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OXIDATION REACTION OF AMINO ACIDS IN AQUEOUS SOLUTION INDUCED BY ARGON ARC PLASMA

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ABSTRACT: It was found that Argon arc plasma induced a powerful and clean stepwise oxidation reaction in aqueous solution containing various amino acids without using any oxidizing agent.

Various types of plasma chemistry have been reported[1], however, these are chemical reactions in the gaseous phase or onto the solid phase. The chemical reactions of inorganic and organic compounds induced by glow discharge against the aqueous solution have been reported[2,3]. However, no organic reactions in aqueous solution by the use of Argon arc plasma have been reported. In this communication, we would like to report the oxidation reactions of organic compounds in aqueous solution induced by Argon arc plasma.

In these plasma induced oxidation reactions, alanine (neutral amino acid), glutamic acid (acidic amino acid), 2,4-diaminobutyric acid (basic amino acid) and methionine (sulfer containing amino acid) were used as the substrates. The apparatus used for the aqueous plasma reaction is shown in Fig. 1. The plasma torch (Nippon Welding Co., Well Pen NP-7) was immersed into the aqueous solution of amino acids (3 - 100 μmol/l, 300ml, pH 3 with HCl) 1 cm below the surface, and the plasma jet was directly applied into the solution. The conditions for the plasma jet formation were : Argon, 1.5 - 2 l/min ; electric current, 40 A ; electric voltage, 10 V. The substrates and the

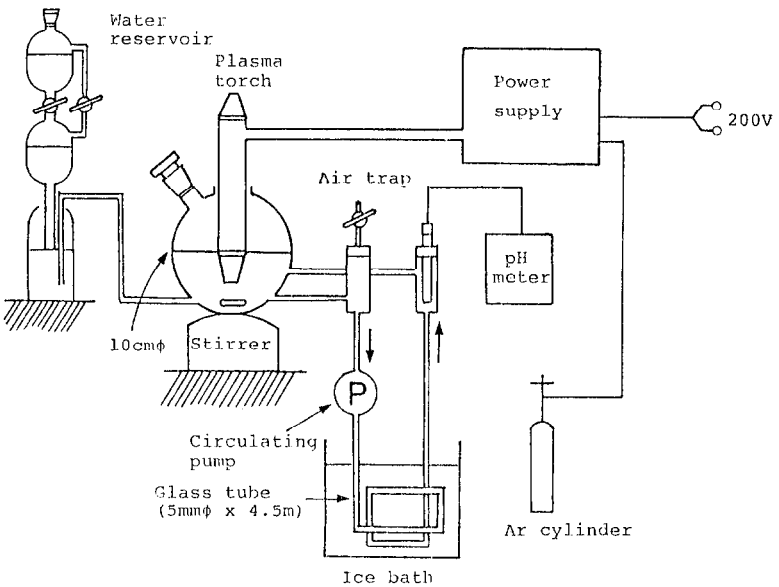

Fig. 1 Apparatus of Plasma-induced Reaction in Aqueous Solution

produced amino acids were analyzed by an amino acid analyzer. The concentration of β-formyl-α-alanine or α-formylalanine was determined from an increase of the corresponding amino acid on sodium borohydride treatment of the reaction mixture. The other reaction products were analyzed by a capillary type isotachophoretic analyzer.

The time course of the oxidation reaction of alanine is shown in Fig. 2. The formation of serine, α-formylglycine, aminomalonic acid and glycine was observed depending on the decrease of alanine. Judging from the time course, serine would be the primary oxidized product in these plasma induced reactions. At the same time, the formation of acetic acid, glycolic acid, glyoxylic acid, pyruvic acid, oxalic acid and formic acid were also observed. The yield of acetic acid reached about 9 %. The time course of the oxidation process of alanine indicates the stepwise oxidation process shown in the scheme in Fig. 2. The organic compounds would be oxidized finally to carbon dioxide.

The time course of the oxidation reaction of glutamic acid is shown in Fig. 3. The formation of aspartic acid, aminomalonic acid and glycine was observed. The yield of aspartic acid reached about 10 %. The oxidation pathway could be described as shown in the scheme in Fig. 3.

