

Concentration of OH Radicals in the Interfacial Region of Cavitation Bubbles

キャビテーション気泡界面領域の OH ラジカル濃度

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1. Introduction

Intense ultrasound in liquids provides a unique environment where high-energy chemical reactions occur.¹⁾ The chemical effects of ultrasound originate from hot spots formed during the collapse of acoustic cavitation bubbles. These hot spots have temperatures of roughly 5000 K, pressures of more than 300 atm, and usually emit bluish light called sonoluminescence (SL).²⁾ Inside cavitation bubbles in an aqueous solution, water vapor is decomposed to form hydrogen atoms (H·) and hydroxyl radicals (OH·), part of which dissolves into liquid.³⁾ Therefore, three different reaction sites are considered to exist, i.e., the inside of cavitation bubbles, the gas-liquid interfacial region of the cavitation bubbles, and the bulk liquid. Since many sonochemical reactions are related to OH radicals in liquid phase, the concentration and the distribution of OH radicals produced by ultrasound may be the important factors in sonochemistry.

In an interfacial region between the cavitation bubbles and the liquid, the high local concentration of 4 mM of OH radicals at 1 MHz ultrasound has been reported by Henglein et al.⁴⁾ However, the local concentration of OH radicals should depend on the ultrasonic parameters that influence cavitation bubble dynamics. In this study, the local concentration of OH radicals in the interfacial region of cavitation bubbles is estimated at different ultrasonic frequency and intensity by the same method as Hengleins'.⁴⁾

2. Experimental

The experimental setup is shown in **Fig. 1**. Ultrasound was irradiated using a commercial apparatus (KAIJO, TA4021), frequencies of which were 200 kHz and 650 kHz with a same transducer in a thermostatic bath (20°C) and the nominal electric power was 200 W maximum and can change with a volume knob. For reference SL at 200 and 600 kHz in 0.5 M NaI solution are shown in **Fig. 2**. The practical ultrasonic power in a vessel was measured by calorimetry. Solutions of 50 mL volume of aqueous potassium iodide solutions at various concentrations were irradiated for 1 min.

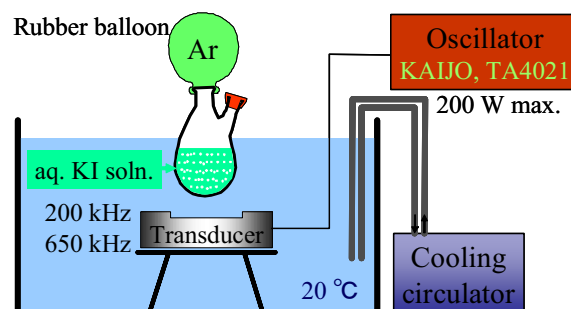


Fig. 1 Experimental setup.

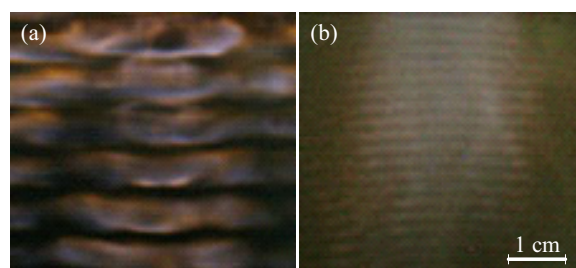


Fig. 2 Sonoluminescence in 0.5 M NaI at (a) 200 kHz and (b) 650 kHz.

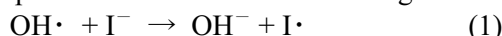
Before irradiation, argon gas was bubbled through the solution. During irradiation, the vessel was closed. The iodine concentration in the irradiated solutions was determined by spectrophotometry (the absorption coefficient of I_3^- at 350 nm being $2.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). In the case of the iodide solutions of lower concentration, 1 mL of 2.5 M KI solution was injected before the absorbance measurement to ensure that I_2 was quantitatively converted into I_3^- . H_2O_2 was subsequently determined by adding 120 μL of a $5 \times 10^{-2} \text{ M}$ ammonium molybdate solution and measuring the increase in the 350 nm absorbance. All the iodide solutions contained phosphate buffer and had a pH of 5.9 to suppress the reaction of H_2O_2 and I_3^- occurring in neutral or alkaline solutions.

3. Results and Discussion

Figure 3 shows the rates of iodine and hydrogen peroxide formation at 650 kHz ultrasound as the function of the iodide concentrations. The ultrasonic intensity is 0.9 W/cm^2 . The sum of the two rates is also shown in **Fig. 3**. It is seen that the sum is almost constant in the all range of iodide concentration. The total yield of H_2O_2 and I_2 is

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independent of the iodide concentration and equal to the H_2O_2 yield in pure water. This result may prove that OH radical reactions under this condition are competitive reactions of the following reactions.



