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Fixation of Molecular Nitrogen in Aqueous Solution Induced by Nitrogen Arc Plasma

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Argon Arc Plasma containing nitrogen gas (nitrogen arc plasma) was directly introduced into water, and a disproportionation reaction of molecular nitrogen took place in aqueous solution to form ammmonia, nitrous acid, and nitric acid. The redox reaction of molecular nitrogen is interesting on the chemical evolutionary point of view as a possible route for the formation of ammonia under non-reducing conditions.

Molecular nitrogen is one of the most inert molecules and it is fundamentally difficult to achieve the reduction of nitrogen to ammonia with water molecules. The difficulty is due to the large positive ΔG^o value in the reaction as shown in Eqs. 1 and 2.

$$N_2 + 3H_2O \longrightarrow 2NH_3 + (3/2)O_2 \qquad \Delta G^o_{298} = 657 \text{ kJ/mol} \qquad (1)$$
$$N_2 + (9/4)H_2O \longrightarrow (5/4)NH_3 + (3/4)HNO_3 \qquad \Delta G^o_{298} = 414 \text{ kJ/mol} \qquad (2)$$

Photolyses of molecular nitrogen in the presence of catalyst[1,2] and hydrolyses of nitrogen-metal complexes[3] 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 this study, it was demonstrated that the argon arc plasma containing nitrogen gas (nitrogen arc plasma) induced the formation of ammonia, nitrous acid, and nitric acid.

The apparatus used for the fixation reaction of molecular nitrogen in an aqueous solution is shown in Fig. 1. Plasma jet genarated by arc electric discharge through flowing argon-nitrogen gas was used as energy and a nitrogen source for the reaction.[5] In order to stabilize the generated nitrogen arc plasma, various amounts of argon gas were previously mixed with nitrogen gas. A half open type reaction vessel was used in order to remove the flow gas and to avoid the contamination of air in the reaction vessel(Fig. 1). The plasma torch was immersed into distilled water (pH 3.0 with H_2SO_4) 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. The volume of the reaction solution was 350 ml and the temperature of the solution was kept below 50 ^oC by the circulation of cooling water. The conditions to produce

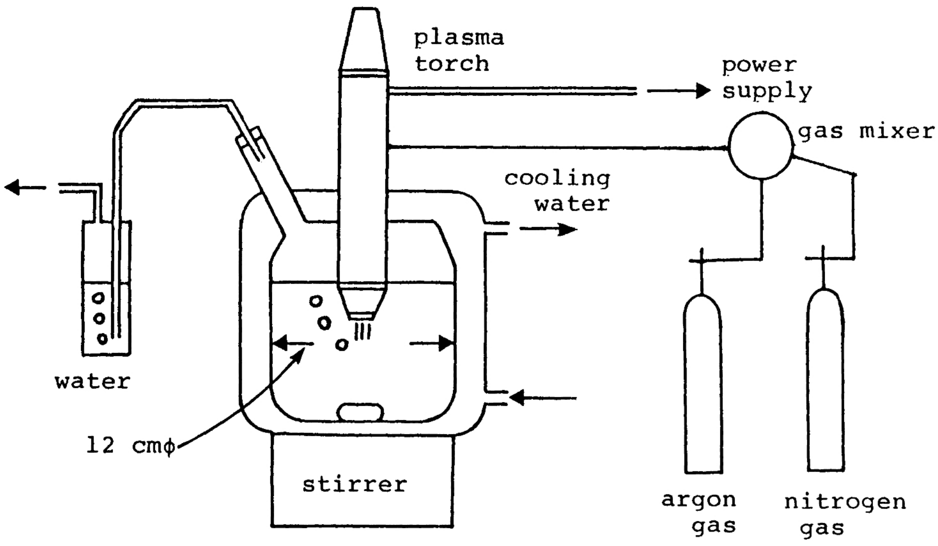

Fig. 1. Apparatus for reductive fixation of molecular nitrogen.

