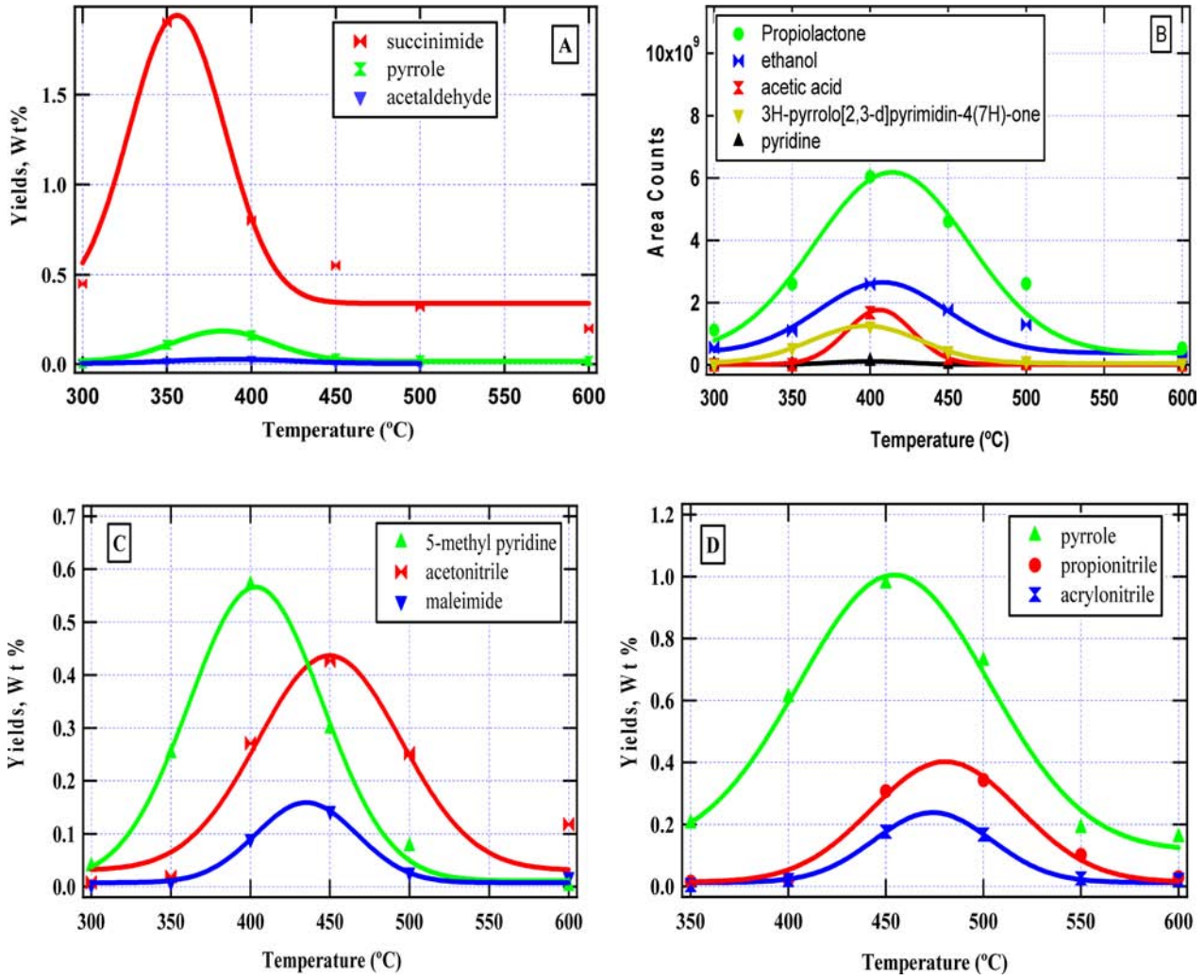

Figure 2. Weight percent yields of major products from the pyrolysis of glutamic (A, C, and D) and yields of other major products (based on GC area counts) (B) from the pyrolysis of glutamic acid in 4% O_2 in N_2 at 1 atm.

heated multiple times, therefore allowing the intermediate neutral, but unstable, products to be collected before they disappear in the secondary processes. The details of this procedure are described in our previous paper.[4]

