Rate Control of Sono-oxidation of KI by adding NaHCO₃

KI の超音波酸化速度に対する NaHCO₃ 添加効果

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1. Introduction

In previous report [1], the rate control of sono-oxidation of potassium iodide (KI) solution in a CO_2-Ar atmosphere was shown. Because carbon hydrogen carbonate ($NaHCO_3$) provides CO_2 by sonication, the possibility of the rate control of sono-oxidation was predicted by adding $NaHCO_3$.

In this presentation, $NaHCO_3$ was added in the system for the rate control of sono-oxidation. Soda water dissolved CO_2 is carbonic acid, namely acidic. The solution dissolved $NaHCO_3$, on the other hand, is basic. Effect of pH on the rate of sono-oxidation will be discussed.

2. Experimental

As irradiation sources, three deferent transducers were used: an ultrasonic atomizer (Honda Electronics HM-303N, 2.4 MHz and 15 W, an ultrasonic extraction apparatus (Honda Electronics UMS, 200 kHz and 15 W), and a sono-reactor system (Kaijo QUAVA mini, 200 kHz and 50 W). In particular, the last one was mainly used. In all cases, ultrasonic irradiation was carried out from the bottom surface of the solution. Reactant was 0.1 M KI solution. First, the matrix gas was introduced through the lower port of the Pyrex glass reactor except an air atmosphere. As matrix gases, Ar, and O_2 was used. In the present study, Ar was mainly used. Before sonication, the reactor was filled with the matrix gas and then, certain amount of $NaHCO_3$ was dissolved in the reactant solution. Almost all the reactions were carried out between 24 ºC and 28 ºC.

The rate of sono-oxidation was evaluated by potassium iodide (KI) dosimetry at 355 nm using a UV-Vis spectrophotometer (JASCO V-730).

3. Results and discussion

It is known that acoustic cavitation is strongly affected by dissolved gas, namely atmospheric gas. For example, as shown in **Fig. 1**, the intensity of multi-bubble sonoluminescence (MBSL) in an Ar atmosphere has higher intensity than air one.

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Fig. 1 also shows their intensity decrease when $NaHCO_3$ is added into the solution. As you know, $NaHCO_3$ reacts to CO_2 by not only heating but also sonication [2] and CO_2 produced has high solubility in water. Then, intensity of cavitation decreases by CO_2.
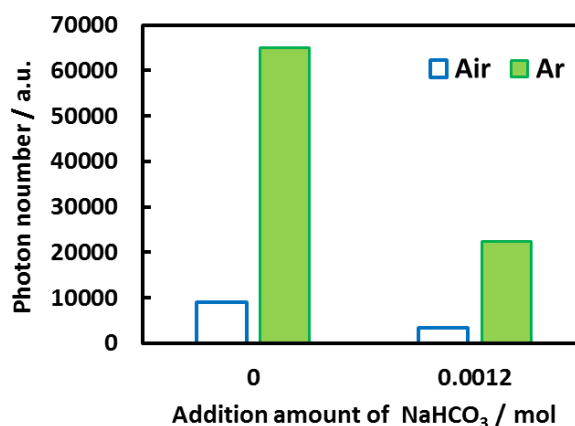

Fig. 1. Decrease in the intensity of MBSL by adding **NaHCO₃**. Ultrasound: 2.4 MHz, 15 W; Reactant: 0.1 M KI solution, 10 mL; Room temperature.

In the case of sono-oxidation of KI solution in an Ar atmosphere, on the other hand, the rate of oxidation increased. **Fig. 2** shows the absorbance as a function of the amount of $NaHCO_3$ at 200 kHz. The absorbance increased with addition of $NaHCO_3$ in low concentration. Then, it had a peak value at about 0.05 M. This behavior is similar to the case of the introduction of CO_2 in an Ar matrix. As reported previously [3], introduction of CO_2 in an Ar matrix is to improve sono-oxidations. Since $NaHCO_3$ reacts to CO_2 as follows, sono-oxidation is expected to improve, namely I^- ions in KI solution are also expected to be oxidized rapidly.

