Enhancement of Sono-oxidation Rate in the Presence of $NaHCO_3$

$NaHCO_3$ 存在による超音波酸化速度の増加

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1. Introduction

Sono-oxidation of $NaHCO_3$-KI was carried out in an Ar atmosphere. Since $NaHCO_3$ reacts to CO_2 as follows, sono-oxidation is expected enhancement, namely I^- ions in KI solution are also expected to be oxidized rapidly. As reported previously [1], introduction of CO_2 in an Ar atmosphere is to increase sono-oxidation rate.

(Sonolysis of $NaHCO_3$)

$$2NaHCO_3 \rightarrow CO_2 + Na_2CO_3 + H_2O$$

In our previous reports [2] - [4], it was reported that higher sono-oxidation rate was obtained when small dose of $NaHCO_3$ was added to the KI solution. Thus, $NaHCO_3$ contributes to increasing in sono-oxidation rate of KI solution as shown in **Fig. 1**. By addition of excess amount of $NaHCO_3$, however, sono-oxidation rate decrease.

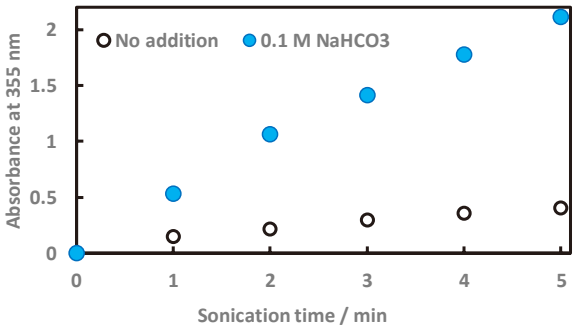

Fig. 1. Deference of sono-oxidation rate of KI solution between with and without $NaHCO_3$. Ultrasound: 500 kHz; Reactant: 0.1 M KI, 10 mL; Atmosphere: Ar; Room temperature.

In this presentation, as following report, we make influences of concentrations about KI and $NaHCO_3$ on the enhancement of sono-oxidation rate clear at 2.4 MHz.

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2. Experimental

Sonication was carried out in a sonochemical reaction system using almosot with a 2.4 MHz transducer (Honda Electric, 15 W and 20 W). Ultrasound was irradiated from the bottom surface of the reactor through a slide glass. A Pyrex glass cylindrical tube (volume: about 60 ml; diameter: 22mm; length: 300 mm; reactant solution: 10 mL – 20 mL) was used as a reactor. All trials were in an Ar saturated closed system at 25°C.

As reactant solutions, 0.01 M KI – 1.0 M KI solution with and without $NaHCO_3$ were used. In the case of a $NaHCO_3$-KI solution, relatively small amount of $NaHCO_3$ (below 0.2 M) was dosed to the solution after Ar gas bubbling. We used extra pure grade reagents (almost all Wako Pure Chemicals) without further purification in all the experiments.

The sono-oxidation rate was evaluated by absorbance at 355 nm. Absorbance was measured using a UV–vis spectrophotometer (JASCO V-730). Most of the data obtained was averaged at least three times by the same routine.

3. Results and discussion

We tried to confirm the most suitable concentration of $NaHCO_3$ for enhancement of sono-oxidation rate. **Figure 2** shows absorbance after sonication with and without $NaHCO_3$. The absorbance incresed with $NaHCO_3$ concentration and the maximum value was at 0.05 M – 0.1 M $NaHCO_3$. After top value, absorbance decreased with the concentration of $NaHCO_3$. The reason for the decline is considered decreasing in sono-chemical power, which means the capability of cavitation. Decreasing in the capability of cavitaion in $NaHCO_3$ solution has been confirmed by the observation of MBSL (multi-bubble sonoluminescence) [3], [4]. The reason for up and down behavior by the concentration of $NaHCO_3$ influence has been reported; that is CO_2 producted from $NaHCO_3$ solution by sonication plays the main role. It is explained shortly that CO_2 plays the scaventer of H radicals produced from solvent

(H_2O) by sonication. Thus, OH radicals, another pair product from H_2O, remain in the system. Those radicals have strong oxidation capability [4], [5].

