Oxidation Reaction of Aliphatic Amines and Aminoalcohols
in Aqueous Solution Induced by Argon Arc Plasma

Michiaki Takasaki and Kaoru Harada[*]
Department of Chemistry, University of Tsukuba, Niihari, Ibaraki, 305, Japan

Abstract: Argon arc plasma induced a powerful and
stepwise oxidation reaction including conversion of methyl
group to carboxyl group, oxidative cleavage of carbon-carbon
bond, and oxidative deamination. Main active species were
considered to be hydroxyl radicals by decomposition of water
molecules.

Many organic reactions using various types of plasmas have been reported.[1]
However, these reactions were mainly carried out in gaseous phase under reduced
pressure. Few organic reactions in aqueous solution using plasma have been
reported except Contact Glow Discharge Electrolysis (CGDE),[2] which is a chemical
reaction due to the glow discharge between an aqueous solution containing a
substrate and an electrode in contact with the solution. Recently, it was found
that argon arc plasma induced a powerful oxidation reaction in aqueous solution
containing organic compounds.[3,4] In this system, argon plasma jet generated by
arc discharge was directly blown into an aqueous solution containing substrates.
The active species produced from water molecules by the action of high energy
plasma react with the organic compounds to afford oxidized products. Therefore,
the plasma induced reaction in an aqueous solution is quite different from that
in the gaseous phase under reduced pressure.

In previous communications,[3,4] oxidation reactions of various amino acids
induced by argon arc plasma were reported. Amino acids used as substrates were
converted to other amino acids and organic acids by the action of argon arc
plasma in aqueous solution. From the isomer distributions of hydroxylations of
aromatic rings, the main active species were considered as hydroxyl radicals
produced by decomposition of water molecules. In this paper, the oxidation
reaction of aliphatic amines and aminoalcohols by this method was reported. The
substrates used were ethylamine, propylamine, 2-aminoethanol, 3-amino-1-propanol,
and 2-amino-1-propanol. Effects of concentration of the substrate, pH of the
solution, and an addition of hydrogen peroxide and formic acid on the oxidation
reaction were also investigated.

Experimentals

The apparatus for the plasma induced reaction in aqueous solution was shown
in Fig. 1. The plasma torch used was a non-transferred type plasma torch (Nippon
Wellding Co., Wellpen NP-7). The argon gas used was of commercial origin (99.999
%). The generated argon arc plasma was stabilized by an argon gas sheath. A
tungsten rod (2.5 mmI.D. x 100 mm) was used as the cathode and a copper nozzle
(1.8 mmI.D.) was used as the anode. The plasma torch was immersed into the
solution of the substrate 1 cm below the surface and the plasma jet was directly
applied into the solution in rounded glass vessel (100 mmI.D.). Argon gas was
previously bubbled through the reaction solution in order to remove oxygen and
the reaction was carried out under argon atmosphere with stirring. The reaction

temperature was kept at 30°C by circulating the solution through a glass tube (4.5 m x 5 mmI.D.) immersed in an ice bath. The volume of reaction solution was 0.3 dm^3 and the pH of the solution was adjusted to 3.0 with 2 mol dm^{-3} HCl or 2 mol dm^{-3} NaOH. Water was supplied continuously from a reservoir to the reaction solution, so as to make supply the solution lost by evaporation. The conditions to produce plasma jet were : argon, 1.5 dm^3 min^{-1}; electric current, 40 A; electric voltage, 10 V. At regular time intervals, 0.5 cm^3 aliquots of the solution were withdrawn and kept in a freezer before analysis.

Analysis of products was carried out by an amino acid analyzer (Irica A-3300) and an isotacophoretic analyzer (Shimazu IP-2A). Electrolytes used for the isotacophoresis

Fig. 1.   Apparatus for plasma induced reaction in aqueous solution.

are : leading electrolyte, 0.01 mol dm^{-3} HCl, 0.02 mol dm^{-3} β-alanine, 0.5 % triton X-100; terminal electrolyte; 0.01 mol dm^{-3} n-capronic acid. The concentration of aminoaldehydes was determined from an increase of the corresponding aminoalcohol on sodium borohydride treatment of the reaction mixture. Other authentic samples of products were purchased. The concentration of hydrogen peroxide in the reaction solution was determined with colorimetric method on treatment of Ti(SO$_4$)$_2$.[5]
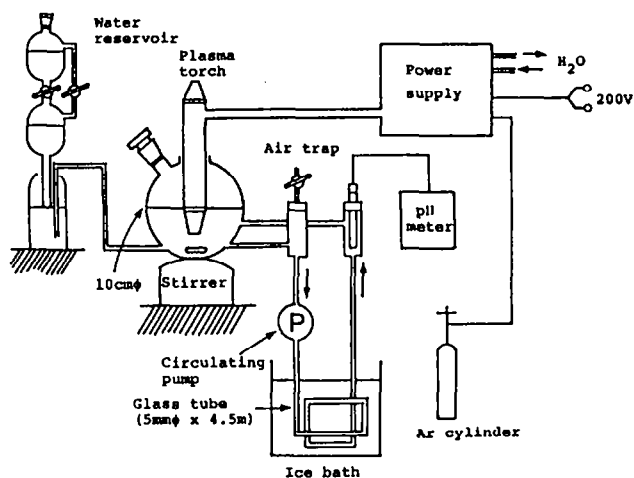
Results and Discussion

