DECOMPOSITION OF POLLUTANTS IN WATER BY PULSED-DISCHARGE PLASMA AND THE CLARIFICATION OF THE DECOMPOSITION PROCESS

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ABSTRACT

Decomposition characteristics of methylene blue in an aqueous solution by the exposure of pulsed-discharge plasma generated above a water surface are investigated for different background-gas (BG) composition. Processes involving OH radicals produced by reaction between high-energy electrons and vaporized H_2O and O_3 contribute to the decomposition of methylene blue. BG molecules and atoms in metastable state, such as N_2 ($A^3\Sigma_u^+$) and Ar ($^3P_2$, $^3P_0$), also contribute to the decomposition through the production of OH radicals by the dissociation of H_2O. NO_x, produced from BG, decomposes O_3 and inhibits O_3 generation, then suppressing the decomposition.

By-products from phenol by the exposure of pulsed-discharge plasma are investigated by gas chromatography mass spectrometry (GCMS), and then the decomposition process of phenol is deduced. In Ar atmosphere, phenol is likely to be converted into catechol and hydroquinone. In an O_2 atmosphere, the benzene rings of the phenol are cleaved by 1,3-dipolar addition involving O_3, and converted into oxalic acid, maleic acid, and succinic acid. In addition formic acid and CO_2 can be produced by the decomposition of oxalic acid.

1. INTRODUCTION

Advanced Oxidation Processes (AOPs) [1] is attracting attention as a method of purifying water polluted by tetrachloroethylene and other volatile organochlorine compounds, as well as PCBs and other persistent chemicals. AOPs consists of processes that decompose toxic chemicals in water by means of OH radicals and other strong oxidants including ozone oxidation, photocatalytic oxidation, wet oxidation and pulsed discharge. In pulsed discharge, accumulated energy is released in a short time and at a high energy density, and electrons are accelerated by a pulsed voltage with a short rise time. As a result, the electrons shift toward higher energies while the increase in collision probability between electrons and gas molecules is restrained, that is, the electron energy distribution is maintained; therefore, high-energy electrons are generated efficiently, and the resulting active species such as OH radicals, O_3, etc. make possible the decomposition of toxic chemicals [1, 2]. Furthermore, one can also expect direct decomposition by high-energy electrons [1], UV radiation, adding to the effectiveness of the process.

In this work, we generate a pulsed-discharge plasma above water containing methylene blue and phenol, which are used as substitutions of the pollutants, and the decomposition characteristics of the substances are investigated for different BG composition to control active species produced in the pulsed plasma. Further, the decomposition products from phenol are analysed in detail to clarify phenol decomposition processes.

2. EXPERIMENTAL SETUP, METHOD AND CONDITIONS

Fig.1 shows the experimental setup. A needle electrode and a water bath electrode are placed in
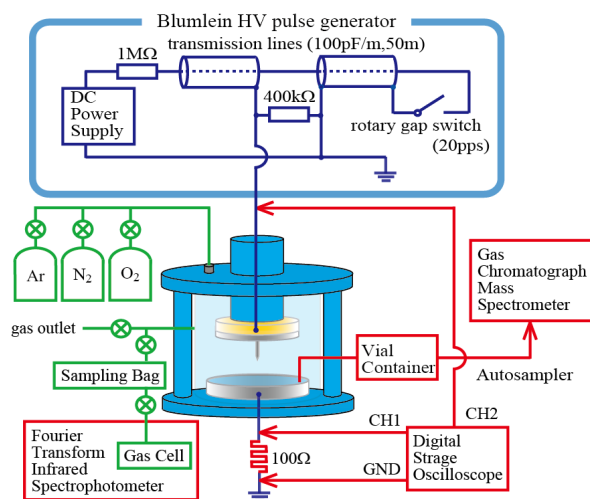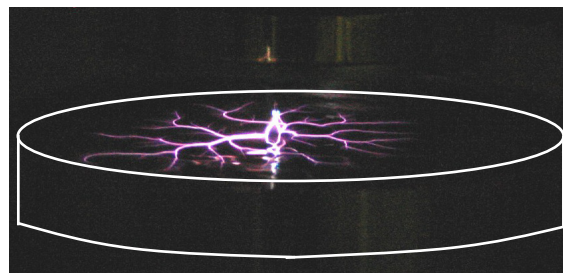
Fig.1 Experimental setup.