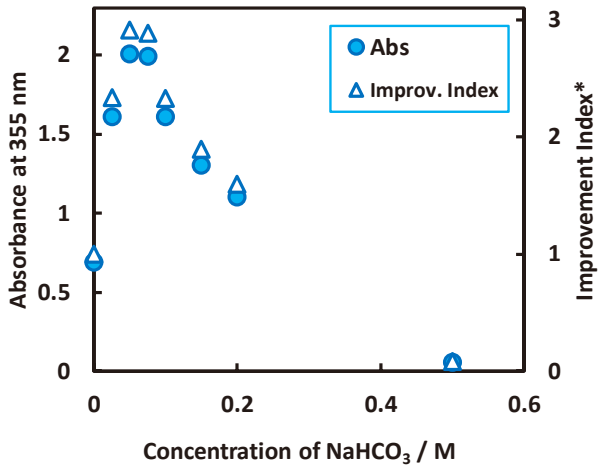

Fig. 2. Additional effects of $NaHCO_3$ to KI solution in an Ar atmosphere on the sono-oxidation rate of KI. Ultrasound: 2.4 MHz, 20 W; Reactant: 0.1 M KI, 20 mL; Sonication time: 10min; Temperature: 25°C. *Improvement index = ratio of absorbance in with $NaHCO_3$ to without $NaHCO_3$.

Figure 2 also shows the dependency of Inprovement index as a function of the concentration of $NaHCO_3$. Both dependencies, namely, absorbance and Improvement index, had similar behavior. The most effective concentration of $NaHCO_3$ (0.05M – 0.1 M) is supported former results in refs. [3], [4].

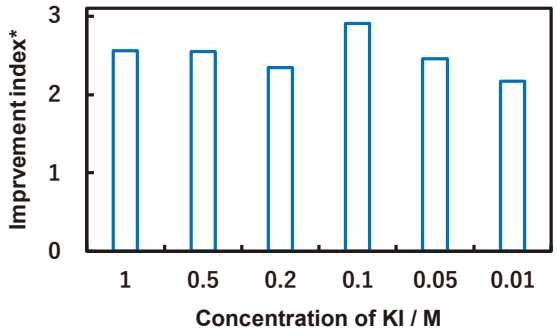

Fig. 3. Influence of KI concentration on the rate of sono-oxidation. *Improvement is explained in the caption of Fig. 2. Ultrasound: 2.4 MHz; Additive reagent: 0.05 M $NaHCO_3$; Atmosphere: Ar; Temperature: 25°C.

As you know, in certain region of reactant concentration, the higher concentration is applied, the higher rate of the reaction is gotten. So far, we had also obtained in favor results below 0.1 M KI solution. Of course, the Improvement index also had similar trend in that concentration region. Accordingly, we checked the effect over 0.1 M KI. It was sure that absorbance increased with KI concentration with and without $NaHCO_3$ by 1 M KI solution. The Improvement indexes, on the other hand, had no relation as shown in **Fig. 3**.

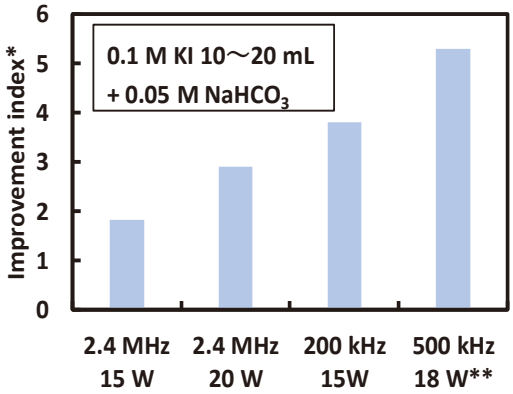

Fig. 4. The improvement indexes in various transducer. *Improvement is explained in the caption of Fig. 2. **Reactant: 10 mL; Sonication time: 10min & **5min; Temperature: 25°C.

According to previous reports [1], [6], by the way, sono-oxidation rate depends on the ultrasonic frequency. They suggested that several hundred kHz gave full performance in sonochemical reaction. It was sure that higher value of absorbance was obtained at those frequencies compared to other range of frequencies. It may get higher enhancement not only for absorbance but also for Improvement index in $NaHCO_3$-KI solution. Accordingly, we introduce our tentative results for the enhancement in the presence of $NaHCO_3$ as shown in **Fig. 4**. The relation between frequency and Improvement index develops a tendency to our expectation.

Acknowledgment

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References

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