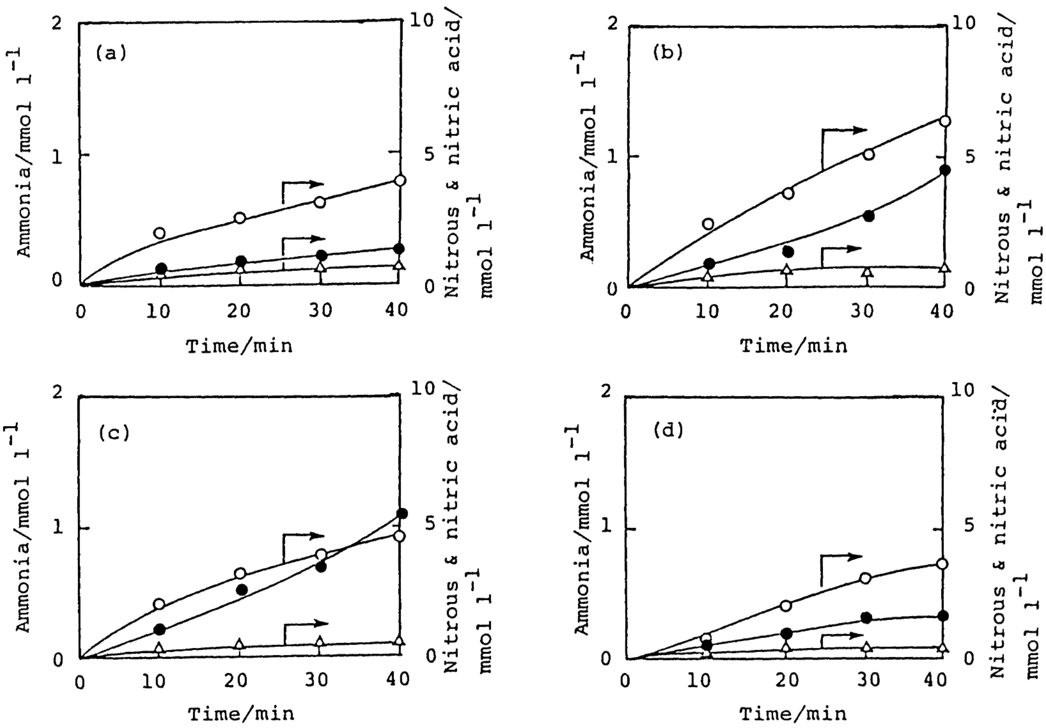

Fig. 2. Formation of ammonia (●), nitrous acid (○), and nitric acid (△) in water (pH 3 with H_2SO_4) induced by nitrogen arc plasma. Flow rates of nitrogen and argon gas were: (a) 0.8 and 1.2 l/min, (b) 0.6 and 1.4 l/min, (c) 0.4 and 1.6 l/min, (d) 0.2 and 1.8 l/min, respectively.

Table 1. Formation of ammonia, nitrous acid, and nitric acid in water induced by nitrogen arc plasma[a]

Flow rate (l/min)		Concentration of products[b] (mmol/l)		
N_2 gas	Ar gas	Ammonia	Nitrous acid	Nitric acid
0.8	1.2	0.26	0.62	3.90
0.6	1.4	0.88	0.72	6.36
0.4	1.6	1.04	0.43	3.58
0.2	1.8	0.35	0.40	3.58
0.0	2.0	0.00	0.00	0.00

a) Conditions to produce plasma jet: total rate of nitrogen and argon gas, 2 l/min; electric current, 40 A; electric voltage, 10 V. Reaction conditions: reaction time, 40 min; solution volume, 350 ml; pH of the solution, 3.0 with H_2SO_4; reaction temperature, 40-50 °C.
b) The products were analyzed by an isotacophoretic analyzer(Shimadzu IP-2A).

plasma jet were : total flow rate of nitrogen and argon gas; 2.0 l/min and various flow rates of nitrogen and argon gas; electric current, 40 A; electric voltage, 10 V. At regular time intervals, 0.5 ml aliquots of the solution were withdrawn and kept in a freezer. Analyses of ammonia, nitrous acid, and nitric acid were carried out by an isotacophoretic analyzer (Shimadzu IP-24). Electrolytes used for the ammonia analysis are: leading; 0.0085 mol/l HCl, terminal; 0.01 mol/l capronic acid (system 1) and leading; 0.006 mol/l cadmium nitrate, terminal; 0.01 mol/l citric acid(system 2). Analyses of ammonia, hydrazine, and hydroxylamine were also carried out by an amino acid analyzer (Irica A-3300).

The analytical results are summarized in Fig. 2. The concentration of ammonia produced is the highest (1.0 mmol/l after 40 min) when the flow rates of nitrogen and argon gas were 0.4 l/min and 1.6 l/min, respectively. In addition, nitrous acid and nitric acid were also obtained. As a control experiment, argon arc plasma containing no nitrogen gas was blown into distilled water(pH 3.0 with H_2O) for 40 min. No fixation product was detected in the reaction mixture. These results are summarized in Table 1.

The nitrogen plasma-induced reaction in aqueous solution is a new type fixation of molecular nitrogen without using any catalyst, and is an unusual 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 could be generated in a plasma jet.[6] Nitrogen atoms produced could react with hydrogen atoms and hydroxyl radicals, which are produced by the dissociation of water molecules, to afford ammonia and nitrous acid in an aqueous solution as in the following equations.

$$N + HO \longrightarrow NO + H \quad (3)$$

$$NO + HO \longrightarrow HNO_2 \quad (4)$$

$$N \xrightarrow{H} (NH) \xrightarrow{H} (NH_2) \xrightarrow{H} NH_3 \quad (5)$$

Nitrous acid could readily be converted into nitric acid under these conditions.

The intermidiates such as NH or NH_2 radicals would react with hydrogen atom to form ammonia. Nitrogen atoms, NH or NH_2 radicals were oxydized by hydroxyl radicals to form nitrous and nitric acid.

The redox reaction of molecular nitrogen induced by plasma is also interesting from the chemical evolutionary point of view. The genesis of the primitive atmosphere of the Earth has been considered to be a result of planetary outgassing, and the main components of the primitive atmosphere on the Earth were CO_2, H_2O, and N_2 ("non-reducing atmosphere").[7-11] Under these conditions, high energy plasma containing nitrogen could be generated by the action of lightning, atmospheric entry of meteors and meteorites, or radiation of solar winds or cosmic rays against the primitive sea. Therefore, the nitrogen plasma-induced reaction in aqueous solution could be regarded as a model experiment of the chemical reactions for the formation of ammonia or nitrogen containing compounds under non-reducing conditions on the primitive Earth.

In conclusion, the arc plasma containing nitrogen gas induced the nitrogen fixation reaction in aqueous solution and the reaction was not controlled thermodynamically. The nitrogen arc plasma-induced reaction is a new type of chemical reaction in aqueous solution and is interesting on the chemical evolutionary point of view.

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