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HYDROXYLATION OF AROMATIC RINGS IN AN AQUEOUS SOLUTION INDUCED BY ARGON ARC PLASMA

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ABSTRACT: Plasma-induced reaction in an aqueous solution of phenyl-containing amino acids resulted in the formation of several hydroxyphenyl amino acids, which was explained by the action of hydroxyl radicals generated by decomposition of water molecules by the high energy plasma.

The Fenton reagent or hydrogen peroxide with UV light has often been used for the hydroxylation of aromatic rings. In both reactions, the active species were regarded as hydroxyl radicals and definite orientation of the hydroxylation to aromatic rings was observed under given conditions[1-3]. The Fe^{2+}-hydrogen peroxide-ethylenediaminetetraacetic acid (EDTA) system and the Fe^{2+}-ascorbic acid-hydrogen peroxide-EDTA system showed hydroxylation of similar orientation as above, however, the Fe^{2+}-ascorbic acid-oxygen-EDTA system showed hydroxylation of different orientation[1,2]. Therefore, the Fe^{2+}-hydrogen peroxide-EDTA system and Fe^{2+}-ascorbic acid-hydrogen peroxide-EDTA system have been confirmed as hydroxyl radical generators in hydroxylation of aromatic rings and the active species of the Fe^{2+}-ascorbic acid-oxygen-EDTA system are not hydroxyl radicals.

In the previous study from this laboratory[4], it was suggested that the active species in the oxidation reaction of organic compounds in aqueous solution induced by Argon arc plasma could be hydroxyl radicals generated by decomposition of water molecules by the high energy plasma. In order to clarify the active species generated during the plasma induced aqueous reaction, hydroxylation reactions of aromatic compounds were studied. The orientation of hydroxylation was compared with the results obtained by the Fe^{2+}-hydrogen peroxide-EDTA system, the Fe^{2+}-ascorbic acid-hydrogen peroxide-EDTA system and the Fe^{2+}-ascorbic acid-oxygen-EDTA system.

The aqueous solutions of phenylalanine and phenylglycine were used as the substrates. The concentrations of the substrates were 2 mmol/l and the pH of the solution were adjusted to 3.0 by hydrogen chloride. The conditions for the formation of Argon arc plasma were : flow rate of Argon, 1.5 l/min ; diameter of plasma nozzle, 1.8 mm ; electric current, 40 A ; electric voltage, 10 V. The Argon arc plasma torch was immersed into the substrate solution

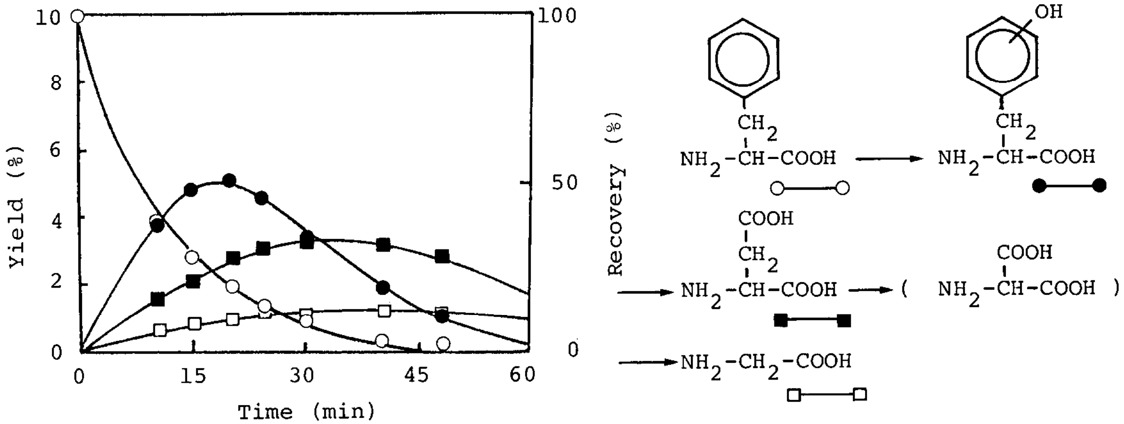

Fig. 1. The time course of the plasma induced reaction of phenylalanine.