<u>Oxidation reactions of aliphatic amines in aqueous solutions.</u>

The time courses of the oxidation products of ethylamine are shown in Fig. 2. Concentration of the substrate was 0.7 mmol dm^{-3}, pH of the solution was adjusted to 3.0 with HCl (Fig. 2-a). Aminoacetaldehyde and glycine were formed depending on the decrease of ethylamine. The yields of aminoacetaldehyde and glycine reached about 1 % and 10 %, respectively. A possible intermediate, 2-
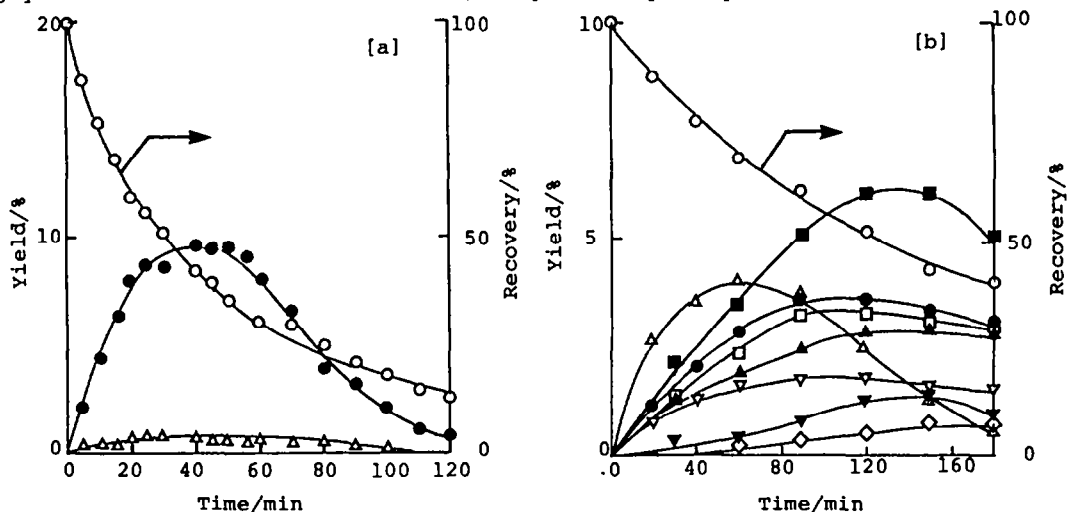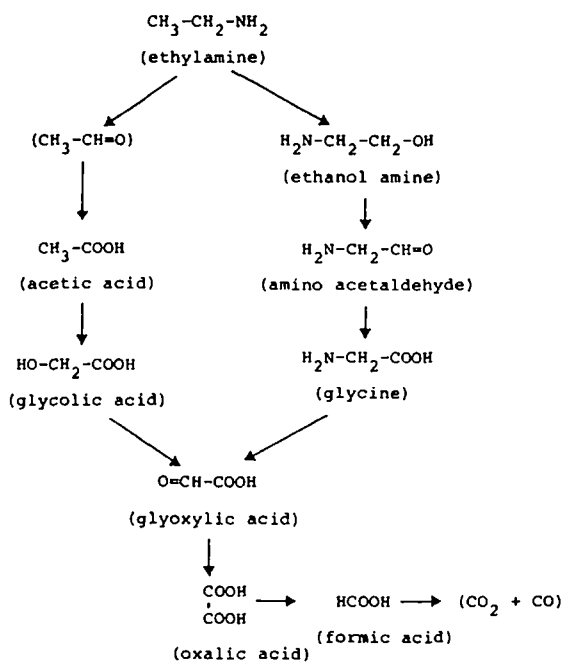

Fig. 2.   Oxidation reaction of ethylamine in aqueous solution (pH 3.0 with HCl) induced by argon arc plasma. Concentrations of substrate were: (a) 0.70 mmol dm^{-3}, (b) 70 mmol dm^{-3}. In reaction (a), aliphatic acids were not identified. (ethylamine: o——o , 2-aminoethanol: ▽——▽ , aminoacetaldehyde: △——△ , glycine: ●——● , acetic acid: ■——■ , glycolic acid: ▼——▼ , glyoxylic acid: □——□ , oxalic acid: ◇——◇ , formic acid: ▲——▲)

aminoethanol was not identified in the reaction mixture, probably because the compound was easily oxidized to amino-acetaldehyde. Determination of organic acids by an isotacophoretic analyzer was not successful, since the concentration of these products was low. On the other hand, in the reaction at higher concentration of substrate (70 mmol dm^{-3}), 2-aminoethanol (maximum yield 2 % at 90 min) was identified with amino-acetaldehyde (yield 4 % at 60 min) and glycine (yield 3.5 % at 120 min) in the reaction mixture as shown in Fig. 2-b. Other organic compounds, formic acid, oxalic acid, acetic acid, glycolic acid, and glyoxylic acid were also obtained in the yields of 3 % (120 min), 0.8 % (140 min), 6 % (120 min), 1.5 % (140 min), and 3 % (120 min). The oxidation process of ethylamine could be explained as shown in Scheme 1.

