Quantitation and evaluation of nitrous acid, nitric acid, and hydrogen peroxide formed in ultrasonic cavitation bubbles

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1. Introduction

When an aqueous solution containing dissolved air is irradiated by ultrasound, active bubbles are generated, where N_2 oxidation and water decomposition occur and result in the formation of NO_2^-, NO_3^-, and H_2O_2. The yields of NO_2^-, NO_3^-, and H_2O_2 are representative indexes to understand the chemical effects of ultrasonic cavitation[1,2], because these yields would be affected by the maximum temperature, maximum pressure, and number of active bubbles. The chemical effects of ultrasonic cavitation have been actively studied for a long time, but the physicochemical properties of active bubbles are still unclear.

In this study, we tried to measure the actual yields of NO_2^-, NO_3^-, and H_2O_2 just after bubble collapse by using the addition of NaOH to a sample solution[3]. The yields of NO_2^- and NO_3^- formed at different solution temperatures and different ultrasonic powers were compared. The temperature in collapsing bubbles, the number of active bubbles, and their chemical effects were discussed.

2. Experimental

Ultrasonic irradiation was performed using a 65 mm ϕ oscillator and an ultrasonic generator (Kaijo 4021 type; frequency: 200 kHz; nominal maximum power: 200 W). The cylindrical reaction vessel (inner diameter: 50 mm) was used and the bottom of the vessel was set at 4.0 mm away from the top of the oscillator. Water containing dissolved air (60 mL) in the presence and absence of NaOH (1.0 mM) was sonicated in a water bath maintained at constant temperature using a cold-water circulation system. The sonication was performed under opened condition. The ultrasonic power applied to the sample solution was measured by a calorimetric method. In this study, the calorimetric power of 3.3, 7.4, 10.3, 13.2, and 15.0 W was used for ultrasonic irradiation. After irradiation, the solution was analyzed. The concentration of NO_2^- and NO_3^- was measured by an ion chromatograph. The concentration of H_2O_2 was measured using a KI colorimetric method by a UV-visible spectrophotometer.

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3. Results and discussion

Fig. 1 shows the changes in concentrations of NO_2^-, NO_3^-, and H_2O_2 in the sonolysis of air-dissolved water, where the ultrasonic irradiation was turned off at 60 min. It can be seen that the concentrations of NO_2^-, NO_3^-, and H_2O_2 increased curvilinearly with irradiation time. This is due to the generation of microbubbles with extremely high temperatures and high pressures[4,5]. The formation of H_2O_2 occurs as follows.

$$H_2O \rightarrow OH + H \quad (1)$$
$$2OH \rightarrow H_2O_2 \quad (2)$$
$$H + O_2 \rightarrow OOH \quad (3)$$
$$2OOH \rightarrow H_2O_2 + O_2 \quad (4)$$

Representative reactions for the formation of HNO_2 and HNO_3 are suggested as follows[4,5].

$$O_2 \rightarrow 2O \quad (5)$$
$$N_2 + O \rightarrow NO + N \quad (6)$$
$$N + O_2 \rightarrow NO + O \quad (7)$$
$$N + OH \rightarrow NO + H \quad (8)$$
$$2NO + O_2 \rightarrow 2NO_2 \quad (9)$$
$$NO + OOH \rightarrow NO_2 + OH \quad (10)$$
$$NO + O \rightarrow NO_2 \quad (11)$$
$$NO + OH \rightarrow HNO_2 \quad (12)$$
$$NO_2 + OH \rightarrow HNO_3 \quad (13)$$
$$2NO_2 + H_2O \rightarrow HNO_2 + HNO_3 \quad (14)$$

In Fig.1, it was also confirmed that the changes of these concentrations occurred even after the irradiation was turned off at 60 min: the concentrations of NO_2^- and H_2O_2 decreased with the standing time, while the concentration of NO_3^- increased with the standing time. On the other hand, in the case of the sum of the concentrations of NO_2^- and NO_3^-, it increased linearly during irradiation and became constant during standing without irradiation. Since the ultrasonic irradiation of air-dissolved water makes the solution acidic[2], the results of Fig. 1 shows that NO_2^- and H_2O_2 undergo a redox reaction in the acidic solution to form NO_3^-, as eq. (15), both during irradiation and during standing without irradiation.

$$NO_2^- + H_2O_2 \rightarrow NO_3^- + H_2O \quad (15)$$

Next, the sonolysis of air-dissolved water was done in the presence of NaOH. It was found that the progress of eq.(15) did not occur in the presence of NaOH[3]: the addition of NaOH was found to be an effective way to measure the actual yields just after bubble collapse.