(a) After 15 minutes plasma exposure.

(b) After 60 minutes plasma exposure.

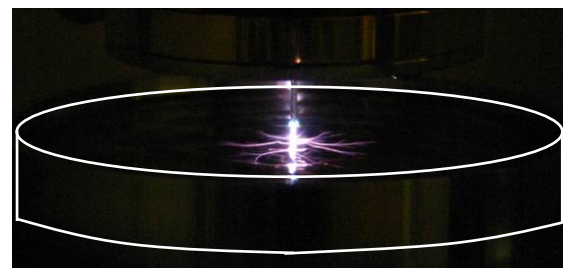*Fig.2 Photographs of a pulsed discharge in N_2-O_2 mixture.*

a cylindrical discharge chamber made of acrylic resin, with 140 mm in inner diameter, 100 mm in height and 1.5 L in volume. The needle electrode is 15 mm in length and 1.5 mm in diameter, and the water bath electrode has 119 mm in inner diameter and 12 mm in depth. Both electrodes are made of stainless steel and the water bath electrode is earthed. Test liquids are 70 g of methylene blue and phenol aqueous solutions with concentrations of 15 ppm and 3000 ppm, respectively. The distance between the needle electrode and the surface of the test liquids is fixed at 4 mm.

The BG gas for methylene blue decomposition is composed of N_2, O_2 and Ar, the purities of which are 99.99 %, 99.5 % and 99.99 %, respectively, and the gas is fed into the chamber with a constant gas flow rate of 6 L/min. The mixture ratios (%) of the BG gas are N_2 (or Ar)/ O_2=100/0, 90/10, 80/20, 60/40, 40/60, 20/80, 10/90 and 0/100. The BG gas for phenol decomposition is composed of Ar and O_2, the purities of which are 99.99 % and 99.5 %, and the gas is fed with the flow rate of 1 L/min. The mixture ratios (%) of the BG gas are Ar/ O_2 = 100/0, 90/10, 50/50 and 0:100.

A Blumlein HV pulse generator is used to produce a pulsed voltage. Using a DC high voltage source (LS40-10, Max-Electronics), HF coaxial cables (Fujikura, 50 m, 100 pF/m) are charged at 14.14 kV, and pulses are generated at a repetition frequency of 20 pps by a rotary gap switch. The pulses are applied to the needle electrode to generate a pulsed discharge above the surface of the aqueous solution.

The test liquids are exposed to the pulsed discharge for 60 minutes (methylene blue) and 120 minutes (phenol), and every 15 minutes, specimen is collected and decomposition rate is measured. The specimen taken from phenol aqueous solution is analysed by gas chromatography mass spectrometry (GCMS-QP2010, Shimadzu Corp., column: DB-17 ms) to examine the by-products in the aqueous solution. In order to analyze the off-gas from the discharge chamber, a Fourier transform spectrophotometer (FTIR-8900, Shimadzu Corp.) fitted with a gas cell with an optical path length of 10 m (10-PA, Infrared Analysis) is used.

3. RESULTS AND DISCUSSION

3.1 DECOMPOSITION CHARACTERISTICS OF METHYLENE BLUE IN AQUEOUS SOLUTION

Figs.2 (a) and (b) show photographs of a pulsed discharge in N_2-O_2 atmosphere after 15 and 60 minutes plasma exposure, respectively. Filamentary discharge reaches from the needle tip to the liquid surface, and the discharges split into several branches. Some of the branch discharges reach the water bath electrode. The extension of the discharge along the liquid surface tends to decrease; the discharge area is about 80mm in diameter after 15 minutes
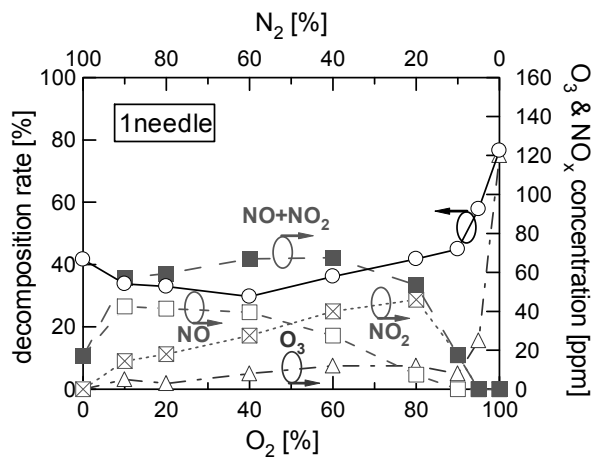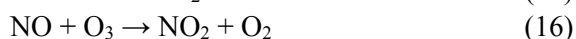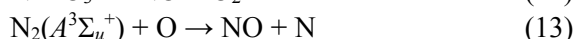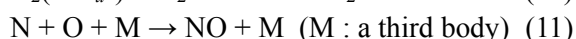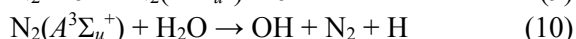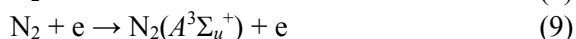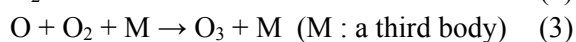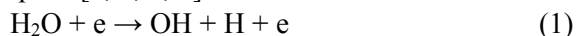
Fig.3 Methylene blue decomposition rate and O_3 and NO_x concentration as a function of mixture ratio of background gas (N_2-O_2).

