Oxidative Decomposition of Organic Compounds by Ozone Microbubbles in Water

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Oxidative degradation of poly(ethylene glycol) (PEG) by ozone microbubbles (O3MBs) was investigated in water. Ozone water are generally effective in oxidation reaction with a variety of organic compounds. O3MBs have promise to improve the efficiency because it seems that O3MBs generates hydroxy radicals, resulting in the higher active oxidative degradation. Herein, oxidative decomposition of PEG by O3MBs in water was carried out and the products were characterized by 1H nuclear magnetic resonance (NMR) and matrix assisted laser desorption/ionization fourier transform ion cyclotron resonance mass spectrometry (MALDI-FT-ICR-MS). Through the continuous struggles, decomposition of PEG was promoted by O3MBs. It was found that O3MBs with hydrogen peroxide added had the largest decomposition effect. The reason has been veiled yet, however, the author reasons that O3MBs have promise as the novel degradation system.

Keywords: Ozone, Microbubbles, Poly(ethylene glycol)

1. Introduction

Microbubbles (MBs) are different from the common mm-order bubbles, and the diameter is approximately 1 – 100 μm. The distinctive features are these; (1) the rising rate is the slower, (2) the pressure inside the bubble are the higher, resulting in the higher miscibility of gas, and (3) the electric bilayer induces the condensation of charges on the surface. In addition, hydroxy radicals are generated at the time when MBs collapse. The feature of hydroxy radicals is the stronger oxidizability against organic compounds [1-4]. However, the life-time is approximately nano-seconds, and continuous generating methodology is needed. The mechanism how to generate hydroxy radicals by MBs has been still unclear, yet hydroxy radicals generated by MBs have promise to be applied to a number of fields such as water treatment, medical, and agricultural technologies.

Ozone has strong oxidizability, and some active species such as hydroxy radicals derived from the autolysis reaction. Ozone water reacts with olefins, resulting in carboxylic acids [5-8].

Given the aforementioned features, ozone inside the MBs (O3MBs) has promise to efficiently generate hydroxy radicals resulting from the higher miscibility, the collapse, and autolysis on the surface (Fig. 1).

Fig. 1. Mechanism of generation of hydroxy radicals by ozone microbubbles (O3MBs).

The details of the effects of O3MBs on the oxidative decomposition of organic compounds has not been elucidated yet [9,10]. Thus, oxidative decomposition of organic compounds having the low degradability has been investigated [11-14].

Herein, the effects of O3MBs on oxidative decomposition in water was studied by decomposing water-soluble polymers, and
poly(ethylene glycol) (PEG) was utilized as a model polymer. Furthermore, the additive effect of H_2O_2 and pH-dependence on the reactions were also investigated. Finally, the decomposition reaction could be controlled by the addition of Na_2CO_3, and the resultant products were simplified.

2. Experimental

2.1. Generating system of O_3MBs

MBs were generated by the pressurized dissolution system (Fig. 2). Ozone was solubilized in the MBs at the pressured condition (0.4 MPa) by the bellows pump (Σ P-15D-V, Sigma Technology, Co., Ltd.). Saturated ozone water was prepared and released to the air by dispersing nozzle to generate O_3MBs (Jpn. Petroleum Exploration Co., Ltd.).

The concentration of O_3 in the aqueous solution was monitored by O_3 monitor (Ebara Jitsugyo Co., Ltd.). Low pressure mercury lamp was utilized as the light source (λ = 253.7 nm). O_3 water was supplied to the detector in the monitor, and the absorption was detected to determine the concentration of ozone in the aqueous solutions.

2.2. Degradation of PEG by O_3MBs in water

O_3MBs (O_3 = 1.0 L/min) were generated at 21 – 23 °C in ion exchanged water (2.5 L). MBs were generated by the pressurized dissolution system. The concentration of O_3 was kept at 4 – 7 or 20 – 23 ppm during the experiments. PEG (M_n ~ 10000 g/mol; 1.5 g, 0.15 mmol) was solubilized in water (500 mL), and it was added to the solution after the constant concentration of O_3. Then, the solution was treated for 90 – 180 min.

2.3. Additive effect of H_2O_2

Similarly, the additive effect of H_2O_2 on the degradation was also studied. An aqueous solution of H_2O_2 (30 wt%, 1.0 mL) had been added to the O_3MBs solution (2.5 L), and an aqueous solution of PEG was added to the mixture. The concentration of H_2O_2 was set as 10 mM.

