

# AMINO ACIDS DERIVATIVES SYNTHESIS FROM NITROGEN, CARBON AND WATER BY ELECTRIC DISCHARGES

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**Abstract.** Electric discharges between a pair of carbon electrodes were continued for 50 days in a vessel of 5 liters in volume which initially contained nitrogen at a pressure of 15 cm Hg and 200 ml of water. The pressure in the vessel was gradually increased to 60 cm Hg at the end of the run. Gas chromatographic analysis showed that the increase of the pressure mainly results from the production of hydrogen and carbon monoxide. The concentration of ammonia in the aqueous sample was increased to 0.05 *M* in 50 days of the discharge. After hydrolysis, glycine and serine were detected at the concentrations of  $3.4 \times 10^{-3}$  *M* and  $0.057 \times 10^{-3}$  *M* in the final solution, respectively, though glycine was found only at the concentration of  $6 \times 10^{-6}$  *M* before hydrolysis. TLC analysis indicated the presence of hydantoic acid, N-formylglycine, diketopiperazine, and polymers of glycine.

Since Miller (1953, 1955) demonstrated the synthesis of amino acids and other organic compounds from ammonia, methane, hydrogen, and water by electric discharges. Similar experiments were performed using various kinds of gas mixtures and energy sources, and the evidence that amino acids are produced if the gas mixtures are in a reducing condition as a whole has been accumulated (Keosian, 1968; Abelson, 1956). However, the volcanic gases of the primitive Earth would not have been reducing enough to form amino acids, as discussed by Rubey (1955). Recently Matsuo (1978) discussed the possibility of the existence of graphite on the primitive Earth, which might have produced a local reducing condition necessary to form organic materials. Harada and Suzuki (1977) reported the formation of amino acids from carbon by means of contact glow discharges at the surface of water under the supply of ammonia which means a considerably reducing condition of the experimental system. We report here the formation of amino acid derivatives by electric discharges between carbon electrodes in nitrogen and water vapour which are neutral with regard to the oxidation-reduction condition.

A discharge vessel of 5-liter flask was prepared with nitrogen at a pressure of 15 cm Hg and 200 ml of water which was refluxed by a heating mantle during the discharge. The discharge was induced by a neon-sign transformer (15 kV) at about 4 cm gap between a pair of carbon electrodes (5 mm  $\varnothing$ ). The primary voltage of the neon-sign transformer and the power supply to the heating mantle were controlled so that the running pressure was kept lower than the atmospheric pressure. The pressure in the vessel measured at room temperature was gradually increased with the discharge time (Figure 1).