exposure, and about 30 mm after 60 minutes plasma exposure.

Fig.3 shows the variations in the decomposition rate of methylene blue and the concentrations of O_3 and NO_x as a function of mixture ratio of N_2-O_2 after 15 minutes plasma exposure. The highest decomposition rate (about 76%) of methylene blue is observed in O_2 atmosphere, and the decomposition rate rapidly decreases with an increase of nitrogen content. In N_2 atmosphere, however, slight increase of the decomposition rate is observed.

Following reactions are known to occur during discharges in N_2-O_2 atmosphere including water vapour [1, 2, 3, 4].

$$H_2O + e \rightarrow OH + H + e \qquad (1)$$
$$O_2 + e \rightarrow 2O + e \qquad (2)$$
$$O + O_2 + M \rightarrow O_3 + M \ (M : \text{a third body}) \quad (3)$$
$$H_2O + O \rightarrow 2OH \qquad (4)$$
$$H_2O + O_3 \rightarrow H_2O_2 + O_2 \qquad (5)$$
$$H_2O_2 + h\nu \rightarrow 2OH \qquad (6)$$
$$H_2O + O(^1D) \rightarrow 2OH \qquad (7)$$
$$N_2 + e \rightarrow N + N + e \qquad (8)$$
$$N_2 + e \rightarrow N_2(A^3\Sigma_u^+) + e \qquad (9)$$
$$N_2(A^3\Sigma_u^+) + H_2O \rightarrow OH + N_2 + H \qquad (10)$$
$$N + O + M \rightarrow NO + M \ (M : \text{a third body}) \ (11)$$
$$N + O_3 \rightarrow NO + O_2 \qquad (12)$$
$$N_2(A^3\Sigma_u^+) + O \rightarrow NO + N \qquad (13)$$
$$NO_2 + O \rightarrow NO + O_2 \qquad (14)$$
$$NO + O \rightarrow NO_2 \qquad (15)$$
$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (16)$$

The variations of the decomposition rate with the BG gas composition can be attributed to the effects of active species. Since the discharge extends along the liquid surface, as shown in Figs.2 (a) and (b), high-energy electrons can collide with vaporized H_2O, OH radicals can be produced by reaction (1), and then OH radicals are probably contribute to methylene blue decomposition. The production of OH radicals is confirmed by the spectra of OH observed at 233, 254, 260, 268 and 283 nm in the emission from the discharge. In O_2 atmosphere, the discharge extends more widely on the liquid surface, as compared to the discharge in N_2-O_2, and this may lead more OH production by reaction (1), thus promoting decomposition. In addition, O and O_3 produced by reactions (2) and (3) and OH by reactions (4) and (7) can promote methylene blue decomposition. In N_2 atmosphere, the discharge develops similarly to that shown in Fig.2, and the effect of OH radicals produced by reaction (1) is nearly the same level. Therefore, the increase of the decomposition rate can be induced by another process, namely, OH radicals produced by nitrogen metastable molecules in reaction (10). In N_2-O_2 atmosphere, O_3 concentration decreases significantly, and considerable amount of NO_x is produced. The mechanism to decrease the decomposition rate of methylene blue is explained as follows. O_3 molecules are decomposed by NO and N respectively in reactions (12) and (16), and O_3 generation is suppressed by the depletion of O because O atoms are consumed for NO_x production in reactions (11), (13), (14) and (15). In this case, methylene blue can be decomposed by OH radicals generated the reaction (1); therefore, the decomposition rate remains low.