To discuss the characteristics of active bubbles, the sonolysis of air-dissolved water was performed at different solution temperature. **Figs. 2** and **3** show the sum of the yields of NO_2^- and NO_3^- and the NO_3^-/NO_2^- ratio as a function of solution temperature at ultrasonic power of 10.3 W. It was confirmed that the sum of the yields of NO_2^- and NO_3^- decreased and the NO_3^-/NO_2^- ratio increased with increasing solution temperature. These results suggested that the temperature in collapsing bubbles and the number of active bubbles decreased with increasing solution temperature.

Next, the effects of ultrasonic power on the formation of NO_2^- and NO_3^- were investingated. It was confirmed that ultrasonic power affected clearly on the yields of NO_2^- and NO_3^-, but it did not affect on the NO_3^-/NO_2^- ratio. These results suggested that 1) the temperature and pressure in collapsing bubbles were not affected by ultrasonic power and 2) the number of active bubbles increased with increasing ultrasonic power up to a certain power.

In multi-bubble cavitation as studied here, when the ultrasonic power increases, it is generally considered that the quality related to the bubble temperature and quantity related to the number of the active bubbles increase simultaneously. Because of the simultaneous changes, it has been difficult to understand the effects of these two factors precisely. The analysis of the yields of NO_2^- and NO_3^- formed in the presence of NaOH would be useful to discuss the quality and quantity of the active bubbles during ultrasonic cavitation.

References

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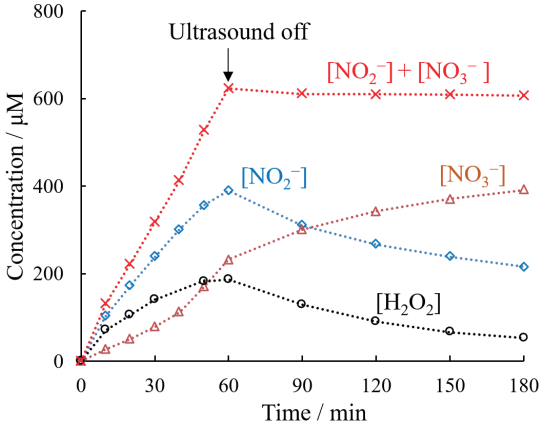

Fig.1 Changes in concentrations of NO_2^-, NO_3^-, and H_2O_2 with irradiation time and with standing time after irradiation. Solution temperature: 20°C.

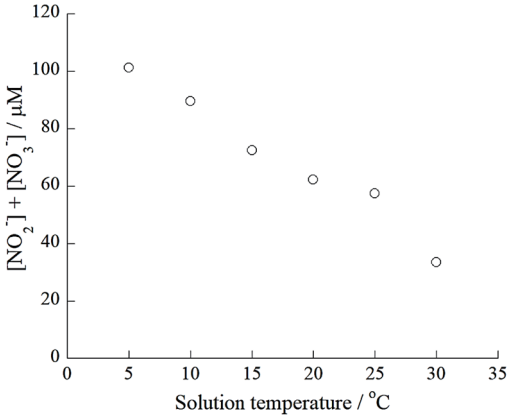

Fig.2 Effect of solution temperature on the sum of the yield of NO_2^- and NO_3^-. Sonication time: 5.0 min.

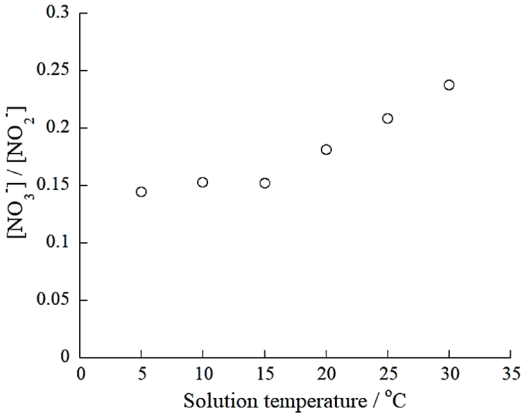

Fig.3 Effect of solution temperature on the NO_3^-/NO_2^- ratio. Sonication time: 5.0 min.