Gas Chromatography–Mass Spectrometry (GC-MS) Characterization of Molecular Products. The GC-MS analysis of the pyrolysate was conducted with an Agilent 6890N gas chromatograph equipped with a 5973N mass selective detector (MSD) with an ion source of electron impact (EI) at 70 eV. Two GC columns, a Gas-pro column (60 m × 0.32 mm i.d. × 0.25 μm) for the analysis of low molecular weight products and a DB5-MS column (30 m × 0.25 mm × 0.25 μm) for the determination of high molecular weight products, were used.[41] To analyze small hydrocarbons, a gas sampling valve was used in place of a cold trap. A detailed description of the procedure for characterization of molecular products has been presented elsewhere.[4] The pyrolysis products were identified using the NIST library. Additionally, standards for pure compounds were used to compare the retention times and mass spectral fragmentation pattern with those of the analyte, and the mass spectral hits were excellent. Each of the compounds identified was thoroughly checked against literature data to ensure the correct reaction product was reported. Accordingly, critical emphasis has been given to those products that can easily be correlated with the structure of the starting material (glutamic acid). The experimental results were averaged of replicates.[38]

Calibration of Molecular Products. Standards for most reaction products were purchased from Sigma-Aldrich. Standards of purity ≥99% were used for the calibration of pyrolysis products. For those pyrolysis products for which standards were not available, the peak area count obtained from integration of respective total ion chromatograms (TIC) was plotted as a function of temperature to determine their yield distribution over the entire pyrolysis temperature range. The percent yield of each calibrated product was evaluated using eq 1. After the compounds were calibrated, product distribution curves displaying the yield of various products with pyrolysis temperature were generated.

$$Y = \left(\frac{\text{wt of product, } w}{\text{wt of sample, } W}\right) \times 100 \quad (1)$$

Y is the yield of the pyrolysis product in wt %.

RESULTS AND DISCUSSION

Fractional Pyrolysis. A series of nitrogen-containing products as well as hydrocarbon products was formed during pyrolysis of glutamic acid in an inert atmosphere. The reaction products from the pyrolysis of glutamic acid can be grouped on the basis of their maximum release temperatures (cf. Figure 2).

Group 1: The maximum release temperature for these products was between 300 and 400 °C with succinimide as the major product, peaking at about 350 °C (cf. Figure 1A). The concentration of compounds in this class peak at low pyrolysis

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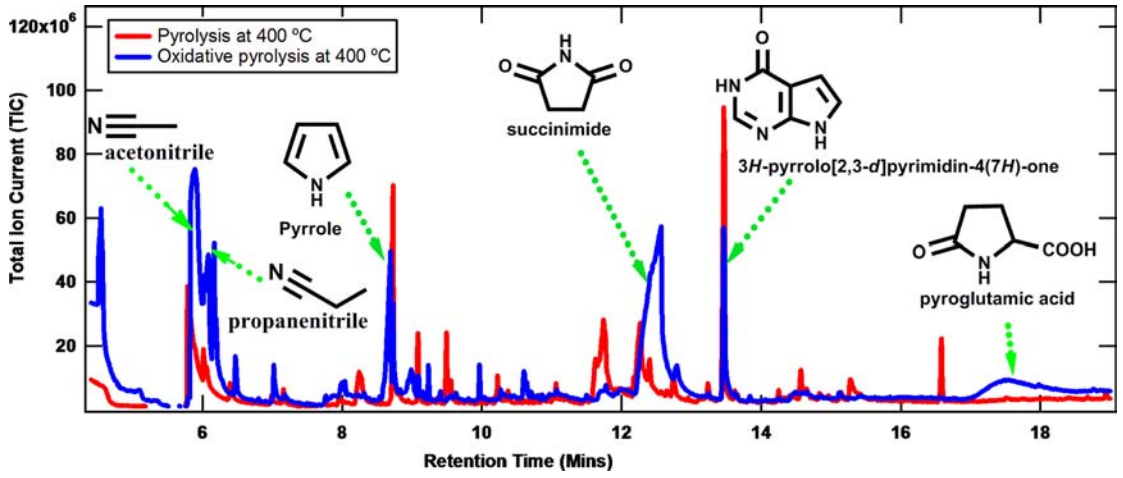

Figure 3. GC-MS chromatogram (DB5-MS column) for pyrolysis (red line) and oxidative pyrolysis (blue line) of glutamic acid in N_2 and 4% O_2 in N_2 at 400 °C.

