

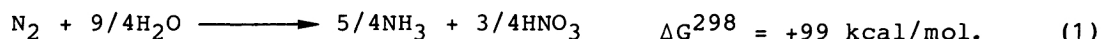
Fixation of Molecular Nitrogen Using Aliphatic Carboxylic Acid by
Nitrogen Arc Plasma. Formation of Amino Acids

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When argon-nitrogen plasma was blown into an aqueous solution containing aliphatic carboxylic acids, formation of several amino acids and amines was identified.

The reductive fixation of molecular nitrogen with hydrogen is well known (Harber-Bosch method), and the reaction is thermodynamically favored. However, the reduction of nitrogen to ammonia with water is fundamentally difficult, because of the large positive ΔG value of the reaction as shown in Eq. 1



Photolyses of molecular nitrogen in the presence of catalysts^{1,2)} and hydrolyses of nitrogen-metal complexes³⁾ are known as possible methods to produce ammonia in an aqueous solution. However, little study has been reported on the reductive fixation of molecular nitrogen with water in the absence of catalyst.⁴⁾

In the previous study,⁵⁾ the formation of ammonia, NO_2^- , and NO_3^- from molecular nitrogen and water by using arc plasma containing nitrogen gas was demonstrated. This is a kind of disproportionation reaction of molecular nitrogen carried out at high energy conditions. In the present study, the formation of amino acids was confirmed on the introduction of nitrogen arc plasma into aqueous solution of various aliphatic carboxylic acids.

The apparatus used for the amination of carboxylic acids by using molecular nitrogen in an aqueous solution is similar to that shown in the previous communication.⁵⁾ Plasma jet generated by arc electric discharge through the flowing nitrogen gas was used as an energy and a nitrogen source for the reaction. In order to stabilize the generated nitrogen arc plasma, various amounts of argon gas were previously mixed with nitrogen gas. The plasma torch was immersed in the aqueous solution 1 cm below the surface and the plasma jet was directly applied into the solution. Nitrogen gas was previously bubbled through the reaction solution in order to remove the dissolved oxygen and the reaction was carried out under nitrogen-argon atmosphere with stirring. Analyses of the products were carried out by an amino acid analyzer and an isotacophoretic analyzer. A part of the reaction mixture was evaporated and the residue was treated with isopropanol/HCl and then trifluoroacetic anhydride(TFAA). The resulting TFA-amino acid isopropyl esters were analyzed by gas chromatography using a chiral stationary phase (Chirasil-Val).

As a typical example, the time course of the formation of amino compounds from an aqueous acetic acid solution (0.3 mol/l) is shown in Fig. 1. The flow

rates of nitrogen and argon gases were 0.6 l/min and 1.4 l/min, respectively. The main amino compounds produced were glycine (198 $\mu\text{mol/l}$) and methylamine (51 $\mu\text{mol/l}$). In addition to these, aspartic acid, β -alanine, formic acid, succinic acid, glycolic acid, oxalic acid and glyoxylic acid were also obtained in the reaction mixture. In order to examine the participation of ammonia produced by the action of nitrogen arc plasma in the amination reaction of acetic acid, argon arc plasma containing no nitrogen gas was directly applied into the aqueous acetic acid solution (0.3 mol/l) containing ammonium acetate (10 mmol/l). The concentration of glycine produced was only 3 $\mu\text{mol/l}$ after 180 min. The result indicates that the ammonia produced in an aqueous solution would contribute little to the formation of amino compounds by nitrogen arc plasma.

Figure 2 shows the time course of the formation of amino compounds from propionic acid (0.3 mol/l). The formation of β -alanine, alanine, ethylamine, methylamine, glycine and serine was observed. The maximum concentration of β -alanine and glycine reach 357 and 186 $\mu\text{mol/l}$, respectively. Other carboxylic acids used for the reductive fixation of molecular nitrogen using arc plasma were acrylic acid, propiolic acid, succinic acid and maleic acid. The results in which the highest yields were obtained are shown in Table 1. In each reaction, amination reactions of substrates proceeded to afford the corresponding amino acids. Particularly, the concentration of amino compounds detected reached 2 mmol/l in the reaction of acrylic acid. From the gas chromatographic analysis using a chiral stationary phase, it was confirmed that alanine and serine obtained from acrylic acid or propionic acid were racemates. This result indicates that amino acids obtained in the reaction mixtures were synthesized by the nitrogen fixation and not by bacterial activity or contamination.