Oxidation reactions of propylamine induced by argon arc plasma were carried out. Fig. 3 shows the time courses of the oxidized products in the reaction mixtures. The initial concentrations of substrate were 0.7 mmol dm^{-3} (Fig. 3-a) and 70 mmol dm^{-3} (Fig. 3-b). Other reaction conditions were simillar to those of ethylamine. In both reactions,
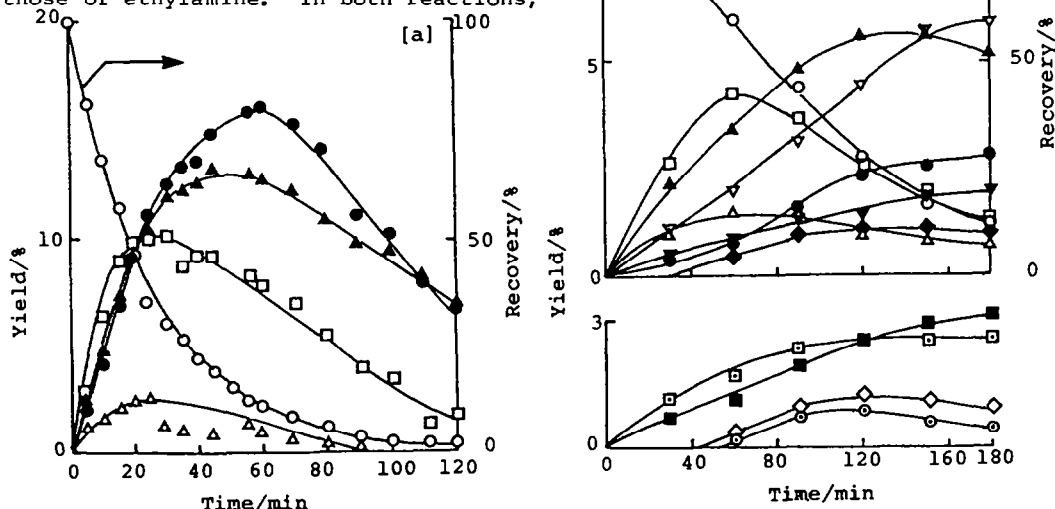
Scheme 1

Fig. 3. Oxidation reaction of propylamine in aqueous solution (pH 3.0 with HCl) induced by argon arc plasma. Concentrations of substrate were: (a) 0.70 mmol dm^{-3}, (b) 70 mmol dm^{-3}. In reaction (a), aliphatic acids were not identified. (propylamine: O——O, 3-amino-1-propanol: □——□, 3-aminopropionaldehyde: △——△, β-alanine: ▲——▲, glycine: ●——●, propionic acid: ▽——▽, 3-hydroxypropionic acid: ◆——◆, acetic acid: ▣——▣, glycolic acid: ◇——◇, glyoxylic acid: ⊘——⊘, oxalic acid: ▼——▼, formic acid: ■——■)

3-amino-1-propanol, 3-aminopropion-
aldehyde β-alanine, and glycine were
obtained depending on the decrease of
propylamine. In the reaction at lower
concentration of substrate, the yields
of products were relatively high as
compared with those obtained in the
reactions at higher concentration of
substrate. Carboxylic acids such as
propionic acid, acetic acid, formic
acid, 3-hydroxypropionic acid,
glycolic acid, glyoxylic acid, malonic
acid, and oxalic acid were also iden-
tified in the reaction mixture at
higher concentration of substrate.
From the time course of the formation
of these compounds, the oxidation of
propylamine induced by argon arc
plasma could be explained as a step-
wise process as shown in Scheme 2.
Other reaction pathways to produce
glycine, such as direct oxidation of
β-carbon of propylamime, could be also
present, although any experimental
results to confirm these pathways were
not obtained.
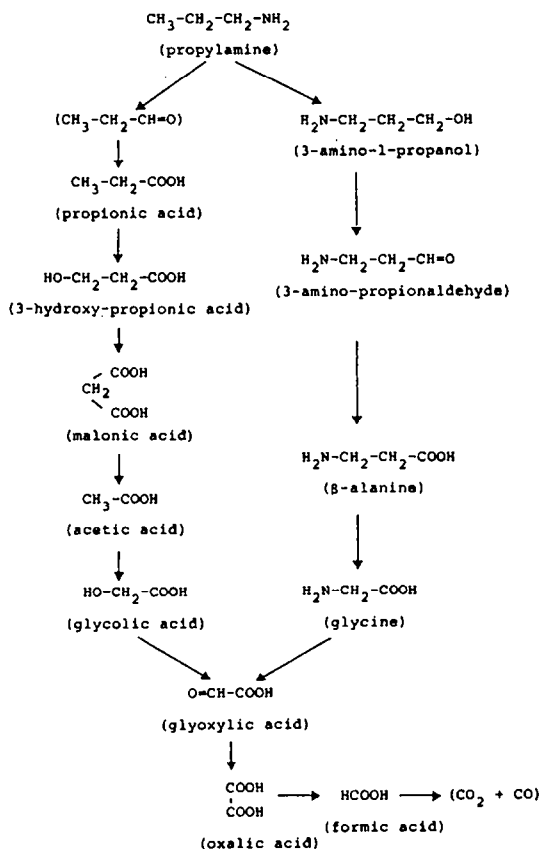
Oxidation reactions of 2-aminoethanol and other aminoalcohols.