The amount of H_2O_2 decreases with increasing iodide concentration, and the amount of I_2 increases correspondingly. The constant amount of OH radicals can reach the aqueous phase. Therefore, at the concentration of iodide where the formation rate of I_2 is equal to that of H_2O_2 , the rates of the reactions of Eqs. 1 and 3 should be equal:

$$k_1[\text{I}^-][\text{OH}\cdot] = 2k_3[\text{OH}\cdot]^2 \quad (4)$$

where k_1 and k_3 are the reaction rate constants of Eqs. 1 and 3, respectively. Then, the concentration of OH radicals is expressed by Eq. 5.

$$[\text{OH}\cdot] = (k_1/2k_3)[\text{I}^-] \quad (5)$$

Using $k_1 = 1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ and $2k_3 = 1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$,⁴⁾ the local concentration of OH radicals can be calculated easily by Eq. 6.

$$[\text{OH}\cdot] = 0.83 \times [\text{I}^-] \quad (6)$$

Figure 4 shows the enlarged graph of Fig. 3 in low concentration range of I^- from 0 to 0.005 M and the similar graph at 200 kHz. The formation rates of I_2 and H_2O_2 are equal at 2 mM for 650 kHz and at 1 mM for 200 kHz. Thus, the local concentration of OH radicals at 650 kHz and 200 kHz are 1.7 mM and 0.8 mM, respectively. All these cases the bulk concentrations of OH radicals, which can be calculated from the formation rates of I_2 by the left hand side of Eq. 4, were in the order of 10^{-15} M .

Table I summarizes the local concentrations of OH radicals together with the total formation rate of H_2O_2 and I_2 , which may be considered as the half rate of total OH radicals released from cavitation bubbles into the liquid.

The local concentration of OH radicals at higher frequency and lower intensity is higher, while $\text{H}_2\text{O}_2 + \text{I}_2$ rate has the opposite tendency. It may be explained by cavitation bubble stability. If bubbles excite shape instability, the interfacial region may be disturbed to decrease the localization of OH radicals while the convection by surface disturbance may promote the diffusion of it.

4. Conclusion

The concentration of OH radicals in the interfacial region at 650 kHz is higher than that at 200 kHz. At 200 kHz it is higher at lower intensity.

Acknowledgment

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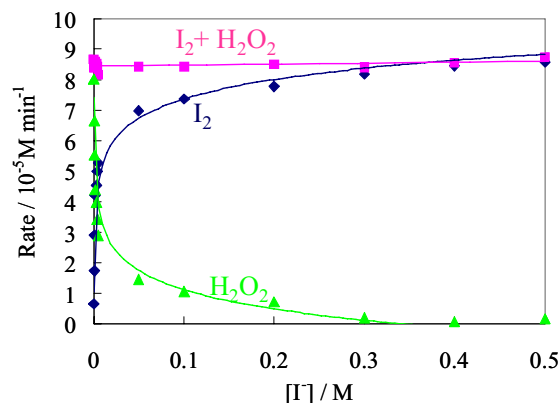


Fig. 3 Sonochemical formation rates of I_2 and H_2O_2 as a function of $[\text{I}^-]$ in the range to 0.5 M.

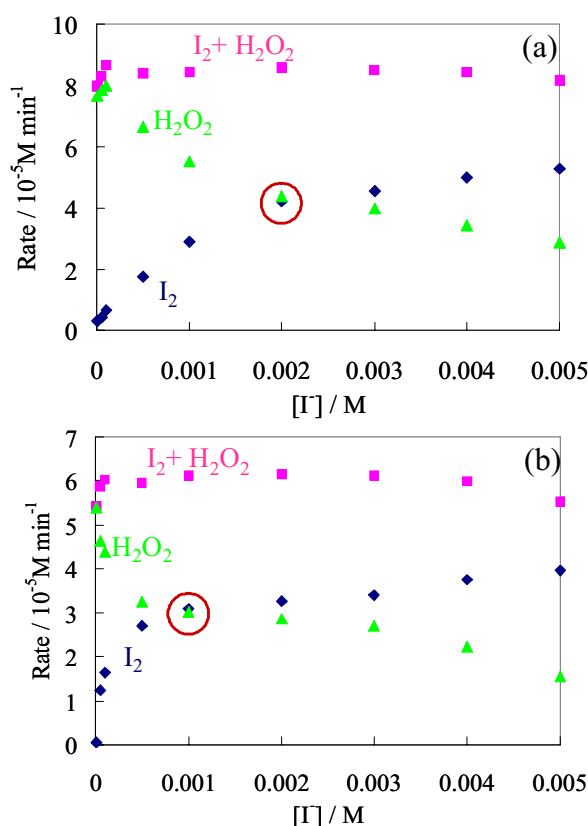


Fig. 4 Sonochemical formation rates of I_2 and H_2O_2 as a function of $[\text{I}^-]$ in the range to 0.005 M at (a) 650 kHz and (b) 200 kHz for 0.9 W/cm^2 .

Table I Local concentrations of OH radicals

Frequency (Intensity)	$[\text{OH}\cdot]$	$\text{H}_2\text{O}_2 + \text{I}_2$
650 kHz (0.9 W/cm^2)	1.7 mM	0.08 mM/min
200 kHz (0.9 W/cm^2)	0.8 mM	0.06 mM/min
200 kHz (1.4 W/cm^2)	0.04 mM	0.1 mM/min

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