(Sonolysis of $NaHCO_3$)
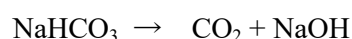
$$NaHCO_3 \rightarrow CO_2 + NaOH$$

Fig. 2 also indicated absorbance decreased after the maximum value. Thus, I see the

rate of sono-oxidation depends on the amount of $NaHCO_3$. Conversely, the amount of $NaHCO_3$ is possible to control the rate of sono-oxidation.
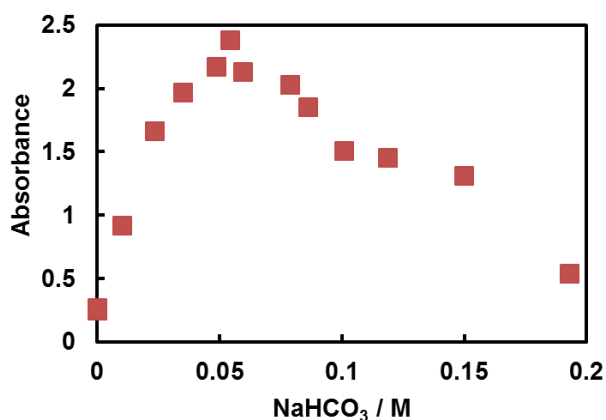

Fig. 2. Effect of adding $NaHCO_3$ to KI solution on the rate of sono-oxidation. Ultrasound: 200 kHz, 50 W; Reactant: 0.1 M KI solution, 100mL; Temperature: 25℃ Irradiation time: 10 min.

Fig. 3 shows the absorbance of KI solution after sonication, namely the rate of sono-oxidation. Although strong MBSL was observed in an Ar atmosphere as shown in **Fig. 1**, lower oxidation rate was obtained compared with air. Air is made up of oxygen (O_2) and other elements. It is known that O_2 is a strong oxidizing agent, namely scavenger about ·H radicals. Thus, since O_2 can quench ·H radicals, ·OH radicals are expected to remain. These radicals remained have considerable oxidation power and acceleration of sono-oxidation of KI solution would be attained.

Interestingly, $NaHCO_3$ addition system had higher rate than O_2 system. It is known that monoatomic gas, such as Ar, have higher heat capacity ratio than polyatomic gas, such as O_2. In other words, Ar has strong cavitation power. Because of strong cavitation power, many radicals are produced in an Ar atmosphere. Thus, number of the rest of ·OH radicals would be large compare to in O_2 atmosphere.

Fig. 4 shows the effects of the ultrasonic frequency and the input power on the rate of sono-oxidation in an Ar atmosphere. As similar to CO_2 addition, an ultrasonic frequency of 200 kHz was higher rate than of 2.4 MHz. The higher input power was applied, the higher rate was also confirmed. As discussed previously, the number of the rest of oxidizing radicals is important. Frequency of 200 kHz and 50 W was the highest improvement. The rate of sono-oxidation was nine times as high as that without $NaHCO_3$.

As conclusion of this presentation, I found the rate of sono-oxidation depends on the amount of $NaHCO_3$. Therefore, the rate of sono-oxidation can controlled by adding $NaHCO_3$.

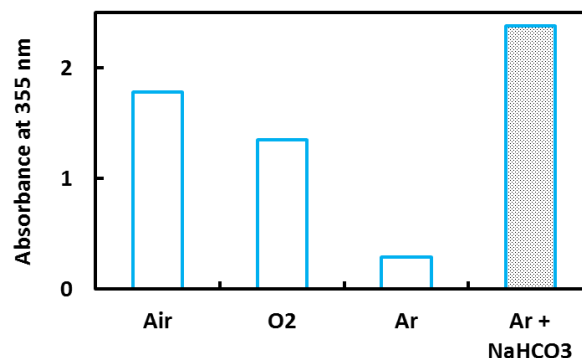Fig. 3. Sono-oxidation rates of KI solution in various atmosphere. Ultrasound: 200 kHz, 50 W; Reactant: 0.1 M KI solution, 100 mL. Temperature: 25℃; Irradiation time: 10 min.
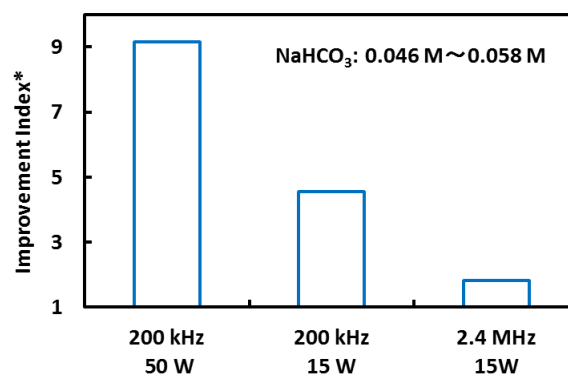

Fig. 4. Effects of frequency and input power on the rate of sono-oxidation. Reactant: 0.1 M KI solution; Added $NaHCO_3$: about 0.05 M; Reaction time: 10min.
*Inprovement index = ratio of absorbance of KI solution with $NaHCO_3$ to without one in an Ar atmosphere.

References
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2. H. Harada: Ultrason. Sonochem. **5**(1998) 73.
3. H. Harada and Y. Ono: Jpn. J. Appl. Phys. **54** (2015) 07HE10.