The oxidation reaction of 2-
aminoethanol in aqueous solution was
carried out by using argon arc plasma
to confirm the explanation of the
oxidation reaction of ethylamine as
shown in Scheme 1. The time course of
plasma induced reaction of 2-
aminoethanol was shown in Fig. 4.
Concentration of the substrate was 70
mmol dm^{-3}, pH of the solution was 3.0
with HCl. Aminoacetaldehyde was
formed first and then glycine was
produced depending on the decrease of
2-aminoethanol. The yield of glycine
reached up to 15 % after one and a
half hours. Other oxidized products,
formic acid, oxalic acid, glycolic
acid, and glyoxylic acid were obtained
in the yields of 7.4 %, 0.8 %, 1.4 %,
and 0.5 %. The yields of these
organic acids also decreased gradually
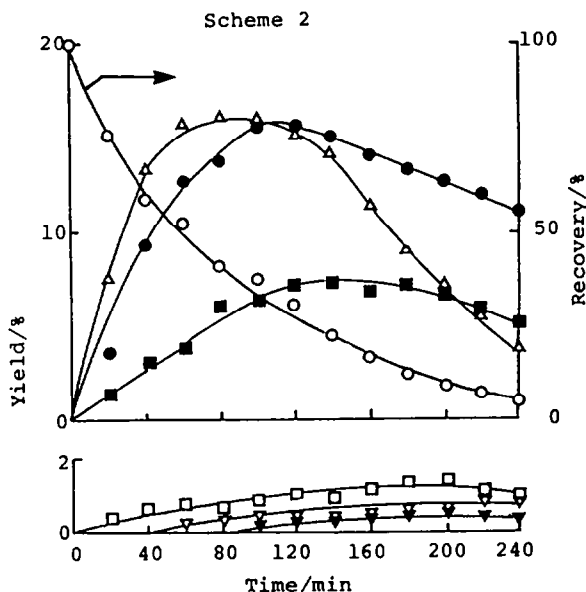on prolonged reaction. Finally,

Scheme 2

Fig. 4. Oxidation reaction of 2-
aminoethanol (70 mmol dm^{-3}) in aqueous
solution (pH 3 with HCl) induced by
argon arc plasma. (2-aminoethanol:
○——————○, aminoacetaldehyde:
△——————△, glycine: ●——————●,
glycolic acid: □——————□, glyoxylic
acid: ▼——————▼, oxalic acid: ▽——
——————▽, formic acid: ■——————■)

Table 1. Oxidation reaction of 2-aminoethanol induced by argon arc plasma[a]

Run	Reaction conditions	Concentration of substrate (mmol dm^{-3})	Initial degradation rate of substrate[b] $\times 10^4$ (mmol dm^{-3} sec^{-1})	Produced amino compounds Maximum yield (%), (reaction time[c]/min)		
				Glycine	Aminoacetaldehyde	Isoserine[d]
1	aqueous solution (pH 3.0 with HCl)	0.07	0.6	34(30)	38(15)	-
2	aqueous solution (pH 3.0 with HCl)	0.27	2.2	31(30)	25(20)	-
3	aqueous solution (pH 3.0 with HCl)	0.70	6.0	29(30)	25(20)	-
4	aqueous solution (pH 3.0 with HCl)	2.1	16.	25(35)	19(25)	-
5	aqueous solution (pH 3.0 with HCl)	7.0	29.	21(50)	18(45)	-
6	aqueous solution (pH 3.0 with HCl)	16.	61.	17(70)	18(60)	-
7	aqueous solution (pH 3.0 with HCl)	70.	125.	15(90)	16(80)	-
8	aqueous formic acid solution (0.02 %)	0.70	5.9	25(30)	21(25)	<1(5)
9	aqueous formic acid solution (0.06 %)	0.70	5.8	25(30)	19(25)	1(5)
10	aqueous formic acid solution (0.2 %)	0.70	4.9	28(40)	16(30)	1(5)
11	aqueous formic acid solution (0.6 %)	0.70	2.8	26(45)	19(45)	7(15)
12	aqueous formic acid solution (2.0 %)	0.70	1.9	19(70)	20(60)	10(15)
13	aqueous formic acid solution (20. %)	0.70	0.16	3(180)[e]	9(180)[e]	7(180)[e]
14	aqueous H$_2$O$_2$ solution (0.015 %, pH 3.0 with HCl)	0.70	5.8	32(30)	31(20)	-
15	aqueous H$_2$O$_2$ solution (0.15 %, pH 3.0 with HCl)	0.70	6.1	34(30)	29(20)	-
16	aqueous H$_2$O$_2$ solution (1.5 %, pH 3.0 with HCl)	0.70	2.1	31(45)	30(35)	-
17	aqueous solution (pH 7.0 with HCl)	0.70	7.8	9(20)	16(15)	-
18	aqueous solution (pH 11.0 with NaOH)	0.70	12.6	1(15)	-	-
19	aqueous solution (pH 3.0 with HCl) and air was bubbled through the solution	0.70	6.1	29(30)	23(25)	-

a) Conditions to produce plasma jet: argon, 1.5 dm^3, electric current, 40 A; electric voltage, 10 V. b) Initial degradation rate was calculated from the concentration of reacted substrate at reaction time 5 min. c) Reaction time at maximum yield. d) Isoserine: 1-hydroxy-2-aminobutyric acid. e) The product did not reach the maximum.

organic compounds produced would be further oxidized to CO and CO_2. The total oxidation pathway of 2-aminoethanol could be described as shown in Scheme 3.