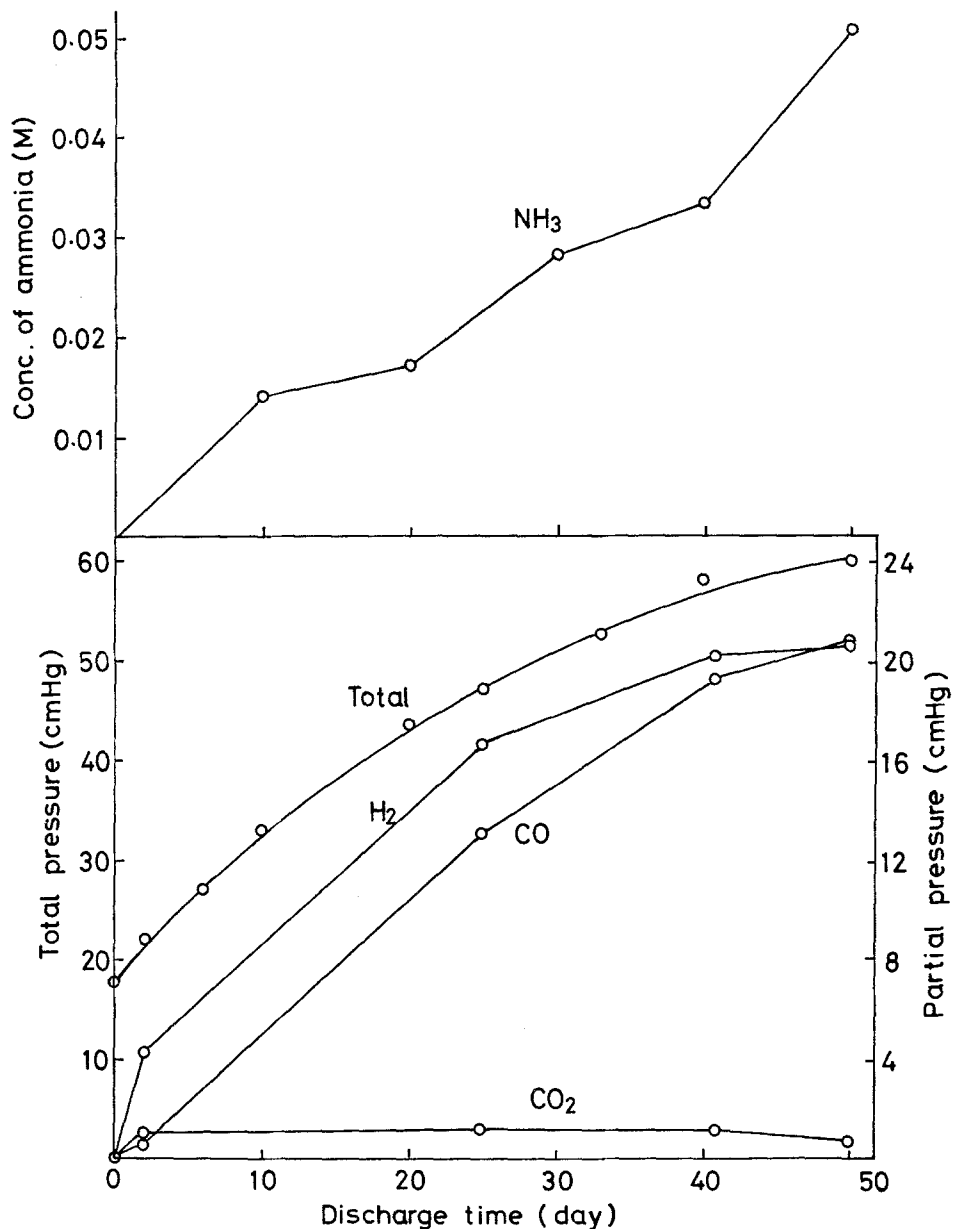


Fig. 1. Change of total and partial pressure and concentration of ammonia produced during discharge.

Gas chromatographic analysis (Shimazu Model GC-6APTF; column: active carbon 3 mm  $\times$  3 m; column temperature 40°–200°C; carrier gas He, 40 ml min<sup>-1</sup>) of the gas component (0.2 ml at atmospheric pressure) indicated the production of hydrogen, carbon monoxide, and carbon dioxide (Figure 2). Methane could not be detected. The results of the gas chromatogram showed that the increase of the pres-

sure is mainly a result of the production of hydrogen and carbon monoxide, and carbon dioxide exists only at a very low level (Figure 1). The partial pressure of nitrogen should have been decreased to about 85% of the initial pressure at the end of the run by mainly the production of ammonia and urea as will be described later, but the decrease could not be confirmed quantitatively because of the experimental errors including the contamination of the air during the sampling of gas at a lower pressure than the atmosphere (Figure 2).