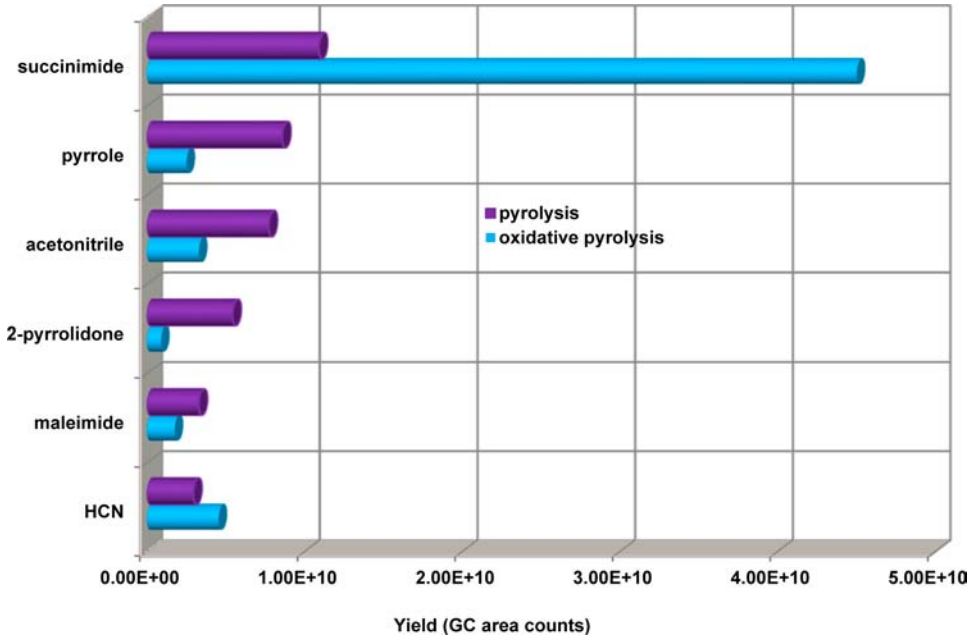

Figure 4. Major product distribution from the thermal degradation of glutamic acid in N_2 and 4% O_2 in N_2 at 1 atm in the temperature region 300–600 °C.

temperature and decrease sharply as the pyrolysis temperature is increased, implying a short release temperature range.

Group 2: This category of compounds included pyrrole, hydrogen cyanide (HCN), propionitrile, and acrylonitrile and generally peaked at about 450 °C (cf. Figure 1B) (the yield of HCN is depicted in GC area counts, the scale on the right). It is notable that amino acids are capable of forming a relatively stable nitrogen–aromatic ring in the early stages of thermolysis, yielding large amounts of hydrogen cyanide.[42] Nitrogen-containing rings are known to break down at high temperatures to give high levels of hydrogen cyanide.[42−44] Previous pyrolysis of intermediates such as pyrrolidone and 2-pyrodone led to observation of high yields of HCN.[44] This suggests the concentration of HCN increases sharply at high temperatures as the concentrations of succinimide, 2-pyrrolidone, 2-pyridone, and pyrrole decrease.

Group 3: The reaction products in this group have similarities to the products discussed in group 2 (cf. Figure 1C). Whereas the maximum release temperature for compounds in group 2 was about 450 °C, the maximum release temperature for those in group 3 was slightly higher than 450 °C, with the major compounds being 2-methylpyrrole and allylcyanide.

Group 4: These products include acetonitrile and 2-pyrrolidone as the major products (cf. Figure 1D). Acetonitrile peaked at high pyrolysis temperatures and may be formed from thermal decomposition of succinimide, pyrrole, and other heterocyclic products such as indole. This observation can be noted from Figure 1A,C,D, which shows the concentration of acetonitrile increased sharply at high temperatures as the concentrations of succinimide, 2-pyridone, and pyrrole decreased. The concentration of compounds in this category reached a maximum at about 500 °C.

Generally, the principal products in order of decreasing abundance in fractional pyrolysis of glutamic acid were as follows: succinimide, pyrrole, acetonitrile, 2-pyrrolidone, 3*H*-

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pyrrolo[2,3-*d*]pyrimidin-4(7*H*)-one, 2-methyl-1*H*-pyrrole, 2-pyridone, and maleimide.