The time course of the oxidation reaction of 2,4-diaminobutyric acid by Argon arc plasma is shown in Fig. 4. The formation of β-alanine, aspartic acid, and glycine was observed. The yields of β-alanine and glycine reached 16 % and

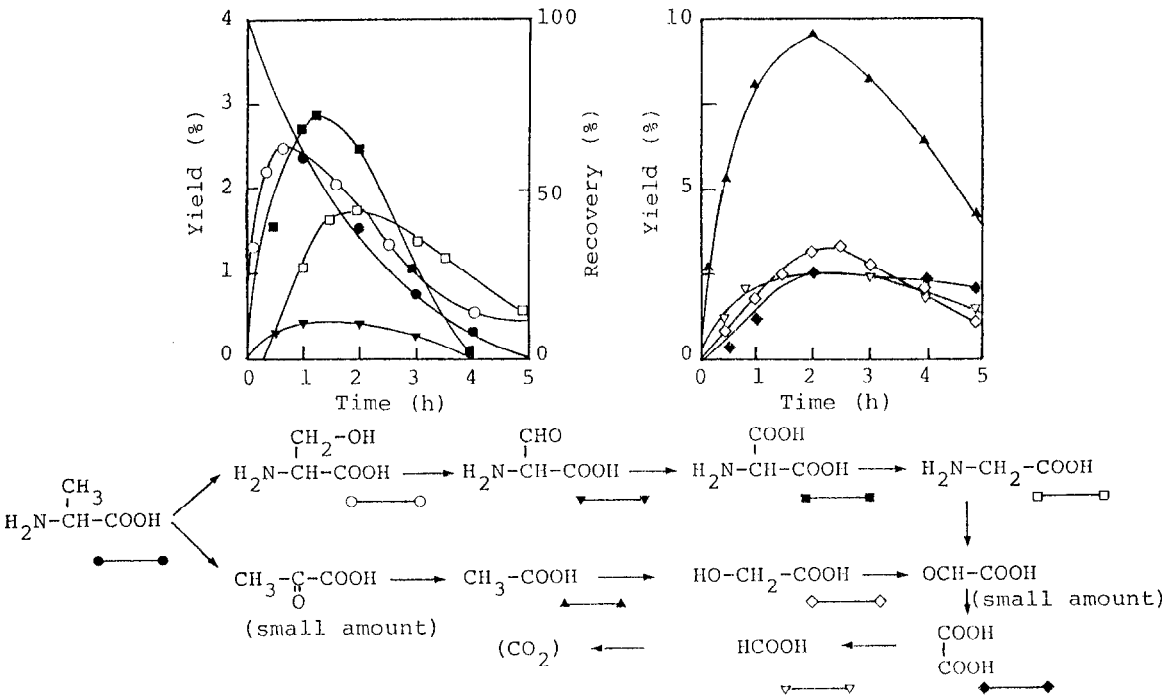

Fig. 2 Oxidation of alanine by Argon arc plasma

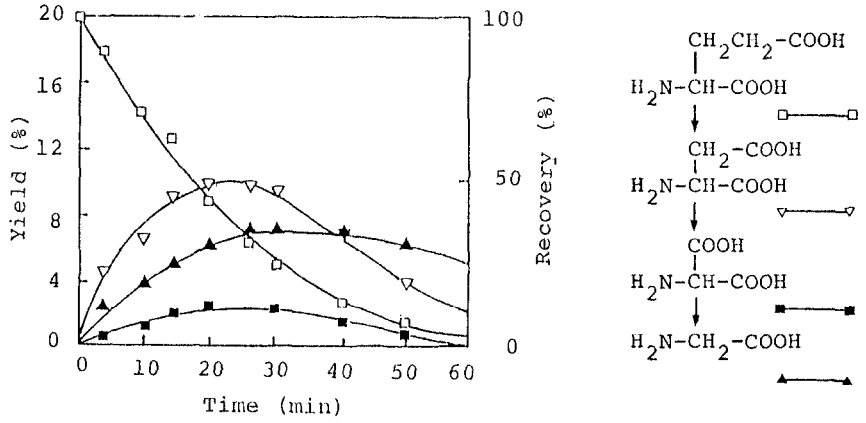

Fig. 3 Oxidation of glutamic acid by Argon arc plasma

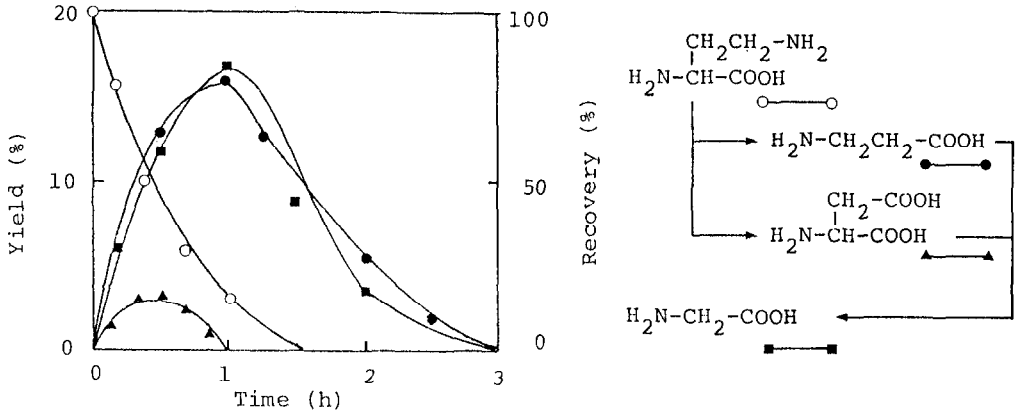

Fig. 4 Oxidation of 2,4-diaminobutyric acid by Argon arc plasma

17 %, respectively. The oxidation pathway could be described as shown in the scheme in Fig. 4.

