Plasma Degradation of Dibromophenols and Interpretation by Molecular Orbital Theory*)

Tetsuya AKITSU1,3), Shin-Ichiro KOJIMA2), Keiko KATAYAMA-HIRAYAMA1), Hiroki KURODA3) and Hiroshi OKAWA3)

1) University of Yamanashi, 4 Takeda, Kofu, Yamanashi 400-8511, Japan
2) Kyushu University, Fukuoka, Fukuoka 812-8581, Japan
3) Happy Science University, 4427-1 Hitotsumatsu-Hei, Chosei, Chiba 299-4325, Japan

(Received 2 January 2019 / Accepted 17 June 2019)

Dielectric barrier discharge was operated in the liquid-gas boundary and applied to the degradation of Dibromophenol (DBP). The brominated aromatic compound shows acute toxicity to aqueous living and, occasionally, carcinogenic and hormone-disruptive effect for human. The plasma degradation provides the advanced oxidation process by charged species, anion as well as neutral radicals. Plasma-degradation with the anion-exchange successfully worked and the controlled the production of BrO$^-$ by NO$_3^-$. Interpretation of the observed difference in the resistance is interpreted using the Molecular Orbital Theory.

© 2019 The Japan Society of Plasma Science and Nuclear Fusion Research

Keywords: plasma electrolysis, aromatic compound, advanced oxidation, molecular orbital theory
DOI: 10.1585/pfr.14.3401132

1. Introduction

Increasing amount of aromatic compounds, with multi benzene rings is produced as flame-retardant plastic materials. 2, 6-Dibromophenom (2, 6-DBP) is detected as a degradation product of Tetrabromophenisholenol-A (TBBP-A) [1,2]. The environmental toxicity is presented by World Health Organization (WHO) [3]. Concern of the animal carcinogenicity is expressed for a product in the oxidative degradation: BrO$_3^-$, by the International Agency for Research on Cancer (IARC) classification Group 2B [4]. Degradation of 2, 6-DBP have been studied using a dielectric barrier discharge in the gas-liquid boundary [5]. In this work, we aim at the confirmation of the reproducibility at lower discharge power, and experimental comparison of DBPs: 2, 4-DBP. Degradation at a higher concentration of DBP solution and a short-cut of the degradation using an anion-exchange polymer have been studied.

2. Materials and Methods

Lukes et al. [6] reported the measurement of $^7$OH radical production and O$_3$ decomposition in the presence of N$_2$ molecules in humid air, through the following reactions.

Dissociation and ionization generating OH anion and radicals

\[
\begin{align*}
H_2O + e & \rightarrow OH^- + H^+ + e \\
H_2O + e & \rightarrow 'OH + 'H + e \\
\end{align*}
\]

Reactions including excited oxygens

\[
\begin{align*}
O(\text{I}D) + H_2O & \rightarrow 2OH^- \\
O(\text{I}D) + O_3 & \rightarrow O_3 \\
\end{align*}
\]

Reactions including metastable state of nitrogen molecules

\[
N_2(A_3^\Sigma) + H_2O \rightarrow N_2 + 'OH + 'H.
\]

Inhibition of O$_3$ production and enhancement of OH$^*$ formation:

\[
\begin{align*}
OH^- + O_3 & \rightarrow 'O_2 + HO_2, \\
O_3 + 3HO_2 & \rightarrow 3OH^* + 3O_2. \\
\end{align*}
\]

Production of superoxide: Oxygen molecule is the primary accepter of electrons and forms $^5$O$_2^-$

\[
O_2 + e \rightarrow ^5O_2^-.
\]

Production of hydroxyl radicals:

\[
\begin{align*}
'OH_2 + H_2O & \rightarrow OH^- + 'HO_2 \\
'HO_2 + 'HO_2 & \rightarrow H_2O_2 + O_2 \\
H_2O_2 + 'O_2 & \rightarrow 'OH + OH^- + O_2 \\
H_2O_2 + e & \rightarrow 'OH + OH^-.
\end{align*}
\]

Dibromophenol + (['OH + OH$^*$])

\[
\rightarrow \text{Produced system.}
\]

Hydroxyl radical and anion are produced in the dissociation of hydrogen peroxide by the electron collision in the gas discharge. In the reactions, in air with humidity, one of the merits is the suppression of ozone generation. Ozone quench is important for the suppression of BrO$_3^-$. The suppression of BrO$_3^-$ is realized by NO$_3^-$ in the advanced oxidation.
Nitrogen reactions including the ozone quench generating the excited state of nitrogen and \( \text{NO}_x \):

\[
\begin{align*}
\text{N}_2 + e & \rightarrow 2\text{N}^* + e, \\
\text{O}^1(\text{D}) + \text{NO} & \rightarrow \text{NO}_2, \\
\text{N}^* + \text{O}_3 & \rightarrow \text{NO} + \text{O}_2, \\
\text{NO} + \text{O}_3 & \rightarrow \text{NO}_2 + \text{O}_2.
\end{align*}
\]