Fractional Oxidative Pyrolysis. The principal reaction products from oxidative pyrolysis of glutamic acid can be classified into three groups.

Group 1: The major product in this class of compounds was exclusively succinimide, which peaked at about 350 °C. Other products in this group included pyrrole and acetaldehyde (cf. Figure 2A). Pyrrole, a major product in pyrolysis, was formed in low amounts under oxidative pyrolysis because an oxidizing atmosphere may retard the formation of pyrrole while enhancing the release of CO_2 according to the literature.[42,45] Previously, intramolecular reactions involving α-lactone followed by decarbonylation were proposed to account for the observed aldehydes,[46,47] although aldehydes (acetaldehyde) were observed as minor products in our experiments (detected only under oxidative pyrolysis).

Group 2: Many of the reaction products detected in this group were mainly oxygenated products, with the major product being propiolactone (reached maximum concentration at about 400 °C) (cf. Figure 2B). An analogous reaction in the presence of water suggested direct deamination occurs via an internal S_N2 mechanism, yielding ammonia and propiolactone.[48] Ethanol and acetic acid were the other oxygenated products observed in this group.

Group 3 comprised the products that are formed above 450 °C and includes 5-methylpyridine, acetonitrile, and maleimide as the principal products (cf. Figure 2C). These products appear to be formed from the thermal decomposition of major products such as succinimide. Early studies postulated pyrolysis of succinimide yielded mainly CO, H_2O, and acetonitrile.[49] This may suggest a secondary route for the formation of acetonitrile. Choud et al. proposed an activation energy of 52 kcal/mol for the ring-opening of succinimide.[49] Subsequently, the ring-opening of succinimide facilitates its decomposition to other poducts including acetonitrile and HCN.

Succinimide was the most abundant product, contributing >40% of the total products quantified from oxidative pyrolysis. The order of abundance for the major reaction products from the thermal degradation of glutamic acid can be seen clearly in the bar graph of Figure 4.

As can be observed from Figure 3 (overlay spectra for pyrolysis and oxidative pyrolysis at 400 °C), pyrolysis and oxidative pyrolysis yielded similar reaction products of different intensities. It is clear from the chromatograms (cf. Figure 3) that although some products were favored by an inert regime (N_2), some were favored by a reactive regime (oxidative). Therefore, a comparison between three major compounds, pyrrole, succinimide, and 3*H*-pyrrolo[2,3-*d*]pyrimidin-4(7*H*)-one, revealed interesting results. Under pyrolysis at 400 °C, for instance, 3*H*-pyrrolo[2,3-*d*]pyrimidin-4(7*H*)-one and pyrrole were exclusively the major products, whereas for oxidative pyrolysis at the same temperature, succinimide was the principal component.

Succinimide was the dominant reaction product from the oxidative pyrolysis of glutamic acid according to Figure 4. The concentration of succinimide was 4 times higher in oxidative pyrolysis compared to pyrolysis. On the other hand, pyrrole was 3 times higher in pyrolysis than in oxidative pyrolysis. Whereas most of the reaction products (succinimide, pyrrole, and 2-pyrrolidone) appear to be formed at low temperature (cf. Figures 1A and 2A), other reaction products (maleimide and acetonitrile) were formed at higher temperatures (cf. Figures 1B–D and 2B).

Decomposition Profile for Glutamic Acid. The decomposition profiles for glutamic acid for both pyrolysis and oxidative experiments were similar (cf. Figure 5). Consequently, glutamic acid appears to exhibit a single decomposition regime, starting at 300 °C and ending at 600 °C. The highest rate of decomposition for oxidative pyrolysis was realized between 300 and 350 °C with a mass loss of 22.4%, whereas the highest rate of decomposition for pyrolysis was achieved between 400 and 450 °C with a mass loss of 21.4%. At the end of the experiment (600 °C), the mass losses for pyrolysis and oxidative pyrolysis were 75.4 and 81.3%, respectively. This suggests that glutamic acid has a higher residue content than most biomass materials such as tyrosine and cellulose[16,50]