A clear concentration effect of the substrate on the yields of aminoacetaldehyde and glycine was observed. These results were shown in Table 1 (run 1-7). The yields of oxidized products increased depending on the decrease of the substrate concentration. In the case of initial concentration of 2-aminoethanol, 0.7 mmol dm^{-3}, the yields of aminoacetaldehyde and glycine were up to 25 % and 30 %, respectively. Table 1 (run 1-7) also shows the initial degradation rates of substrate at several concentrations of substrate.

$$H_2N-CH_2-CH_2-OH$$
(2-aminoethanol)

$(O=CH-CH_2-OH)$ $\qquad$ $H_2N-CH_2-CH=O$
(amino acetaldehyde)

$HO-CH_2-COOH$ $\qquad$ H_2N-CH_2-COOH
(glycolic acid) $\qquad\qquad$ (glycine)

O=CH-COOH
(glyoxylic acid)

COOH
COOH
(oxalic acid)

HCOOH $\longrightarrow$ (CO + CO_2)
(formic acid)

Scheme 3

The initial degradation rate of 2-aminoethanol decreased depending on the decrease of the substrate concentration.

Oxidation reaction of 2-aminoethanol induced by argon arc plasma was carried out in aqueous formic acid solution (0.02 - 20 %). The initial degradation rate of substrate decreased with the increase of formic acid concentration. In the reactions at higher concentrations of formic acid, the reaction times which were necessary to reach the maximum yields of products were longer compared with those obtained in the reactions at lower concentrations of formic acid. These results indicate that the plasma induced oxidation reaction was inhibited by the presence of formic acid. In addition to this result, at higher concentration of formic acid, a carboxylated product, isoserine was obtained in the reaction mixture. The yield of isoserine was about 10 % when the initial concentration of formic acid was 2 %. These results were summerized in Table 1 (run 8-13).

It was found that argon arc plasma induced a formation of hydrogen peroxide (H_2O_2) in water as shown in Fig. 5. The concentration of H_2O_2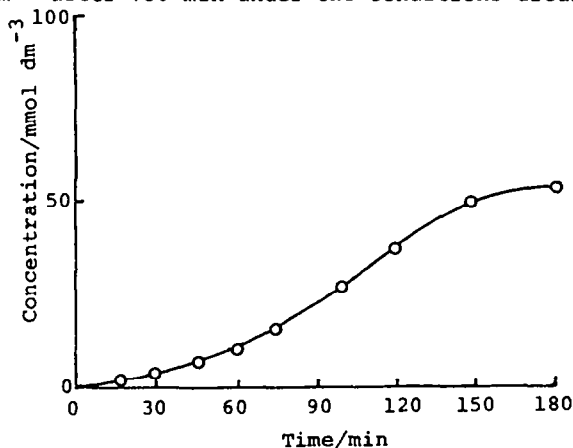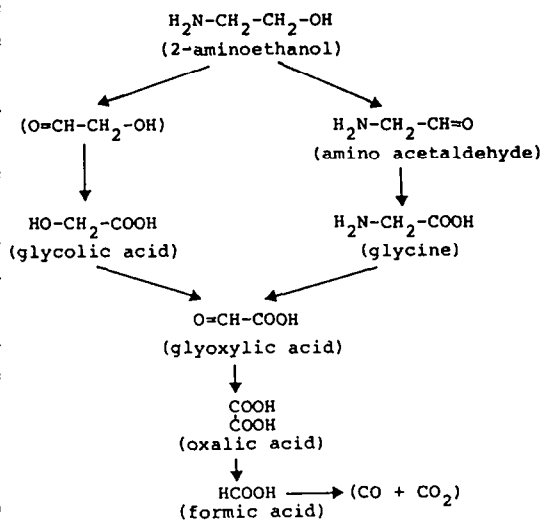 reached to 50 mmol dm^{-3} after 180 min under the conditions used. Hydrogen peroxide was an oxidizing agent, and which would be generated from water molecules by the action of argon arc plasma. In order to examine the participation of H_2O_2 in the oxidation reaction of the substrate, the plasma induced reaction of 2-aminoethanol was carried out in aqueous H_2O_2 solutions. The results were shown in Table 1 (14-16). In the reaction at lower concentrations of H_2O_2, the oxidation reaction was not affected by the addition of H_2O_2. However, at a higher concentration (1.5 %), the oxidation reaction of 2-

Fig. 5. Formation of hydrogen peroxide in aqueous solution (pH 3 with H_2SO_4) induced by argon arc plasma.

aminoethanol was inhibited by the addition of H_2O_2.

The clear pH dependence on the yields of aminoacetaldehyde and glycine in the oxidation reaction of 2-aminoethanol was observed. The yield of glycine decreased considerably and aminoacetaldehyde was not indentified in the basic condition (pH 11.0). The results were summerized in Table 1 (run 3, 17, and 18). In order to examine the participation of dissolved oxygen in the oxidation reaction of 2-aminoethanol, air was bubbled through the reaction solution containing the substrate throughout the oxidation reaction. As shown in Table 1 (run 19), the
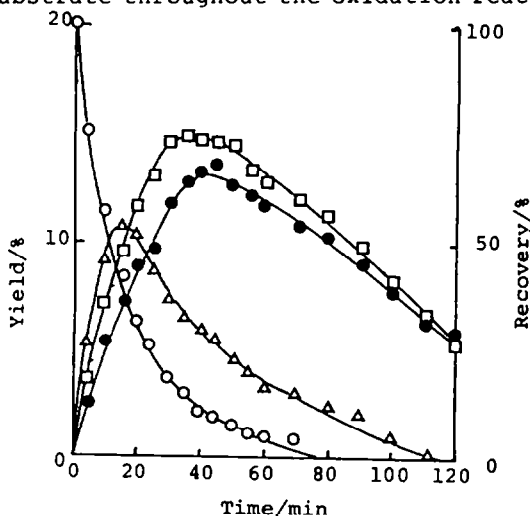