Fig.4 shows a photograph of a pulsed discharge in Ar-O_2 atmosphere. Filamentary discharges reach from the needle tip to the liquid surface, and extends along the liquid surface. Large number of branch discharges are observed during plasma exposure, as compared to Fig.2, and many OH radicals are found to be produced by the reaction (1). Fig.5 shows methylene blue decomposition rate and the concentration of O_3 as a function of mixture ratio of Ar-O_2 after 15 minutes plasma exposure. It is found that higher decomposition rate is achieved, and that the decomposition rate of methylene blue rises with an increase of Ar concentration in the mixture
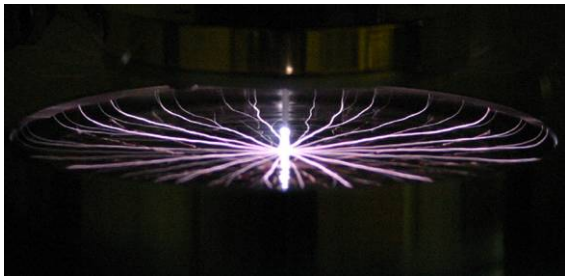
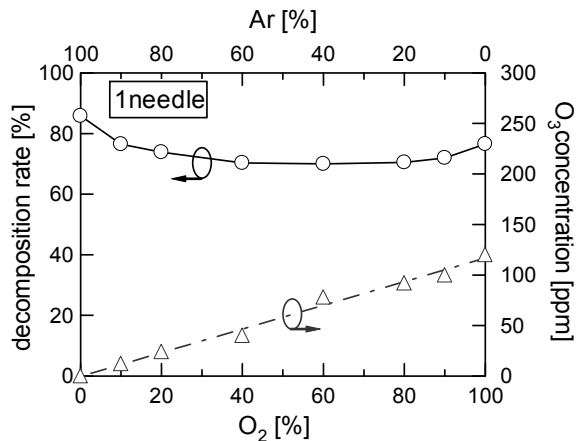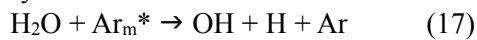*Fig.4 Pulsed discharge in the Ar-O₂ mixture.*

Fig.5 Variations in methylene blue decomposition rate and O₃ concentration as a function of mixture ratio of Ar-O₂.

(a) Ar (0 minutes)

(b) Ar (60 minutes)

(c) O₂ (0 minute)

(d) O₂ (15 minutes)

Fig.6 Photographs of pulsed discharges.

Fig. 7 Decomposition rate of phenol.

though O_3 concentration decreases at the same time. This means that some species in Ar-O_2 discharge contribute to the decomposition. Considering that Ar is an inert gas, Ar atoms in metastable states (Ar_m*) have possibility to decompose methylene blue directly and indirectly. Namely, $^3P_2$ and $^3P_0$ react directly with methylene blue, as shown by McCorkle *et al*.[5], and OH radicals produced by the reaction between H_2O vapour and $^3P_2$ and $^3P_0$, as shown in (17), contribute to decomposition of methylene blue.