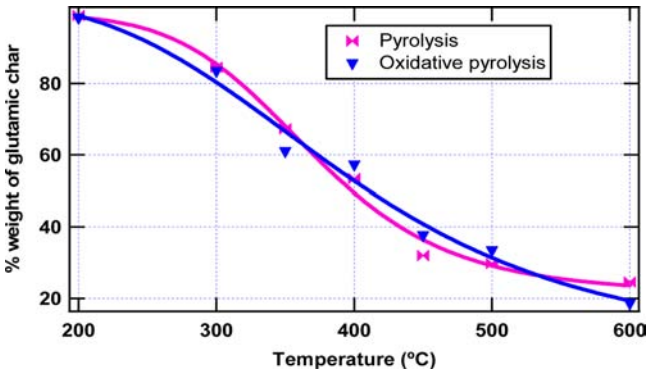


Figure 5. Weight percent yield of glutamic acid char as a function of temperature.

An observation of glutamic acid after heat treatment revealed a waxy substance (probably polyglutamic acid or diketopiperazine) that stuck to the walls of the reactor. Accordingly, this would imply the gas–solid interface changes during heat treatment and any pores present in the sample disappear so that oxygen acts only on the surface but does not penetrate into the matrix of the (polymer) sample.[50,51] Thus, the degradation of glutamic acid is independent of oxidative reactions.[50] Consequently, we believe the mass loss due to an oxidizing and an inert environment will certainly not change significantly in the entire temperature range. For comparison, it was observed that the mass loss of cellulose below 300 °C was due to oxidative reactions, but at temperatures above 300 °C the rate of pyrolysis was essentially the same in both air and nitrogen, indicating thermal degradation is independent of oxidative reactions.[50,51] This observation is remarkable and agrees well with observations made during the thermal degradation of glutamic acid.

Mechanistic Description. The major reactions for glutamic acid are dehydration, decarboxylation, and deamination.[18] Glutamic acid contains two acidic ($-CO_2H$) groups and one basic ($-NH_2$) group, which can react to form large molecules at high temperature.[3,52] Therefore, different functional groups are expected to have different pyrolysis characteristics as well as to give different pyrolysis products.[53] For example, at low temperatures (about 300 °C) low molecular weight heterocyclic compounds are formed, whereas at high temperatures (≥500 °C), polycyclic aromatic hydrocarbons are expected to form.[31]

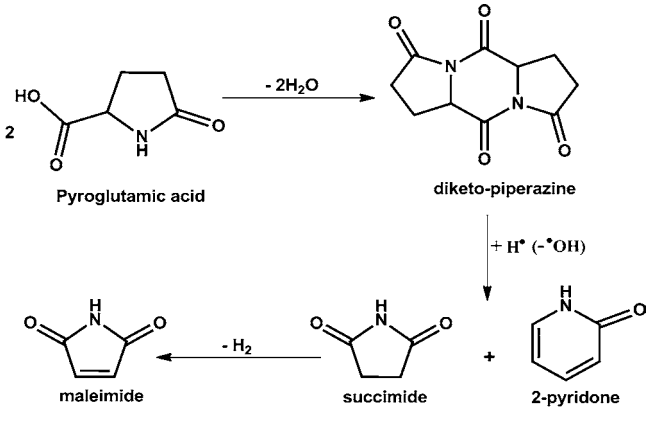
Decarboxylation Reactions for Amino Acids. The mechanistic considerations for pyrolysis experiments of amino

acids have been extensively studied.[3,16,34,46,47,54,55] More recently, a statistical mechanical investigation (QM/MM) has shown that the most likely pathway for decomposition of amino acids occurs via direct decarboxylation, where CO_2 departure is the first as well as the rate-determining step.[48] The use of ^{14}C-labeled amino acids provides excellent evidence that decarboxylation is the predominant decomposition pathway for amino acids.[35] Decarboxylation reactions of amino acids yield an amine as the major product[35] and clearly constitute the major decomposition pathway as evidenced from the yield of CO_2.[47]