Fig. 6. Oxidation reaction of 3-amino-1-propanol (0.70 mmol dm^{-3}) in aqueous solution (pH 3 with HCl) induced by argon arc plasma. Aliphatic acids were not identified in the reaction mixture. (3-amino-1-propanol: O———O , 3-aminopropionaldehyde: △———△ ,β-alanine: □———□ , glycine: ●———●)
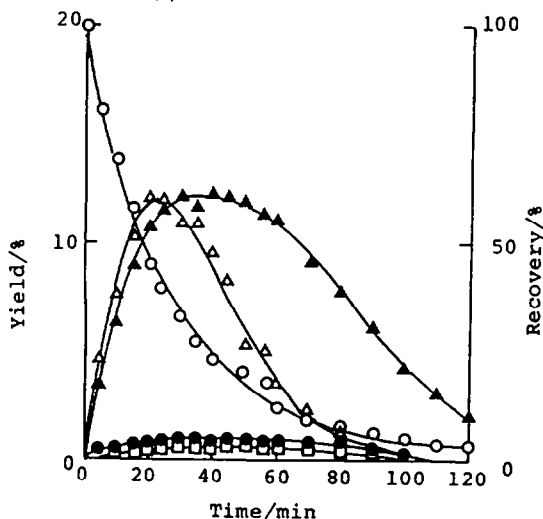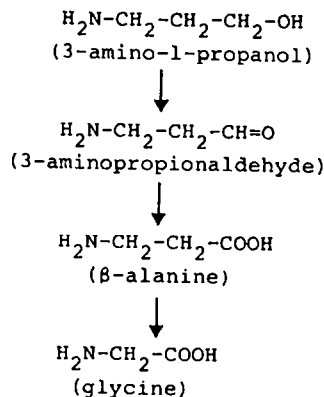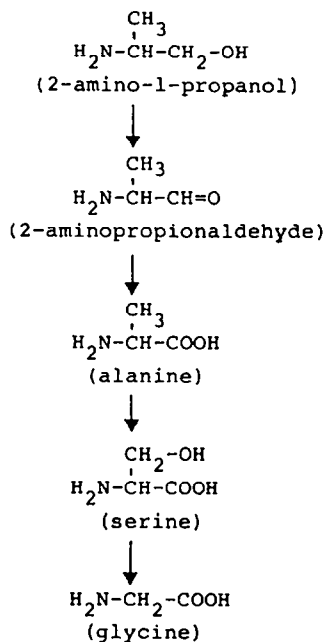

Fig. 7. Oxidation reaction of 2-amino-1-propanol (0.70 mmol dm^{-3}) in aqueous solution (pH 3.0 with HCl) induced by argon arc plasma. Aliphatic acids were not identified in the reaction mixture. (2-amino-1-propanol: O———O , 2-aminopropionaldehyde:△———△ , alanine: ▲———▲ ,serine: ●———● , glycine: □———□)

$H_2N-CH_2-CH_2-CH_2-OH$
(3-amino-1-propanol)

↓

$H_2N-CH_2-CH_2-CH=O$
(3-aminopropionaldehyde)

↓

$H_2N-CH_2-CH_2-COOH$
(β-alanine)

↓

H_2N-CH_2-COOH
(glycine)

Scheme 4

CH_3
$H_2N-CH-CH_2-OH$
(2-amino-1-propanol)

↓

CH_3
$H_2N-CH-CH=O$
(2-aminopropionaldehyde)

↓

CH_3
$H_2N-CH-COOH$
(alanine)

↓

CH_2-OH
$H_2N-CH-COOH$
(serine)

↓
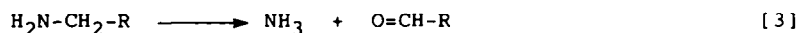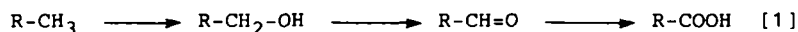
H_2N-CH_2-COOH
(glycine)

Scheme 5

effect of bubbled air on the oxidation reaction was not observed.

The time course of the oxidation reactions of 3-amino-1-propanol was shown in Fig. 6. The initial concentration of the substrate was 0.7 mmol dm^{-3}. Formation of 3-aminopropionaldehyde, β-alanine, and glycine were confirmed. The formation of these compounds could be explained as shown in Scheme 4. Detection of carboxylic acids by an isotacophoretic analyzer was not successful, since the concentrations of these products were low.

Oxidation reaction of 2-amino-1-propanol induced by argon arc plasma was carried out. The concentration of substrate was 0.7 mmol dm^{-3}. Alanine, serine, glycine, and 2-aminopropionaldehyde were identified. The time course of the oxidation reaction was shown in Fig. 7. The formation of these amino compounds could be explained as shown in Scheme 5.

Mechanism of plasma induced reaction in aqueous solution.