2.4. Additive effect of NaOH

An aqueous solution of NaOH (conc. ~ 1.0 M) was added to the O_3MBs water to keep pH ~ 10. Then, an aqueous solution of PEG (500 mL, 0.15 mmol) was added to the solution, and the mixture was treated by O_3MBs for 180 min.

2.5. Additive effect of Na_2CO_3

Na_2CO_3 (10 g) had been added to the O_3MBs water, and an aqueous solution of PEG (500 mL, 0.15 mmol) was added to the mixture.

2.6. Characterization

The decomposition of PEG in the solution was characterized by TOC (total organic carbon), 1H NMR, and MALDI-TOF-FT-ICR-MS.

3. Results and discussion

3.1. Characterization of mineralization by TOC

To confirm whether PEG was decomposed to gases (ex. CO_2) or not, the reaction was evaluated by TOC (Fig. 3). PEG hardly suffered from O_3MBs without any additives. In the condition with H_2O_2 and NaOH, PEG was slightly decomposed to inorganic compounds.

3.2. Characterization by 1H NMR

The resultant products were characterized by 1H NMR to confirm the structure. The products after the reaction showed the peaks from PEG (δ = 3.6 ppm) and new peaks (δ = 4.15 – 4.35 ppm). The
results indicated that aldehyde and ester groups were generated after the treatment of O3MBs. In addition, those intensity depended on the treatment-time, suggesting that some compounds were generated through the oxidative degradation of PEG. It was also found that H2O2 accelerated the oxidative decomposition of PEG by O3MBs in water.

3.3. Characterization by MS analysis
3.3.1. Effects of MBs on the decomposition

The resultant products were further characterized by MALDI-TOF-FT-ICR-MS to elucidate the detail. After the reaction with O3MBs, the monomodal peak of PEG \((M_p \sim 8000\ m/z; M_p\), molecular weight at the peak top) changed to the bimodal peaks whose \(M_p\)’s were 4000 and 2000 \(m/z\). Both peaks had the series of some peaks at constant interval corresponding the MW (molecular weight) of ethylene glycol \(44\ m/z\) in the spectrum. As results from \(^1\)H NMR and MS measurements, it seemed that PEG with lower MW (○), PEG with the ester- (●) and carboxylic acid-terminal (■) were gained (Fig. 4a). After the treatment for 180 min, almost all peaks disappeared, suggesting that PEG was decomposed to the low MW compounds \(< 1000\ m/z\) (Fig. 4b).

Compared to the above results, PEG was treated by ozone water without MBs. After the treatment for 1 min, the result was almost same with the results with O3MBs (Fig. 5a). This indicated that the resultant products were almost same in both conditions. On the other hand, the peak series from the products were still observed in the spectrum after the treatment for 180 min (Fig. 5b). The result was different from that with O3MBs, therefore, it was found that MBs accelerated the oxidative decomposition of PEG in water, yet the concentration of ozone was same in both conditions. This would be because ozone gas more efficiently encountered PEG by generating MBs in water.

3.3.2. Effects of H2O2 and NaOH

H2O2 accelerated the oxidative degradation of PEG by O3MBs in water, resulting from the increment of hydroxyl radicals. On the other hand, NaOH inhibited the degradation reaction. This would be because the autolysis of ozone was accelerated in the base condition. This would result in the shorter life-time of radicals, inducing the lower concentration of ozone. In both cases, the decomposing rate with MBs was faster than that without MBs. Therefore, MBs were effective for the oxidative decomposition of PEG in water.

3.3.3. Effects of Na2CO3

Finally, the effect of Na2CO3 on the reaction was investigated. The MS spectrum showed only two series and the intervals corresponded to MW of ethylene glycol, suggesting that the mechanism in the condition was different from the non-additive condition, and simplified by addition of Na2CO3 (Fig. 6).
Fig. 6. MALDI-TOF-ICR-MS spectra of PEG decomposed by O₃MBs in the presence of Na₂CO₃.

4. Conclusion

In conclusion, oxidative decomposition of PEG by O₃MBs in water, and the effect of MBs on the reaction was investigated. MBs accelerated the reaction, yet PEG was not completely mineralization. After the reaction, not only PEG with the lower MW but also PEG with ester- and carboxylic acid-terminals were yielded, confirmed by ¹H NMR and MALDI-TOF-FT-ICR-MS measurements. The effect of additives on the reaction was also investigated, and it was found that H₂O₂ accelerated the reaction. Furthermore, the resultant products were simplified by addition of Na₂CO₃, indicating that the mechanism would be controlled by additives.

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