1 cm blow the surface and the plasma jet was directly applied into the solution. The time course of the plasma induced reaction of phenylalanine is shown in Fig. 1. Tyrosine, aspartic acid and glycine were formed depending on the decrease of phenylalanine. The stepwise oxidation reaction of phenylalanine could be described as shown in the scheme in Fig. 1. The three isomers of tyrosine (ortho, meta and para) were separated by an amino acid analyzer as shown in Fig. 2. The analysis of o-tyrosine, which was close to the peak of phenylalanine on the chromatographic analysis, was carried out by using a calibration curve for the peak hight. The results are shown in Table 1.

A similar hydroxylation reaction of phenylglycine was carried out by using Argon arc plasma. The time course of the oxidation process of phenylglycine is shown in Fig. 3. The formation of hydroxyphenylglycine and glycine was observed depending on the decrease of phenylglycine. The three isomers of hydroxyphenylglycine (ortho, meta and para) were separated by an amino

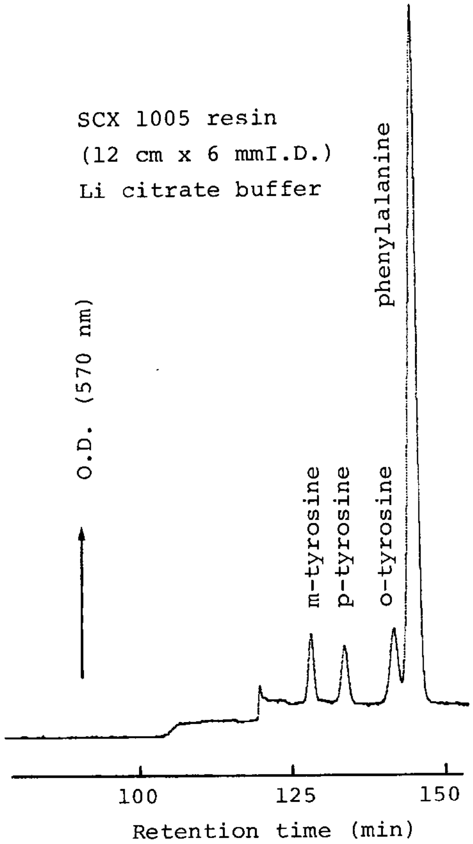

Fig. 2. The amino acid analysis of hydroxylation products of phenylalanine by plasma-induced reaction.

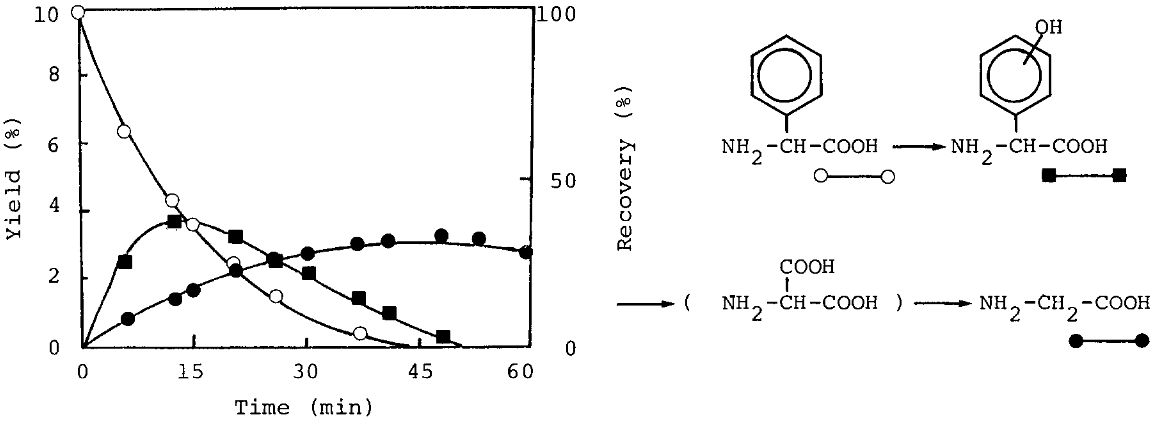

Fig. 3. The time course of the plasma induced reaction of phenylglycine.

acid analyzer. The ratio of the isomers are listed in Table 1.