Figure 1 shows the experimental layout. The apparatus consists of a quartz tube 3.0 mm in outer diameter, 1.4 mm in inner diameter and W-Re electrode inserted coaxially. This part is submerged in the DBP water solution in a test vial, 100 mL. Discharge is excited with a quasi-sinusoidal high voltage generated by a fly-back transformer oscillator, at 16.94 kHz, 7.68 to 7.84 kV. Figure 1 (b) shows the High voltage is supplied to a W-Re wire inserted along the center. Discharge current was measured with a current probe and pre-amplifier TCP312 and TCPA300. High-side terminal voltage was measured with P-3000 high voltage probe. Discharge power was estimated by integrating the multiplied waveform and digitized Q versus V Lissajous figure. The electronic charge Q was measured as the voltage-drop across a ceramic capacitor, \( C_r = 4200 \text{pF} \) connected to the outer electrode surrounding the vial.

In the experiment, DBP sample was solved in NaOH solution, and diluted with pure-water. The concentration was measured at 20 mg/L. After plasma-injection, the concentration of the solution of DBP was measured by the high-performance liquid chromatograph (HPLC). The total organic carbon (TOC) was measure as the amount of CO2 from the incinerated organic materials. The concentration of Br\(^-\) and \( \text{BrO}_3^- \) was measured by the ion-chromatography. The concentration of the DBPs were measured by HPLC, L-6000 equipped with UV detector, L-4200 (Hitachi Co., Japan) with column X-bridge 4.6, 250 mm (Waters, Japan).

TOC measurement was carried out by TOC-LCSH/CSN and auto sampler, ASI-L, (Shimadzu Co., Japan) Ion chromatography for the anion ICS-1100 ( Dionex), with column IonPac AS22 (Dionex), and guard column, IonPac, AG22 (Dionex) installed with the electro-conductivity detector. The reproducibility of the time elapsed measurement and the experiment with high density samples was examined by HPLC Prominence-I LC-2030 Plus (Shimadzu Co., Japan) installed with UV-detector and a reverse mode column: Xbridge C-18, 5 \( \mu m \).

3. Experimental Results

Figure 2 shows the time-evolution of 2, 6-DBP concentration and TOC as a measure of remaining organic compounds. In Fig. 2 (a), oxygen and air discharge case, one can find that the bromine detachment is completed in 20 minutes. The decomposition in nitrogen (green-diamond) and Ar (blue-triangle symbols) discharge are inefficient compared with the oxidative media.

Decrease in the TOC in the oxygen discharge is almost 100%. Figure 3 shows the result of the ion-chromatography: Br\(^-\), and \( \text{BrO}_3^- \). \( \text{NO}_3^- \) was measured in the air discharge. In the oxygen discharge, the increase in the concentration of Br- anion is observed initially. Then, turned to decrease. This change indicates the production of \( \text{BrO}_3^- \) by oxidation. In the air-discharge, 40% of the initial TOC is remaining, but the suppression of \( \text{BrO}_3^- \) production was observed. This difference is attributed to the increase in \( \text{NO}_3^- \) density. The power estimated with the Q versus V Lissajous is summarized in Table 1.

Next object is the comparison of DBPs structure and the operation at lower discharge power < 6 W. Figure 4 shows the degradation of 2, 4-DBP and 2, 6-DBP, in the initial 20 minutes.

The power estimated with the Q versus V Lissajous is summarized in Table 2, at low discharge power < 6 W.

In Figs. 4 (b) and (c), our small finding is the bromine detachment in shorter time in the case of 2, 6-DBP. In the industrial bi-product, hazardous concentration of DBP may be observed. Let's say 10 times the observed case. Table 3 shows the result of the combination of the plasma degradation and the anion exchange using gel-type tri-methyl ammonium polymer, after the air-discharge.
Fig. 2 Comparison of the degradation of 2, 6-DPB by multi-gas plasma: (a) Concentration of 2, 6-DPB. Black-cross symbol indicate the control in a case air bubbling; (b) TOC.

Using the combination of plasma and anion exchange, high density sample can be degraded to 25% of the initial concentration successfully. Thus, a short cut of the degradation have been achieved. Figure 5 shows poly-styrene base anion exchange polymer, capable to exchange Br⁻.