Mechanistic Channel for Formation of Succinimide and Maleimide. The major product during fractional pyrolysis as well fractional oxidative pyrolysis was succinimide, surprisingly nondetected in previous studies.[31] Our studies, however, have since shown that pyrolysis of glutamic acid in N_2 and 4% O_2 in N_2 would in fact yield succinimide and maleimide. Maleimide was formed in much lower amounts than succinimide. The yields of maleimide did not change significantly when the pyrolysis environment was changed from N_2 to 4% O_2 in N_2 (Figures 1D and 2). Succinimide was exclusively the major product under oxidative pyrolysis, contributing about 40% of the products analyzed, whereas under pyrolysis it contributed >20% of the products analyzed. Whereas previously succinimide has been detected from the thermal degradation of aspartic acid, asparagine, and glutamine, no succinimide has been detected from the thermal degradation of glutamic acid.[31] The mechanistic channel for succinimide and maleimide formation from aspartic and asparagine is known, however; succinimide and maleimide formation from glutamine and glutamic acid is not yet understood.[31]

Succinimide and maleimide, nevertheless, are structures that are characteristic of amino acids with additional carboxylic or amino functional groups.[3] Accordingly, we propose the formation of succinimide proceeds via an intermediate, tricyclic diketopiperazine (DKP), which is a highly unstable intermediate evidenced in the literature.[31] We hypothesize that DKP would eventually decompose to succinimide and 2-pyridone in the presence of hydrogen atoms pool through the reactions of the addition of H to DKP and further disproportionation reactions (cf. Scheme 1). From this pathway, maleimide appears to be formed from the dehydrogenation of succinimide and may explain why succinimide was formed in higher concentrations than maleimide. It was previously proven experimentally by Sharma et al. that direct degradation of succinmide yielded maleimide.[31]

Scheme 1. Formation of Diketopiperazine (DKP) from Pyroglutamic Acid and of Succinimide and Maleimde from the Unstable DKP Intermediate



The formation of DKP requires two molecules of pyroglutamic acid.[31] This product forms in trace and significant amounts in pyrolysis and oxidative pyrolysis, respectively (Figure 3). Peptide-forming reactions occur readily because they involve simple dehydration reactions.[31] DKPs also form promptly upon heat treatment of proteinaceous foods.[15] In principle, peptides will be nondetectable intermediates in amino acid pyrolysis because of their high thermal reactivity and low volatility, which keeps them in the thermal zone until they react further.[31] Consequently, we postulate DKP thermally degrades to succinimide and 2-pyridone (cf. Scheme 1). 2-Pyridone was one of the major products from the thermal degradation of glutamic acid under pyrolysis but a minor product under oxidative pyrolysis. This is because, although an oxidizing environment accelerates the formation of pyrolysis products, it may also oxidize certain reaction products into water, CO, or CO_2 and subsequently decrease their yields.

Scheme 1 predicts equal amounts of succinimide and 2-pyridone. Experimentally it was found the yields of succinimide prevailed over the yields of 2-pyridone by a factor of 2. This may be possible because 2-pyridone is susceptible to hydrogenation in the presence of an abundant pool of hydrogen atoms in pyrolysis and char. Also, the high polarizability of 2-pyridone[56] in comparison with succinimide (symmetric structure)[57] enhances its absorptivity on the GC column and consequently minimizes its detection. The marked difference in yields between succinimide and 2-pyridone is evident in oxidative pyrolysis. 2-Pyridone may be easily oxidized by oxygen or most importantly by abundant hydroxyl radicals (characteristic of oxidative processes) into water, CO, or CO_2 and subsequently decrease its yield, making it a minor product.

The key finding during oxidation is that the yield of succinimide increases rapidly, predominating over all other product yields significantly (Figure 4). Pyroglutamic acid, an important precursor for the formation of succinimide, was observed experimentally in detectable amounts in oxidative conditions (Figure 3, blue chromatogram at RT ~ 17.3 min) but in trace amounts under pyrolytic conditions. As an important intermediate product, pyroglutamic acid may form from internal cyclization of glutamic acid via dehydration processes.[2,58,59] Dehydration is a very common reaction for amino acids and may occur in the gas phase through a four-centered concerted mechanism as presented in the Supporting Information provided with this paper. It is expected that hydroxyl radicals during oxidative pyrolysis will facilitate this concerted mechanism toward the formation of pyroglutamic acid (by increasing the polarizability of the hydroxyl O−H bond in the carboxylic group).