Similar hydroxylations of phenylalanine and phenylglycine by using a Fe^{2+}-hydrogen peroxide-EDTA system, a Fe^{2+}-ascorbic acid-hydrogen peroxide-EDTA system and Fe^{2+}-ascorbic acid-oxygen-EDTA system were carried out. The yields of hydroxylated amino acids and the ratios of ortho-, meta- and para-isomers of tyrosine and hydroxylphenylglycine are shown in Table 1. In the case of phenylalanine, the ratio of ortho : meta : para tyrosine by using Argon arc plasma was 46 : 26 : 32. This ratio agreed well with the results obtained by reactions using the systems which involved the hydroxyl radicals as a hydroxylating agent (Fe^{2+}-hydrogen peroxide-EDTA system and Fe^{2+}-ascorbic acid-hydrogen peroxide-EDTA system). However, the orientation of hydroxylation was different from the result obtained by using a Fe^{2+}-ascorbic acid-oxygen-EDTA system in which the active species were not hydroxyl radicals. In the case of phenylglycine by using Argon arc plasma, the ratio of ortho : meta : para was found to be 36 : 38 : 26 which agreed well with the results obtained by oxidations by using a Fe^{2+}-hydrogen peroxide-EDTA system and a Fe^{2+}-ascorbic acid-hydrogen peroxide-EDTA system, however, the ratio was different from the results obtained by using a Fe^{2+}-ascorbic acid-oxygen-EDTA system.

The results obtained in Table 1 indicate that the active species, which have properties similar to hydroxyl radicals, are participating in the hydroxylation reactions of aromatic rings in aqueous solution by using Argon arc plasma. In conclusion, the hydroxylation reaction could be considered to be due to the hydroxyl radicals which are produced by decomposition of water molecules by the high energy plasma. Therefore, the other subsequent oxidation process shown in the schemes in Fig. 1 and 2 could also be explained by the action of hydroxyl radicals generated easily in aqueous solution by Argon arc

Table 1. Hydroxylation reaction of aromatic rings in aqueous solution

1) Hydroxylation of phenylalanine

reaction system	reaction time	recovery (%)	total yield[a] (%)	o : m : p
Argon arc plasma	20 min[b]	20	5.2	42 : 26 : 32
Fe^{2+}-H_2O_2-EDTA[c]	24 hrs	73	11.5	41 : 29 : 30
Fe^{2+}-ascorbic acid-H_2O_2-EDTA[d]	24 hrs	18	9.8	41 : 27 : 32
Fe^{2+}-ascorbic acid-O_2-EDTA[e]	24 hrs	26	11.7	40 : 35 : 25

2) Hydroxylation of phenylglycine

reaction system	reaction time	recovery (%)	total yield[a] (%)	o : m : p
Argon arc plasma	10 min[b]	40	3.5	36 : 38 : 26
Fe^{2+}-H_2O_2-EDTA[c]	36 hrs	56	3.7	36 : 39 : 25
Fe^{2+}-ascorbic acid-H_2O_2-EDTA[d]	24 hrs	37	6.5	35 : 39 : 26
Fe^{2+}-ascorbic acid-O_2-EDTA[e]	24 hrs	53	8.9	32 : 49 : 18

a) Total yield of o-, m-, and p-hydroxyphenylamino acid based on initial amounts of substrate

b) Reaction time taken to reach the maximum yield.

c) Aqueous H_2O_2 solution (0.3 %) under nitrogen atmosphere, pH 3 with 2N HCl, substrate, 2 mmol/l; $FeSO_4$, 2 mmol/l; EDTA, 10 mmol/l.

d) Substrate, EDTA and H_2O_2 same as ref. c and in addition: $FeSO_4$, 0,2 mmol/l; ascorbic acid, 10 mmol/l.

e) Same as ref. d except that air bubbled through the solution instead of adding H_2O_2 to the reaction mixture.

plasma in relatively high concentration. The new plasma induced reaction could be appicable in many radical reactions of organic and inorganic compounds in aqueous solution. On the other hand, from the chemical evolutionary point of view, the plasma induced reactions could be considered as chemical reactions in the hydrosphere on the primitive earth which was striked by high energy charged particles such as cosmic rays or solar winds at the time when the primitive earth did not have a magnetic field.

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