Abiotic Asparagine Formation from Simple Amino Acids by Contact Glow Discharge Electrolysis

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(Received December 13, 1996)

Asparagine, one of the most important amino acids for prebiotic peptide formation in aqueous media, was formed using Contact Glow Discharge Electrolysis (CGDE) against aqueous solutions containing simple amino acids and carboxylic acid amides.

Many simulative experiments on the prebiotic formation of amino acids have been carried out over the last forty years since Miller's experiments.[1,2] However, the formation of asparagine and glutamine as well as basic amino acids is still under discussion.[3-5] Among the twenty protein amino acids, only glycine[6] and asparagine[7-9] can polymerize by itself, respectively, in aqueous media without catalysts upon heating . The resulting polyglycines might not have been important for protein-precursor formation in aqueous environment on the primimitive Earth, since the longer polyglycines than tetramer are not very soluble (solubility < 1 mM) in aqueous media at neutral pH and room temperature. On the other hand, asparagine forms polyaspartic acids[7-9] which are quite water-soluble. In addition, asparagine can act as glue linking to other amino acids.[9,10] In spite of having such significant roles during prebiotic peptide formation, prebiotic formation of asparagine has not been understood well. Harada et al. carried out the amination of succinic acid mono-amide (yield of asparagine was 1.1%) by Contact Glow Discharge Electrolysis (CGDE).[11] Sanchez et al. Reported asparagine formation (5-10 %) using cyanoacetylene[12] which is a typical product in many electric discharge experiments using gas mixtures containing methane and nitrogen. However, it has been noticed that such a reducing atmosphere containing methane had not existed on the primitive Earth.[13-17]

In this paper, we wish to report the formation of asparagine from aqueous solutions containing simple amino acids and carboxylic acid amides by contact glow discharge electrolysis (CGDE), which is a suitable method[18,19] for simulating lightning between the atmosphere and the hydrosphere of the primitive Earth. We have chosen three amino acids (glycine: Gly, alanine: Ala, β-alanine: β-Ala) and two carboxylic acid amides (formamide, acetamide) as the substrates for the CGDE reactions. The three amino acids are abundant in the carbonaceous meteorites[20-22] and the two carboxylic acid amides are the hydrolyzed products of nitriles which are considered to be important starting materials for prebiotic amino acid formation.[3]

The reaction apparatus is shown in Figure 1. CGDE was carried out against 20 ml aqueous solutions containing an amino acid (Gly, Ala, or β-Ala), a carboxylic acid amide (formamide or acetamide), and 12 mM H_2SO_4 under an argon stream. The reaction solution was stirred during the CGDE experiments and pH of the reaction solution was maintained in the range between 2.5 and 3.0. The glass apparatus was cooled[18] in an ice-water bath to maintain the temperature at 0-10 °C. A known volume of reaction solution was taken from the solution at 30 min interval and was analyzed with an amino acid analyzer.

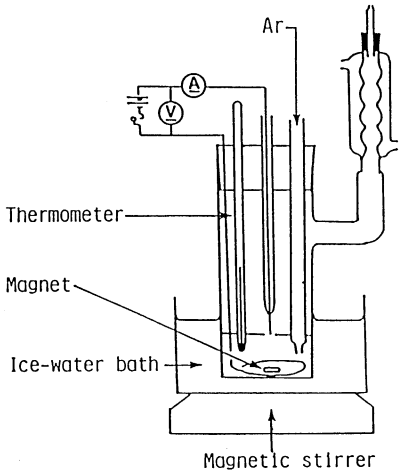


Figure 1. Apparatus for contact glow discharge electrolysis.

In the case of 100 mM Gly and 200 mM acetamide, glycine decomposed and ammonia was formed with the increasing time of CGDE (460 V, 20 mA). No other amino acids than Gly were detected at all during 240 min of CGDE with the amino acid analyzer.