$$H_2O + Ar_m* \rightarrow OH + H + Ar \qquad (17)$$

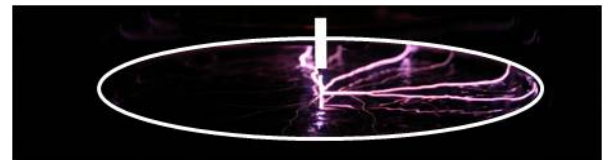## 3.2 DECOMPOSITION PROCESS OF PHENOL IN AQUEOUS SOLUTION

Figs.6 (a) - (d) show photographs of discharges in Ar and O_2 atmospheres. In Ar atmosphere, the discharge branches when it reaches the surface of the phenol aqueous solution and extends along the liquid surface as shown in Fig.6 (a). The shape changes over time, and the discharge length halves after 60 minutes, as shown in Fig. 6 (b). In O_2 atmosphere, there are thick discharges reaching the rim o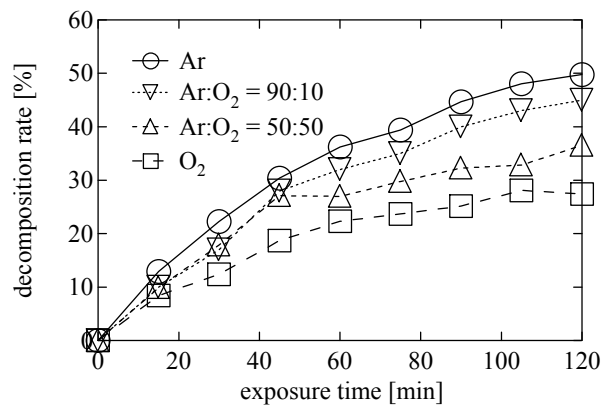f the water bath electrode, as shown in Fig.6 (c). After 15 minutes, there remain only thin discharges that do not reach the rim of the water bath electrode, as shown in Fig. 6 (d).

Fig. 7 shows the phenol decomposition rates for different BG gas compositions. The highest decomposition rate is obtained in Ar atmosphere, being 50% after 120 minutes of the plasma exposure. As the O_2 content increases the decomposition rate decreases, and the lowest rate of 27% is observed in O_2 atmosphere.
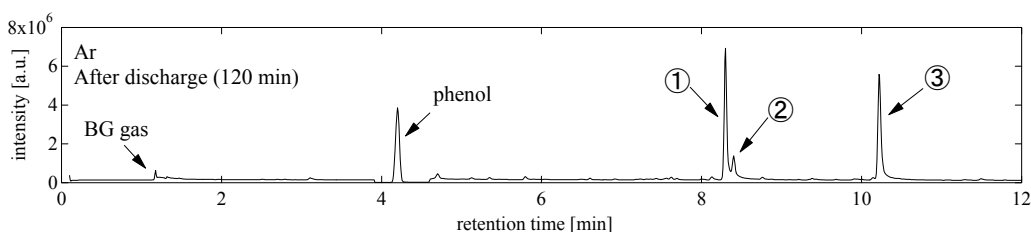
Fig. 8 Chromatogram of phenol aqueous solution after plasma exposure in Ar atmosphere
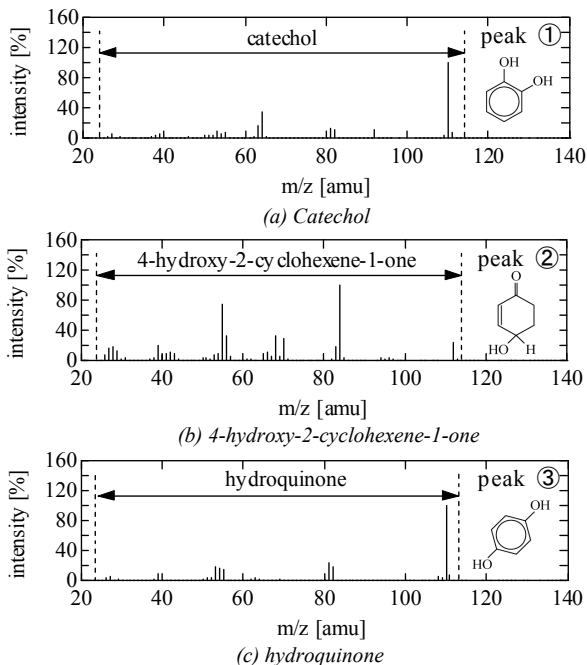

(a) Catechol

(b) 4-hydroxy-2-cyclohexene-1-one

(c) hydroquinone

Fig. 9 Mass spectra at peaks ①-③.

Fig. 10 Decomposition process of phenol in Ar atmosphere.

Fig. 8 shows a chromatogram of the sampled phenol aqueous solution after 120 minutes of plasma exposure in Ar atmosphere. There are peaks with retention times of ① 8.3 minutes, ② 8.4 minutes and ③ 10.2 minutes, in addition to the peaks for BG gas and phenol that appear at retention times of 1.2 and 4.2 minutes. These peaks are assumed to represent phenol decomposition products.

Figs.9 (a), (b) and (c) respectively show the mass spectra of peaks ①, ② and ③ observed in the chromatogram. From the comparison with reference spectra, the peaks ①, ② and ③ are found to represent catechol, 4-hydroxy-2-cyclohexene-1-one and hydroquinone, respectively.