The results observed indicate that the plasma induced reaction of several aliphatic amines and aminoalcohols proceeded by a stepwise oxidation reaction containing conversion of methyl group to carboxyl group [1], oxidative cleavage of carbon-carbon bond [2], and oxidative deamination [3] as shown below.

$$R-CH_3 \longrightarrow R-CH_2-OH \longrightarrow R-CH=O \longrightarrow R-COOH \quad [1]$$

$$R-CH_2-COOH \longrightarrow R-COOH \quad [2]$$

$$H_2N-CH_2-R \longrightarrow NH_3 + O=CH-R \quad [3]$$

Finally the products obtained would be oxidized to NH_3, CO, and CO_2. The powerful oxidation of alkyl group of aliphatic amines is an unusal oxidation reaction. The main active species of the plasma induced reaction were considered as hydroxyl radicals produced by decomposition of water molecules by argon arc plasma as shown in the equations below.

$$H_2O \longrightarrow H_2O^+ + e^- \quad [4]$$

$$H_2O \longrightarrow H_2O^* \longrightarrow 2H\cdot + HO\cdot \quad [5]$$

$$H_2O^+ \longrightarrow 2H^+ + HO\cdot \quad [6]$$

The hydroxyl radical is one of the strongest oxidizing agent and has a strong electrophilic property. In acidic condition (pH 3.0), the hydroxyl radical subtracts hydrogen more easily from the β-, or γ-carbon rather than from the α-carbon of aliphatic amines, because most of the amino groups are protonated and the charged nitrogen atom attracts electrons strongly. The resulting substrate radicals react with hydroxyl radicals to form oxidized amino compounds. Therefore, the water molecule acts as a solvent and as a powerful oxidizing agent to produce oxidized amino compounds in acidic condition. (equation [7])

$$R-CH_3 \xrightarrow[-H_2O]{HO\cdot} R-CH_2\cdot \xrightarrow{HO\cdot} R-CH_2-OH \quad [7]$$
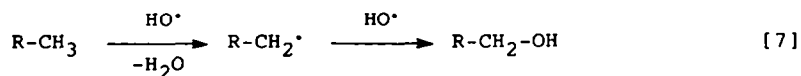
On the other hand, the α-carbon and the amino group of the substrate are both oxidized by plasma induced reaction in basic condition (pH 11.0), since non-protonated amino groups have an electron-donating property and the electron

density of the α-carbon becomes high as compared with those in acidic condition. Consequently, the yields of amino compounds in the reaction in basic condition are relatively low as compared with in acidic condition.   Formation of hydroxyl radicals in the reaction mixture was also suggested by isomer distributions of hydroxylation of aromatic rings in aqueous solution by using argon arc plasma in the previous report.[4] The ratios of ortho, meta, and para-hydroxyphenyl amino acids by plasma induced reactions were similar to those obtained by other hydroxyl radical generation systems such as the Fenton reagent.

Formation of hydroxyl radicals by decomposition of water molecules in the plasma induced reaction was considered to proceed in the vicinity of the plasma jet in the aqueous solution. Since the high energy of the plasma jet was focused in a fixied position in the solution, the hydroxyl radicals produced from water molecules would exist in a small zone formed between the solution and the plasma jet. The substrate in the solution reacts with hydroxyl radicals in the small zone to afford oxidized products.   Therefore, the oxidation reaction induced by argon arc plasma would be a kind of heterogeneous reaction proceeded in the small reaction zone, which was located in a fixed position and constantly renewed by the generation of new active species.

The kinetics of the plasma induced reaction were explained by the assumptions that the oxidation reaction of the substrate proceeded only in the reaction zone and the adsorption of substrate to the reaction zone followed the adsorption isotherm represented by the Freundlich's equation.[6] If the Freundlich isotherm could be applied to the plasma induced reaction, the volume of the substrate in the reaction zone, v_s was given by the following equation,

$$v_s = a \cdot (C_s)^b \qquad\qquad [8]$$

where C_s was the concentration of the substrate in the reaction solution and a and b were constants.   Since the rate determination step was considered to be the attack of active species to the substrate, the degradation rate of substrate (R_d) would be proportional to the concentrations of active species (C_a) and the substrate (v_s) in the reaction zone.   Therefore, the following second-order rate equation can be written.

$$R_d = k \cdot C_a \cdot v_s \qquad\qquad [9]$$

thus,

$$R_d = k \cdot a \cdot C_a \cdot (C_s)^b \qquad\qquad [10]$$

The values of C_a in the reaction zone was not known, however, which would be constant throughout the reaction under the conditions used.   Therefore, the following pseudo first-order rate equation can be written,

$$R_d = k' \cdot (C_s)^b \qquad (k' = k \cdot a \cdot C_a) \qquad\qquad [11]$$

where k' includes all the proportionality constants.   Logarithmic form of equation [11] was

$$\ln(R_d) = b \cdot \ln(C_s) + \ln(k') \qquad\qquad [12]$$

Comparison of theory with experiment is shown in the logarithm plot of initial

degradation rate of substrate (R_d) against initial concentration of substrate ($C_s{}^o$) from the results in Table 1 (run 1-7) (Fig. 8). In the concentration range from 0.07 to 70 mmol dm^{-3}, the plot was almost linear. From the plot, constant b and k' were 0.77 and 6.36 x 10^{-4} sec^{-1}, respectively. The linear correlation with b value, 0.77 demonstrates that the adsorption of substrate to the reaction zone follows the Freundlich isotherm. The kinetics described above support that the plasma induced reaction is a kind of heterogeneous reaction proceeded in the reaction
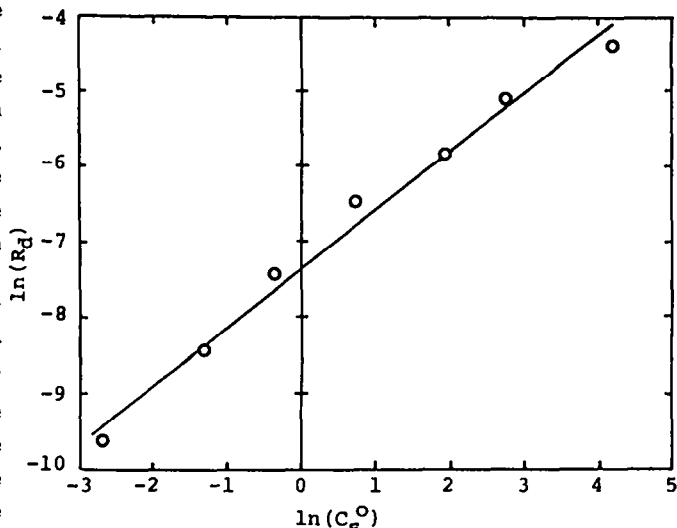