The nitrogen plasma-induced reaction in an aqueous solution is a new type fixation of molecular nitrogen without using any catalyst, and is an unusual

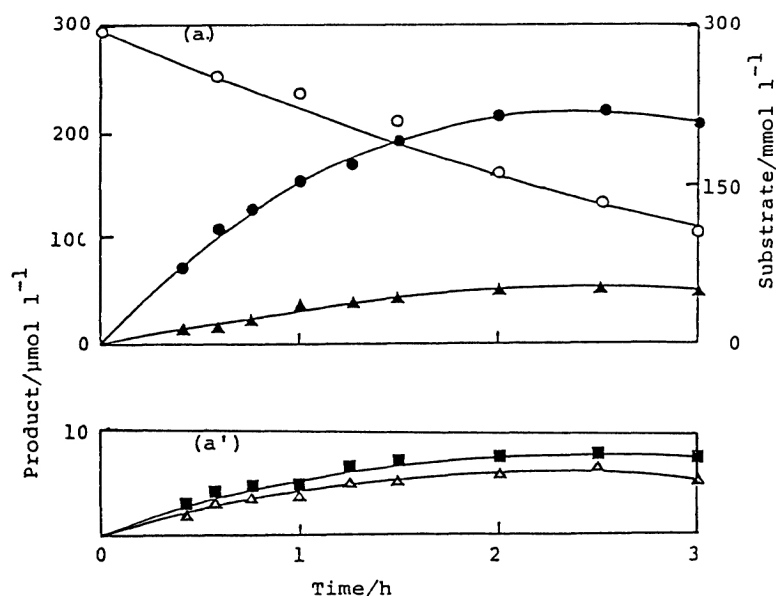


Fig. 1.

Formation of amino compounds (a and a') from acetic acid (300 mmol/l) in aqueous solution (pH, 2.6) induced by nitrogen arc plasma (nitrogen gas, 0.6 l/min; argon gas, 1.4 l/min). Acetic acid: \circ , glycine: \bullet , methylamine: \blacktriangle , aspartic acid: \blacksquare , β -alanine: \triangle .

Table 1. Formation of amino acids induced by nitrogen arc plasma^{a)}

Starting materials ^{b)}	Produced amino acids ^{c)} ($\mu\text{mol/l}$)							Other amino compounds ($\mu\text{mol/l}$)	
1 CH_3COOH	Asp (7)	Gly (198)	β -Ala (6)					MeNH ₂ (51)	
2 $\text{CH}_3\text{CH}_2\text{COOH}$	Ser (13)	Gly (15)	Ala (186)	i-Ser (6)	β -Ala (357)			MeNH ₂ (31)	EtNH ₂ (81)
3 $\text{CH}_2=\text{CHCOOH}$	α -Formylgly (105)		Ser (194)	Gly (66)	Ala (1159)	i-Ser (63)	β -Ala (284)	MeNH ₂ (56)	EtNH ₂ (168)
4 $\text{CH}\equiv\text{C}-\text{COOH}$	Ser (17)	Gly (58)	Ala (77)	i-Ser (6)	β -Ala (18)			MeNH ₂ (12)	EtNH ₂ (168)
5 $\begin{array}{c} \text{CH}_2-\text{COOH} \\ \\ \text{CH}_2-\text{COOH} \end{array}$	Asp (210)	OH-Asp (75)	Gly (27)	Ala (12)	β -Ala (56)			MeNH ₂ (7)	
6 $\begin{array}{c} \text{CH}-\text{COOH} \\ \\ \text{CH}-\text{COOH} \end{array}$	Asp (443)	OH-Asp (382)	Ser (7)	Gly (219)	Ala (17)	i-Ser (17)	β -Ala (22)	MeNH ₂ (7)	

a) Conditions to produce plasma jet: flow rate of nitrogen gas, 0.6 l/min; argon gas, 1.4 l/min; electric current, 40 A; electric voltage, 10 V. Reaction conditions: reaction time, 180 min; solution volume, 350 ml; reaction temperature, 40 - 50 °C. b) Concentration of the starting materials, 0.3 mol/l. c) Products were analyzed by amino acid analyzer (Irica-A300). Asp: aspartic acid, Thr: threonine, Ser: serine, Glu: glutamic acid, Gly: glycine, Ala: alanine, β -Ala: β -alanine, i-Ser: isoserine, α -Formylgly: α -formylglycine, OH-Asp: β -hydroxyaspartic acid, MeNH₂: methylamine, EtNH₂: ethylamine.