Fig.10 shows phenol decomposition process in Ar atmosphere, inferred from the decomposition products. Since O_3 is not detected in off-gas analysis in the case of the Ar atmosphere, phenol can be decomposed by active species other than O_3. Hoeben et al. [6] reported that OH radicals produced by a pulsed discharge cause the
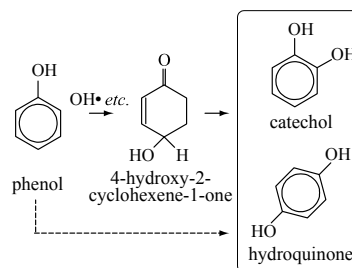
generation of dihydroxycyclohexadienyl radicals (structures in which a hydroxyl group is added to one of the C atoms making up the benzene ring of phenol); after that, catechol and hydroquinone are generated via some intermediate products. In this work, the electrical discharge is generated above a water surface, and hence active species derived from H_2O, such as OH, O, and HO_2 radicals, H_2O_2, etc., as well as high-energy electrons produced by the discharge, contribute to phenol decomposition. The 4-hydroxy-2-cyclohexene-1-one detected in this work is a structure very similar to the intermediate products assumed by Hoeben et al. [6]. Phenol is, therefore, likely to be converted into 4-hydroxy-2-cyclohexene-1-one, and then into catechol and hydroquinone. In addition, when a trace of O_2 is mixed in the BG gas, the production of catechol and hydroquinone is confirmed but 4-hydroxy-2-cyclohexene-1-one is not detected. Thus we can assume a production process of catechol and hydroquinone that does not involve 4-hydroxy-2-cyclohexene-1-one as an intermediate stage.

Fig.11 shows a chromatogram of the sampled phenol aqueous solution after 120 minutes of plasma exposure in O_2 atmosphere. Here the substances identified previously in the Ar atmosphere are also shown in the diagram. There are peaks with retention times of ① 1.3 minutes, ② 3.6 minutes, ③ 7.3 minutes, and ④ 7.6 minutes, which are regarded as decomposition products of phenol in O_2 atmosphere.

Figs.12 (a) - (d) show mass spectra of peaks observed in the chromatogram. From the
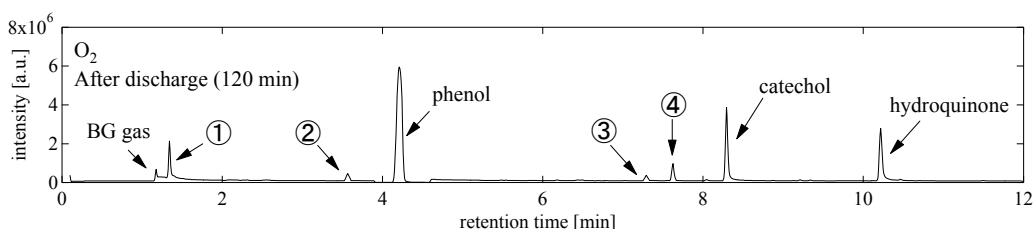
Fig. 11 Chromatogram of phenol aqueous solution after plasma exposure in O_2 atmosphere.

(a) formic acid

(b) maleic anhydride

(c) succinic anhydride

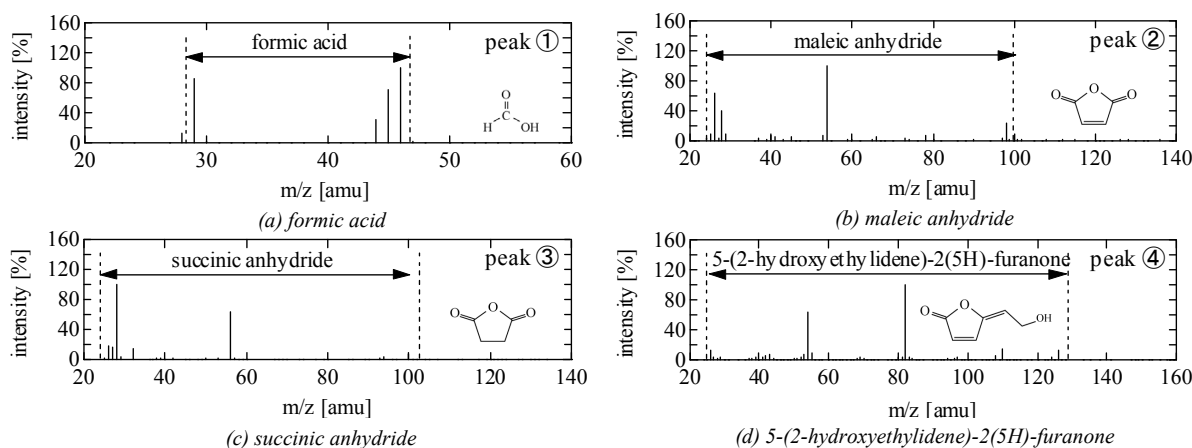*(d) 5-(2-hydroxyethylidene)-2(5H)-furanone*
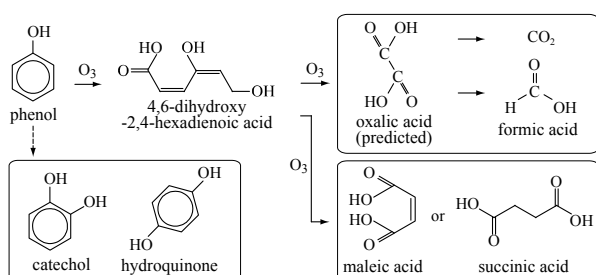
Fig.12 Mass spectra at peaks ① - ④.