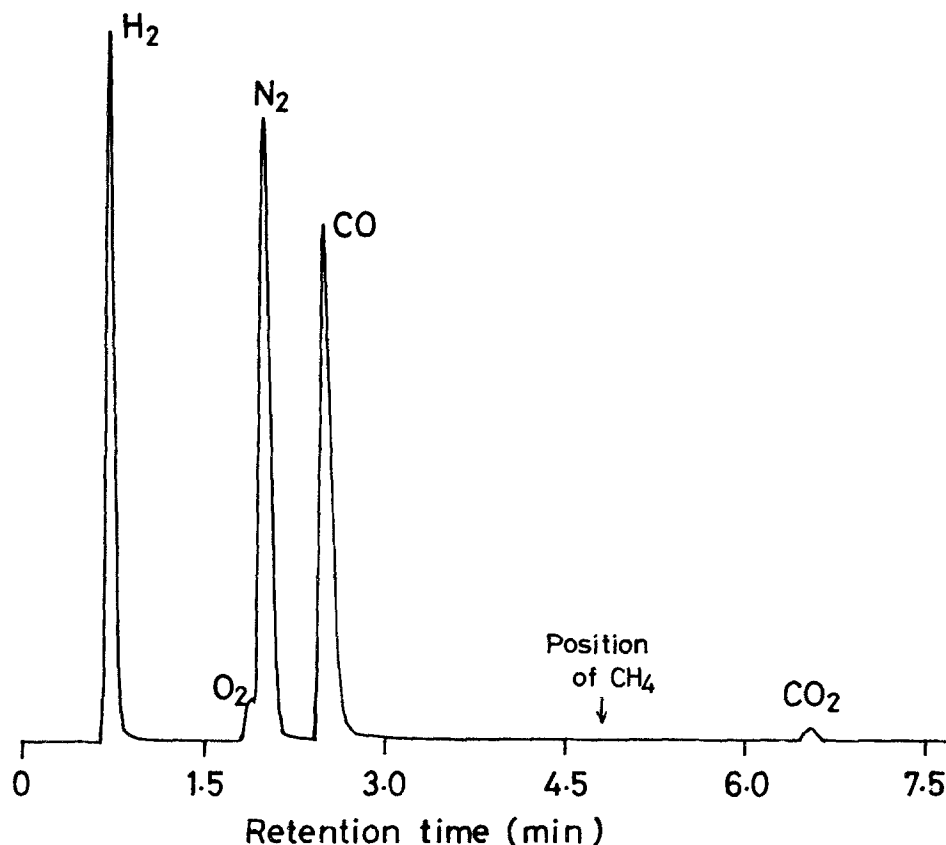


Fig. 2. Gas chromatogram of gas components at 50 days of discharge. Sensitivity of detector for hydrogen peak is forty times larger than for the others. Oxygen indicates the contamination of air during the sampling.

Each 10 ml of the aqueous sample was pumped out in each ten days after the start of the discharge, and the concentration of ammonia (or ammonium ion) was estimated by the titration of dilute sulfuric acid which absorbed ammonia ejected from the sample by adding sodium hydroxyde (Figure 1). The ammonia free final solution was analyzed with an amino acid analyzer (Hitachi 835). The chromatogram revealed only a very small peak corresponding to glycine, from which the concentration is estimated to be about  $6 \times 10^{-6} M$ , besides several unknown ninhydrin positive

peaks. After hydrolysis (90°C, 15 h) of the sample with 5N sodium hydroxide, however, the chromatogram showed the presence of glycine and serine, and the concentrations in the final solution were estimated to be  $3.4 \times 10^{-3} M$  and  $0.057 \times 10^{-3} M$ , respectively. The presence of glycine was also confirmed on a silica gel TLC.

These results indicate the production of some N-blocked glycine and serine derivatives. In fact, the products behaving like hydantoic acid (N-carbamoylglycine), N-formylglycine and 2,5-diketopiperazine were observed on silica gel TLC (1st solvent; isobutyric acid, 2nd solvent; ethyl acetate 10: acetic acid 4) by using the color development with ninhydrin after hydrolysis by spraying 6N HCl on to the plate, followed by heating at 100°C for 10 h. A ninhydrin positive spot was also observed at the origin, which seems to be polymers of glycine. Further, a part of the final solution was evaporated to dryness and the residue was treated (75°C, 5 h) with p-nitrobenzyl bromide and triethylamine in N, N-dimethyl-formamide (Fosker and Law, 1965). UV-Absorbing spots corresponding to p-nitrobenzyl ester of hydantoic acid and N-formylglycine were found on silica gel TLC (solvent, ethyl acetate 9: ethanol 1), besides several unknown spots.

Hydantoic acid is formed by the reaction of glycine with cyanic acid,



Support of the formation of cyanic acid was found in the detection of urea, which is formed by the reaction of cyanic acid and ammonia. The concentration of urea was estimated by the amount of ammonia produced by an addition of urease to be 0.02 M in the final solution. N-formylglycine might be produced by the condensation

reaction,  $\text{HCOOH} + \text{H}_2\text{N}-\text{CH}_2-\text{COOH} \rightarrow \text{HC}-\overset{\text{O}}{\parallel}{\text{N}}-\text{CH}_2-\text{COOH}$ . Formic acid was detected on silica gel TLC (solvent, ethanol 77: concd. ammonia 23) as a black spot developed by spraying ammonia solution of silver nitrate (silver mirror reaction). From the comparison with standard ammonium formate, the concentration of formate was estimated to be about 0.008 M in the final solution.

The absence of other amino acids, especially of alanine, a high concentration of which was produced in Miller's (1955) experiment, can be explained by the absence of methane in the present experiment. The preferential production of serine relative to other amino acids is presumably a result of the addition reaction of glycine to formaldehyde (Miller and Orgel, 1974).

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