Mechanistic Pathways for the Formation of Pyrrole and Methylated Pyrroles. The thermal degradation of glutamic acid appears to be a major process in the pyrosynthesis of not only succinimide but also pyrroles (pyrrole, 2-methylpyrrole, 2,4-dimethylpyrrole, and 2,5-dimethylpyrrole). The production of pyrrole from glutamic acid clearly indicates one carboxyl group is lost as carbon dioxide (cf. Scheme 2), whereas the second carboxyl group is incorporated into the 2-pyrrrolidone ring before converting to pyrrole.[42,43] In this study, we propose the precursor for the formation of pyrrole is pyroglutamic acid through the formation of 2-pyrrolidone. Pyrrole ultimately undergoes methylation to

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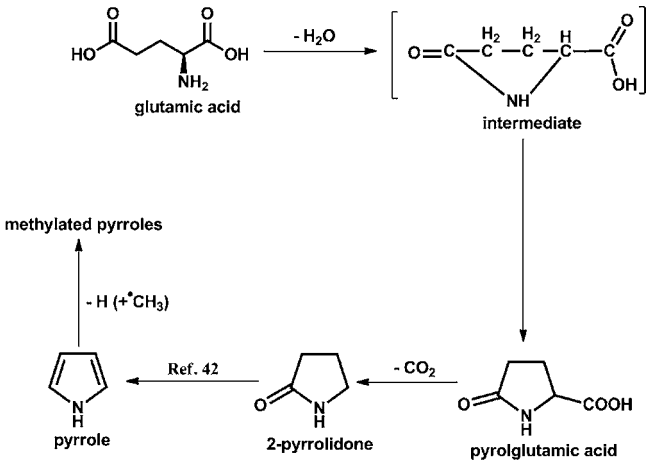
Scheme 2. Proposed Mechanism for the Formation of Pyroglutamic Acid, 2-Pyrrolidone, Pyrrole, and Methylated Pyrroles[42,43]



form 2-methylpyrrole and 2,5-dimethylpyrrole as indicated in Scheme 2.

It was proposed previously that pyrrole decomposes to yield predominantly HCN in addition to hydrocarbon products.[60] This implies the pyrrole yield peaks at lower temperatures, whereas that of HCN and hydrocarbons (propane, propene, etc.) is expected to peak at high temperatures, remarkably consistent with the results presented in this study.

Toxicological Consequences of Molecular Products. Whereas succinimide, 2-pyrrolidone, and maleimide have no known toxicological impacts,[61,62] HCN, acetonitrile, acrylonitrile, and benzene are known to be precursors for health-related problems.[63,64] The biological activity of HCN has mostly been correlated with the inhibition of the terminal cytochrome oxidase in the mitochondrial respiratory pathway and attacks the nervous system and thyroid glands.[63] Acrylonitrile is known to cause respiratory effects, whereas benzene is an established human carcinogen.[65,66] Acetonitrile (methyl cyanide) upon ingestion can lead to mental abnormalities, lethargy, tightness of the chest, and vomiting.[67,68] In the gas phase, acetonitrile has a very high ability to convert to the highly toxic compounds hydrogen cyanide and cyanogen.[68] Additionally, acetonitrile is an Environmental Protection Agency (EPA)-classified toxic compound.[68] There is no clear record in the literature that pyrrole is toxic; nevertheless, it is an important precursor for the formation of the toxic compounds hydrogen cyanide and acetonitrile.[60] The toxicological effects of some of the molecular products analyzed in this study, including those that were not analyzed but believed to be formed (ammonia, HNCO, NO(x), and CO), are critical for understanding biomass burning, cigarette smoking, and high-temperature cooking of proteinaceous foods.

This study proposes that the major product succinimide from pyrolysis and oxidative pyrolysis of glutamic acid may actually be formed from the thermal degradation of the intermediate peptide, a tricyclic diketopiperazine (DKP). We conclude pyroglutamic acid is an important intermediate product from the thermal degradation of glutamic acid, which polymerizes to diketopiperazine before ultimately decomposing to high yields of succinimide, especially during oxidative pyrolysis. Maleimide, which was also detected for the first time, is most probably a minor product resulting from the dehydrogenation of succinimide as predicted in the literature.

■ ASSOCIATED CONTENT

Supporting Information

Hydrocarbon products from pyrolysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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