Fig. 13 Decomposition process of phenol in O_2 atmosphere.

comparison with the reference spectra, the peaks ①, ②, ③ and ④ respectively represent formic acid, maleic anhydride, succinic anhydride, and 5-(2-hydroxyethylidene)-2(5H)-furanone. In the GCMS employed here, liquid samples are vaporized in a chamber heated up to 150 °C, then separated in a column for mass spectrometry. Therefore, we may conclude that substances with two hydroxyl groups located close to each other undergo dehydration due to intramolecular reaction, that is, the two hydroxyl groups form an ether bond, and one water molecule is separated. Hence maleic acid, succinic acid, and 4,6-dihydroxy-2,4-hexadienoic acid are likely to exist in the aqueous solution.

Fig.13 shows the decomposition process of phenol in an O_2 atmosphere, inferred from the decomposition products. Hoeben *et al*. [6] predicted that O_3 and phenol enter into a reaction of 1,3-dipolar addition so that the benzene ring is

cleaved, and unsaturated aliphatics are produced. These are then further decomposed into formic acid, oxalic acid, glyoxylic acid, and glyoxal. In this work, O_3 is detected in the off-gas at about 100 ppm in O_2 atmosphere; thus we may infer the existence of decomposition processes initiated from benzene ring cleavage caused by O_3. The 4,6-dihydroxy-2,4-hexadienoic acid observed in this work is similar in structure to unsaturated aliphatics; therefore this acid is likely to be a product of a 1,3-dipolar addition reaction between phenol and O_3. In addition O_3 reacts selectively with C=C double bonds [7], and then 4,6-dihydroxy-2,4-hexadienoic acid may be decomposed into maleic acid or succinic acid with 4 carbon atoms, or oxalic acid with 2 carbon atoms. Considering that formic acid is detected in this work while oxalic acid is not, and that formic acid is reported to be produced from oxalic acid in accordance with reaction (18) [8], oxalic acid is probably produced by the same processes as formic acid.

$$HOOCCOOH \rightarrow HCOOH + CO_2 \qquad (18)$$

The generation of catechol and hydroquinone in O_2 atmosphere has been confirmed. Lukes *et al*. [9] reported that dihydroxycyclohexadienyl radicals are generated from phenol due to OH radicals, and that catechol and hydroquinone are generated due to O_2 in the water. In our work, too, catechol and hydroquinone may be generated in that manner in O_2 atmosphere.
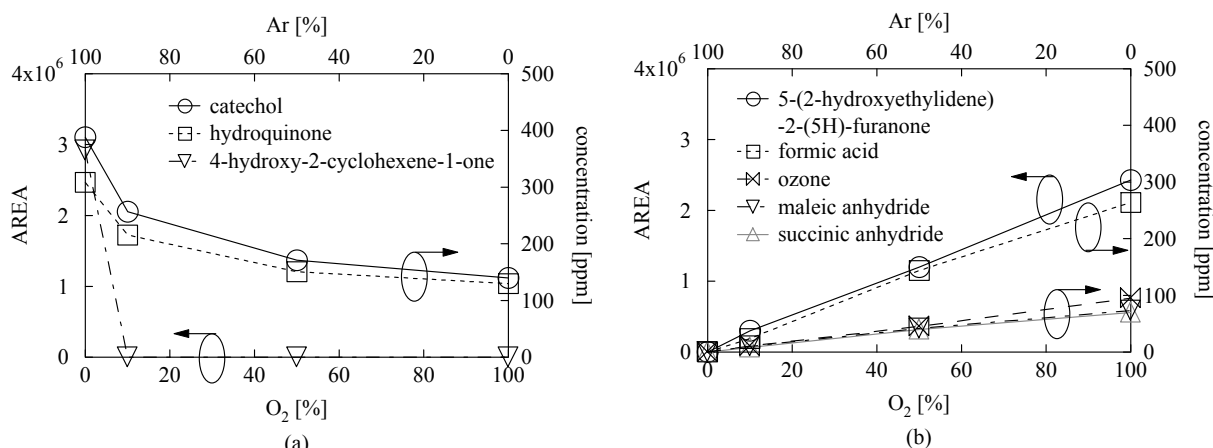
Fig.14 Concentrations of byproducts and O_3 as functions of mixture ratio of Ar-O_2.