Figure 2 shows the time course of the reaction using 100 mM Ala and 200 mM formamide by CGDE (520 V, 20 mA). Alanine

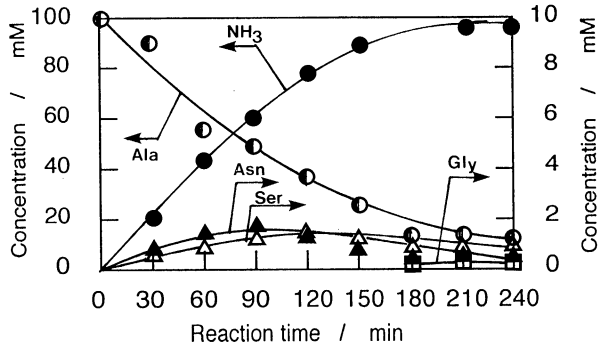


Figure 2. Time course of the reaction using Ala (100 mM) and formamide (200 mM) by CGDE (520 V, 20 mA).

decomposed to 20% of the original amount and a significant amount of ammonia was formed after 240 min of reaction. The ammonia formation could be explained by the decomposition of Ala and formamide. On the other hand, the yield (1.5 mM) of Asn reached 3% of the reacted Ala during 90 min and serine (Ser) was formed up to 1.8% of the reacted Ala during 120 min. It is possible to explain that Asn was formed by alkylation of the methyl group of Ala with formamide and Ser was formed by the oxidation due to hydroxyl radical. In addtion, Gly formed later than 180 min seemed to be produced by the decomposition[18] of Asn, Ser, or Ala.

The reaction using a solution of 100 mM β-Ala and 200 mM formamide was also carried out by CGDE (520 V, 30 mA). The time course is shown in Figure 3. While Asn was not detected, *iso*-Asn (0.14%, 90 min), ammonia, *iso*-Ser (1.4%, 150 min), and Gly (16%, 180min) were formed in this reaction. An unknown peak supposed to be another isomer of *iso*-Asn was

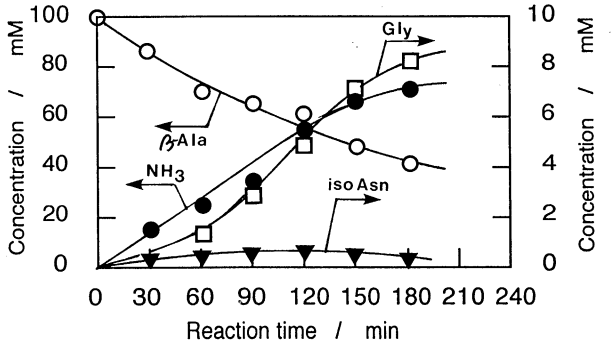
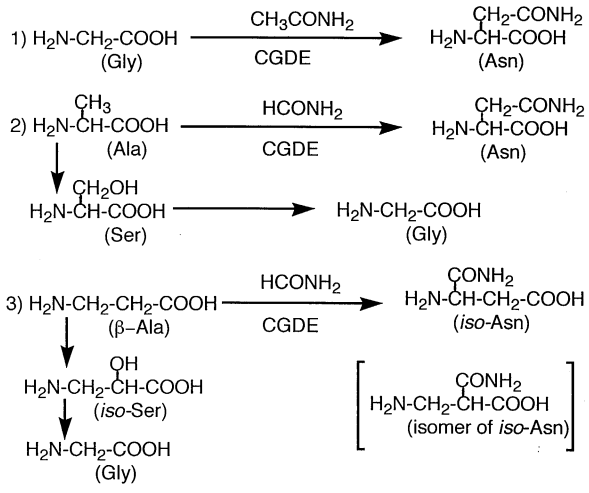


Figure 3. Time course of the reaction using β–Ala (100 mM) and formamide (200 mM) by CGDE (520 V, 30 mA).



Scheme 1. Possible reaction pathways.

detected on the amino acid chromatogram. The possible pathways of the CGDE reactions of this study are sumarized in Scheme 1.

In conclusion, this study has demonstrated that asparagine can be formed by alkylation of alanine with formamide during CGDE. The result indicates that lightning against the primitive hydrosphere containing alanine and formamide could have produced asparagine.

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