Table 1 Discharge power.

| Gas  | Energy (mJ/s) | Frequency (kHz) | Power (W) |
|------|---------------|-----------------|-----------|
| Air  | 0.608         | 16.88           | 10.26     |
| Ar   | 0.293         | 16.69           | 4.89      |
| N₂   | 0.410         | 16.94           | 6.94      |
| O₂   | 0.749         | 16.91           | 12.67     |

Table 2 Discharge power.

| Gas  | Energy (mJ/s) | Frequency (kHz) | Power (W) |
|------|---------------|-----------------|-----------|
| Air  | 0.363         | 16.89           | 6.13      |
| Ar   | 0.224         | 16.99           | 3.81      |
| N₂   | 0.314         | 16.99           | 5.33      |
| O₂   | 0.354         | 16.92           | 5.99      |

degradation in 10 minutes, at discharge power < 13 W.
and NO$_3^-$ anion with OH$^-$ anion.

4. Discussion

4.1 Interpretation by frontier electron density calculation

The replacement reaction of Br$^-$ and OH$^-$ is determined by the energy difference in the starting system, DBP+OH-. Consequently, the reversed reaction in the produced system, bromophenol + OH$^-$ (in NaBr). Hydroxyl radical and anion are excited in the gas region. The excited state of hydroxyl radicals is singly occupied molecular orbital (SOMO) and directed to the electrophilic reaction. Figure 6 shows the energy diagram of the excited state of hydroxyl anion and DBP. The lowest unoccupied molecular orbital, LUMO energy of the starting system, 2, 4-DBP is $-0.540 \text{ eV}$ and excited energy of OH$^-$ is $4.045 \text{ eV}$. Difference between the highest occupied molecular orbital, HOMO and LUMO energy gives the activation energy, $4.585 \text{ eV}$. LUMO energy of the produced system, 1, 2-OH-4 bromophenol is $-0.332 \text{ eV}$ and HOMO energy of Br$^-$ is $-10.197 \text{ eV}$. This calculation indicates the reaction...
proceeds in the forward direction, while supplies of OH$^+$ radical and excited OH$^-$ ion lasts. Figure 7 shows the energy diagram of the starting system of 2, 6-DBP + OH$.\ \text{LUMO energy is slightly lower.}$

Figure 8 shows iso-surface of 2, 6-DBP. (a) the nucleophilic susceptibility, (b) electrophilic susceptibility reaction frontier electron density.
**Appendix A**

Figure A shows 3-D LUMO/HOMO model of 2, 6-DBP.

![Figure A](image)

(a) LUMO surface, $-0.737 \text{ eV}$; (b) HOMO surface, $-9.481 \text{ eV}$.

**Appendix B**

Figure B shows 3-D LUMO/HOMO model of 2, 4-DBP.

![Figure B](image)

(a) LUMO surface, $-0.540 \text{ eV}$; (b) HOMO surface, $-9.287 \text{ eV}$.

[1] WHO (World Health Organization) (1995) In: Van Esch GJ, ed., “Tetrabromobisphenol A and Derivatives. Geneva: WHO International Programme on Chemical Safety”, Environmental Health Criteria 172, 25 (1995).

[2] K. Katayama-Hirayama, A. Suzuki, S. Mukaiyama, K. Hirayama and T. Akitsu, Sustainable Environment Research 20(4), 221 (2010).

[3] K. Katayama-Hirayama, N. Toda, A. Tauchi, A. Fujioka, T. Akitsu, H. Kaneko and K. Hirayama, J. Environ. Sci. 26, 1284 (2014). http://DOL.ORG/10.1016/S1001-0742(13)60600-2

[4] IARC section 172.730 Potassium Bromate. https://www.accessdata.fda.gov/scripts/cdrh/cfdocs/cfcfr/CFRSearch.cfm?fr=172.730

[5] S. Kojima, K. Katayama-Hirayama and T. Akitsu, World J. Eng. Technol. 4, 423 (2016). http://DOL.ORG/10.4236/wjet.2016.43042

[6] P. Lukes and B.R. Locke, Ind. Eng. Chem. Res. 44(9), 2921 (2005). https://DOL.ORG/10.1021/ie0491342

[7] Biomedical CAChe 6.0 Users Guide (2003), Fujitsu.

[8] K. Somekawa, Molecular Orbital Calculation of Organic Molecules and The Applications (MOCOM) (Kyushu University Press, 2013) ISBN978-4-7985-0089-8.

[9] U. von Gunten, Water Res. 37(7), 1443 (2003). PMID: 12600374.

[10] U. von Gunten, Water Res. 37(7), 1469 (2003). PMID: 12600375.

[11] U. von Gunten and J. Holgne, Environ. Sci. Technol. 28(7), 1234 (1994). http://DOL.ORG/10.1021/es00056a009

[12] F. Parrino, G. Camera - Roda, V. Loddo, V. Augugliaro and L. Palmisano, Appl. Catal. B Environmental 178, 37 (2013). http://DOL.ORG/10.1016/j.apcatab.2014.10.081