Fig.14 (a) and (b) show the concentrations of decomposition products in the sampled phenol aqueous solution after 120 minutes of the plasma exposure at various BG gas compositions, and the O_3 concentration in the gas phase. Here quantitative data could not be obtained for 4-hydroxy-2-cyclohexene-1-one and 5-(2-hydroxyethylidene)-2(5H)-furanone, and hence the chromatographic areas are shown instead. As can be seen from Fig.14 (a), the concentrations of catechol and hydroquinone are highest in the case of Ar atmosphere, and decrease considerably with an increase of O_2 content. Furthermore, 4-hydroxy-2-cyclohexene-1-one is not produced in the presence of O_2. Fig.14 (b) indicates that formic acid, succinic anhydride, maleic anhydride, and 5-(2-hydroxyethylidene)-2(5H)-furanone are produced in O_2 atmosphere. Their concentrations increase with the content of O_2 and the concentration of O_3. This can be explained by the fact that the concentrations of decomposition products produced by cleavage of benzene rings due to 1,3-dipolar addition involving O_2 and O_3 depend on the O_3 concentration. The same decomposition products are also obtained in case of pure O_2 and Ar-O_2 mix, and hence we may infer that the same decomposition processes take place in both cases.

4. CONCLUSIONS

In this work, a pulsed-discharge plasma is generated above water containing methylene blue and phenol, and the decomposition characteristics of methylene blue are investigated for different BG composition. Further, the decomposition products from phenol are

processes. The results of the work are summarized below.

(1) Methylene blue is probably decomposed by OH radicals produced by the reaction between high-energy electrons and vaporized H_2O. In addition, the decomposition is enhanced by O and O_3 in O_2 atmosphere and OH produced by the reaction between vaporized H_2O and molecules (atoms) in metastable in metastable state in N_2 and Ar atmosphere. The decomposition, however, is suppressed in N_2-O_2 atmosphere due to O_3 depletion by NO_x.

(2) Phenol in aqueous solution is converted into catechol, 4-hydroxy-2-cyclohexene-1-one and hydroquinone in Ar atmosphere by the pulsed-discharge plasma exposure. In O_2 atmosphere, catechol, hydroquinone, CO_2, formic acid, oxalic acid, maleic acid, succinic acid, and 4,6-dihydroxy-2,4-hexadienoic acid are produced.

(3) In Ar atmosphere, phenol is likely to be converted into 4-hydroxy-2-cyclohexene-1-one, and then into catechol and hydro-quinone. In addition, phenol may be converted into catechol and hydroquinone thorough another process that does not involve 4-hydroxy-2-cyclohexene-1-one as an intermediate stage.

(4) In an O_2 atmosphere, the benzene rings of the phenol are cleaved by 1,3-dipolar addition involving O_3, thus producing 4,6-dihydroxy-2,4-hexadienoic acid. Subsequently, oxalic acid, maleic acid and

succinic acid are likely to be produced by reaction between C=C double bonds and O_3. In addition, we may infer the decomposition of oxalic acid into formic acid and CO_2, and the production of catechol and hydroquinone from phenol due to OH radicals and O_2 molecules present in the water.

(5) In Ar-O_2 atmosphere, the decomposition products are the same as in O_2 atmosphere. The concentrations of the decomposition products depend on the O_2 content and the O_3 concentration.

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