Fig. 5 shows the time course of the oxidation of methionine. The formation of methionine sulfoxide, methionine sulfone, homocysteic acid, aspartic acid and glycine were confirmed as shown in Fig. 5. In addition to the above mentioned products, small amounts of homoserine, β-formyl-α-alanine and aminomalonic acid were identified. Therefore, the oxidation pathway of methionine could be described as shown in the scheme in Fig. 5.

The results indicate that the oxidation reaction of amino acids induced by Argon arc plasma is a very powerful and clean oxidation process without adding any oxidizing agent. The results suggest strongly that the active oxidizing species are hydroxyl radicals produced by dissociation of water by high energy Argon arc plasma. The time courses of the oxidation reactions indicate relatively controlled stepwize reactions, which is a quite different type of reaction from the gaseous plasma chemistry. The chemical reactions in aqueous solution induced by Argon arc plasma is a new type of chemistry and the new

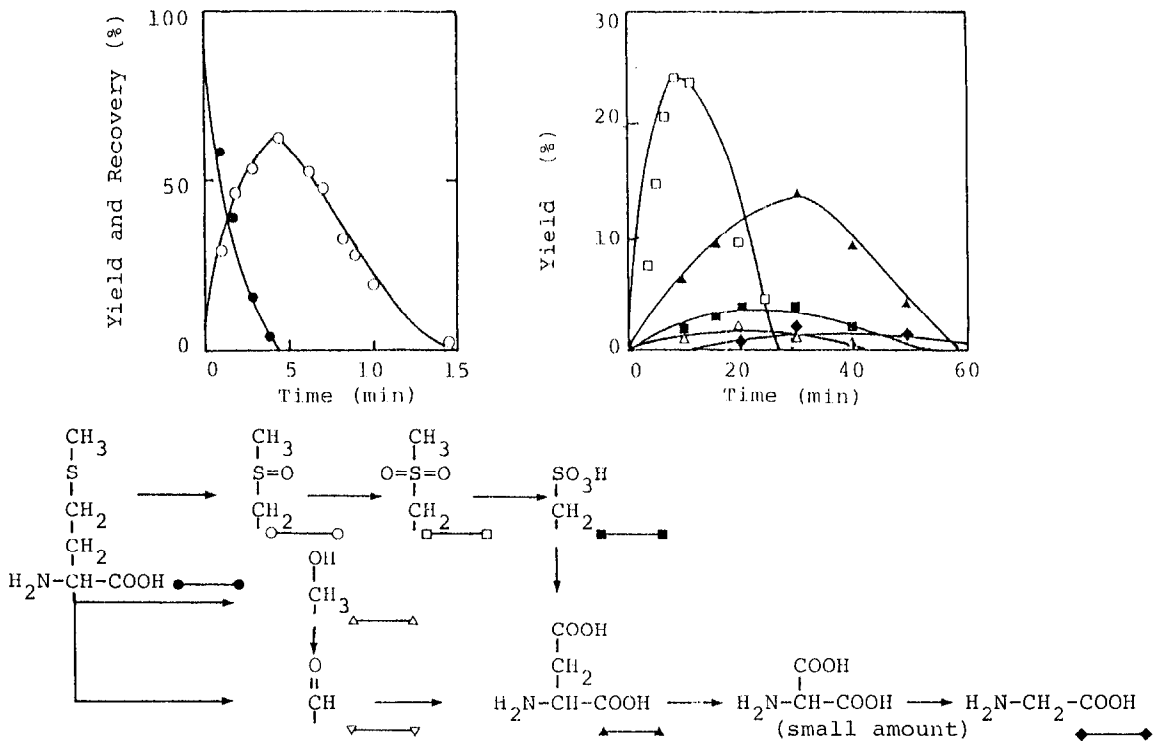

Fig. 5 Oxidation of methionine by Argon arc plasma

chemistry might be applied in many fields of chemical reactions in aqueous solution. On the other hand, based on the chemical evolutionary point of view, this type of plasma chemistry could be regarded as a model reaction of organic compounds in aqueous solution irradiated by high energy charged particles such as cosmic rays or solar winds when the primordial earth did not have magnetic field.

Acknowledgment

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