Reductive Fixation of Molecular Nitrogen by Glow Discharge against Water

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The reductive fixation of molecular nitrogen by glow discharge against water resulted in the formation of ammonia; amino compounds were also formed when the aqueous solution contained carboxylic acids.

Molecular nitrogen is one of the most inert diatomic molecules, and the reductive fixation of molecular nitrogen with water is thermodynamically difficult because of the large ΔG° value, equation (1). Photochemical conversion of molecular nitrogen in the presence of a catalyst[1,2] and hydrolysis of nitrogen–metal complexes[3] are known examples of the reductive fixation of molecular nitrogen, but little study has been made on this reaction in the absence of a catalyst.[4]

$$4/5N_2 + 9/5H_2O \rightarrow NH_3 + 3/5HNO_3$$
$$\Delta G^\circ(298) = +86.2 \text{ kcal/mol} \quad (1)$$

In the present study, the reductive fixation of molecular nitrogen with water using glow discharge was carried out. It was found (i) that ammonia and nitrate ions were formed in the aqueous solution, and (ii) that amino acids were formed by using the same reaction in the presence of carboxylic acids.

Contact glow discharge was applied on the surface of water (20 ml) containing a small amount of sulphuric acid (0.025 mmol) under a nitrogen atmosphere. The applied electric current range was 50—60 mA in the range 500—600 V. The reaction temperature was kept in the range 25—40 °C by cooling the reaction mixture in an ice water bath. The reaction mixture withdrawn was analysed using an amino acid analyser for ammonia and by ion chromatography for nitrate ions. The experimental results are summarized in Figure 1. The amount of ammonia and nitrate ion found in the reaction mixture increased with the reaction time, and the concentrations of ammonia and nitrate ion were 0.45 mmol/20 ml and 0.38 mmol/20 ml, respectively after 24 h. Nitrite ions were not found in the reaction mixture, probably owing to rapid oxidation to the nitrate ion. As a control reaction the glow

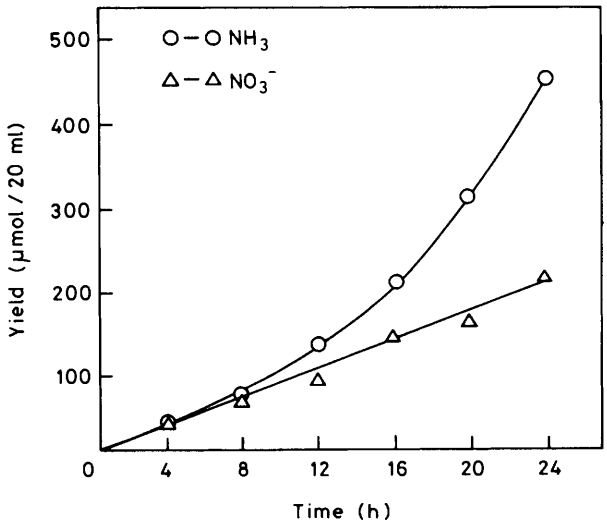

Figure 1. Formation of NH_3 and NO_3^- from N_2 and H_2O by glow discharge. Reaction conditions: 520—600 V, 50 mA, 35—45 °C. Substrate: H_2SO_4, 0.025 mmol/20 ml H_2O–N_2.

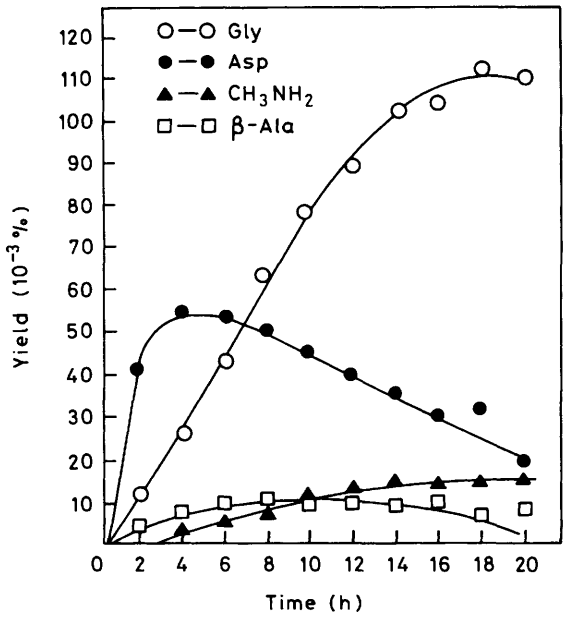

Figure 2. Amination of maleic acid by glow discharge. Reaction conditions: 460—500 V, 20 mA, 10—20 °C. Substrate: maleic acid 10 mmol/20 ml H_2O–N_2. Gly = glycine, Asp = aspartic acid.

discharge reaction was carried out under an argon atmosphere, and neither ammonia nor nitrate ions were found in the reaction mixture. The whole process was also carried out without glow discharge, and again neither ammonia nor nitrate ions were identified.

When some organic compounds were added to the aqueous solution, the glow-discharge reaction resulted in the formation of amino compounds. Aliphatic carboxylic acids, such as acetic acid, propionic acid, and maleic acid were used as the amino acceptors. The resulting amino compounds are as follows (maximum yields quoted): methylamine (0.31 μmol/20 ml), glycine (0.27 μmol/20 ml) from 1.8 M aqueous acetic acid; methylamine (1.18 μmol/20 ml), glycine (0.78 μmol/20 ml), alanine (Ala, 0.19 μmol/20 ml), β-alanine (0.38 μmol/20 ml) from 1.3 M aqueous propionic acid.

A typical time course of the amination reaction with maleic acid by molecular nitrogen is shown in Figure 2.

The formation of ammonia and nitrate ions from molecular nitrogen and water could be regarded as a disproportionation reaction under high-energy conditions. A possible mechanism for the formation of ammonia and nitrate ions could be explained by the decomposition of the nitrogen and water molecules and the recombination of the resulting radicals. The active species in the amination reaction could be NH or NH_2 radicals, which could be formed by the coupling reaction of nitrogen and hydrogen atoms generated by glow discharge. The ratio of Ala : β-Ala produced from propionic acid (1 : 2) was similar to that in the NH-radical reaction (1 : 1.6).[5]

The experimental results indicate clearly that the reductive fixation of molecular nitrogen to yield ammonia and amino compounds took place by the glow-discharge reaction, and the reaction is not controlled thermodynamically. The new fixation reaction of molecular nitrogen is not only interesting chemically, but also interesting from the chemical evolutionary point of view. This type of reaction could be regarded as a model experiment of lightning striking on the hydrosphere under a non-reducing atmosphere (mainly H_2O, N_2, and CO_2) on the primitive Earth.

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