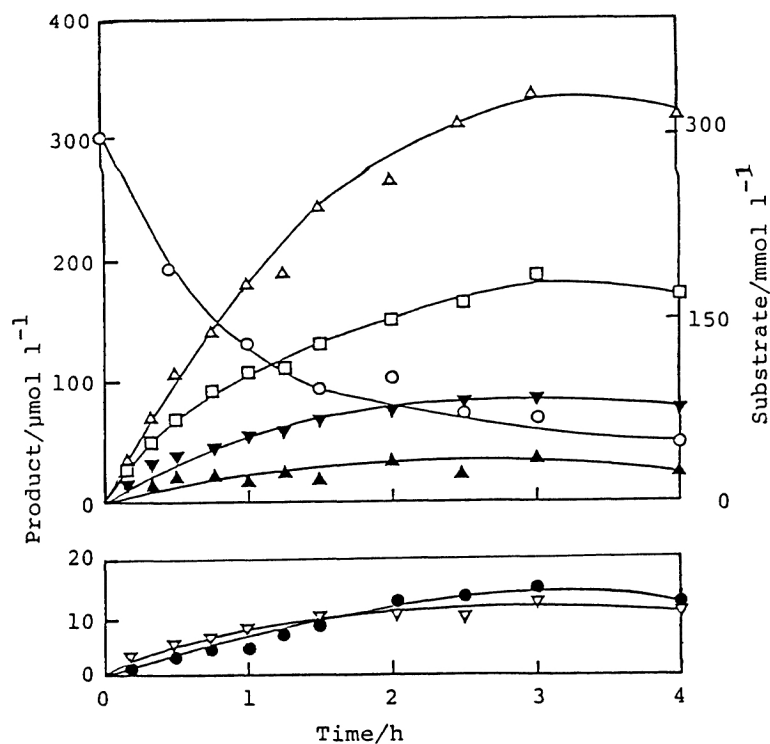


Fig. 2.

Formation of amino compounds from propionic acid (300 mmol/l) in aqueous solution (pH, 2.7) induced by nitrogen arc plasma (nitrogen gas, 0.6 l/min; argon gas, 1.4 l/min). Propionic acid:

○, β -alanine: △, alanine: □, ethylamine: ▼, methylamine: ▲, glycine: ●, serine: ▽.

disproportionation reaction which affords oxidized and reduced nitrogen products simultaneously. These chemical behaviors are considered to be due to the action of localized high energy. At the present time, the active species are considered to be nitrogen atoms which is generated in a plasma jet.⁷⁾ Nitrogen atoms produced could react with hydrogen atoms or hydroxyl radicals, which are produced by the decomposition of water molecules, to afford ammonia and nitrous acid in an aqueous solution. Nitrous acid could readily be converted into nitric acid under these conditions. The intermediates to produce ammonia, such as NH or NH₂ radicals, could react with aliphatic carboxylic acids to afford amino acids. Indeed, the ratio of alanine : β -alanine produced from propionic acid (1 : 1.9) was similar to that in the NH radical reaction (1 : 1.6).⁷⁾

The results obtained would also be interesting in connection with the origins of ammonia, amino acids, nitrous acid and nitric acid on the primitive Earth. The primitive atmosphere of the Earth has been considered to be a result of planetary outgassing, and the main components of this were considered to be CO₂, H₂O, and N₂ ("non-reducing atmosphere").⁸⁻¹¹⁾ In these conditions, high energy plasma containing nitrogen gas could be generated by the action of lightning, atmospheric entry of meteors and meteorites, or radiation of solar winds or cosmic rays on the primitive sea. Therefore, the nitrogen plasma-induced reaction in an aqueous solution could be regarded as a model experiment of the chemical reactions of the molecular nitrogen in the "non-reducing atmosphere" on the primitive Earth.

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