Fig. 8. Kinetics of 2-aminoethanol oxidation in aqueous solution induced by argon arc plasma. $C_s{}^o$: initial concentration of substrate (mmol dm^{-3}), R_0: initial degradation rate of substrate (mmol dm^{-3} sec^{-1})

zone, which is formed in the vicinity of plasma jet in aqueous solution.

In the oxidation reaction by argon arc plasma, the sum of the yields of products detected and the recovery of the substrate did not reach 100 % at any reaction times. There were two possible reasons: 1) part of the substrate was rapidly decomposed to CO, CO_2, and NH_3 in the reaction zone, and 2) undetectable products such as aliphatic aldehyde, were formed from the substrate in the aqueous solution.

The oxidation reaction of 2-aminoethanol by argon arc plasma was inhibited by the presence of formic acid, and a carboxylated product, isoserine, was obtained as shown in Table 1 (run 8-13). It is known that formic acid is a scavenger of hydroxyl radicals.[7] The scavenging reaction could be described as shown in equation [13].

$$HO^{\cdot} + HCOO^{-} \longrightarrow H_2O + CO_2{}^{\cdot} \qquad [13]$$
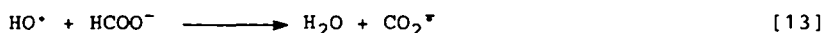
The resulting $CO_2{}^{\cdot}$ would undergo a carboxylation reaction with the substrate radicals produced.[8]

$$CO_2{}^{\cdot} + H_3N^+-CH_2-\overset{\cdot}{C}H-OH \longrightarrow H_3N^+-CH_2-\underset{\underset{OH}{|}}{CH}-COO^- \qquad [14]$$
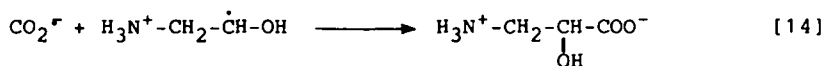
Therefore, the plasma induced reaction of 2-aminoethanol in the presence of formic acid could be explained on the basis of the reaction of hydroxyl radicals with formic acid.

Formation of H_2O_2 in aqueous solution induced by argon arc plasma could result in the coupling reaction of hydroxyl radicals as shown below.

$$2HO^{\cdot} \longrightarrow H_2O_2 \qquad [15]$$

The participation of H_2O_2 as an oxidizing agent in the oxidation reaction of 2-aminoethanol was considered to be relatively small, since the degradation rate

of substrate was not accelereted by the addition of H_2O_2 to the reaction mixture. Particularly, at higher concentration of H_2O_2 (1.5 %), it was considered that the reaction proceeds as a scavenging reaction of hydroxyl radicals.[9] Hydrogen peroxides react with hydroxyl radicals in the reaction zone and convert to hydroperoxyl radicals (HOO·) as shown equation below.

$$H_2O_2 + HO· \longrightarrow HOO· + H_2O \qquad\qquad [16]$$
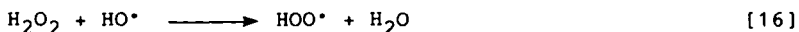
Hydroperoxyl radicals (HOO·) produced would further scavenge hydroxyl radicals and afford oxygen molecules as shown in equation [17],[10,11] and the degradation rate of 2-aminoethanol decreases in the reaction at higher concentration of H_2O_2.

$$HOO· + HO· \longrightarrow H_2O + O_2 \qquad\qquad [17]$$
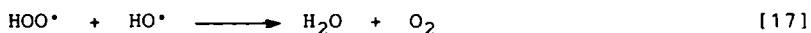
Judging from the air bubbling effect (Table 1, run 19), the dissolved oxygen would contribute little to the oxidation reaction of the substrate. This result indicates that oxidizing species generated from oxygen molecules, such as excited oxygen, were not main active species of the oxidation reaction induced by argon arc plasma.

The formation and role of the reducing species, such as hydrogen radical and hydrated electron, in the plasma induced reaction have not yet been clarified under the conditions used. These reducing species might also participate to subtract hydrogen from the substrate molecules. The reactions of these reducing species produced in the plasma induced reaction are a problem should be solved.

The results obtained above are summerized as follows. The argon arc plasma induces a powerful oxidation reaction including a conversion of methyl group to carboxyl group in aqueous solution. These oxidation reactions are inhibited by the addition of formic acid or hydrogen peroxide (above 1.5 %). The main active species are considered to be hydroxyl radicals produced by decomposition of water molecules. The plasma induced reaction is considered to be a kind of heterogeneous reaction proceeded in a reaction zone, which is located in the vicinity of plasma jet in the aqueous solution.

The chemical reaction induced by argon arc plasma could be regarded as a new chemistry in aqueous solution. It is possible to consider that the new chemistry could have great potentialities in its application to many kinds 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 the primitive hydrosphere irradiated by high energy charged particles such as cosmic rays, soler winds, or lightning striking on the sea.

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