1. Introduction

We have studied improving the rate of sono-oxidation through the oxidation of KI solution. Authors reported that sono-oxidation rate increased in a CO₂-Ar atmosphere, especially very low concentration of CO₂. As the acceleration mechanism, we assumed that CO₂ scavenges ·H radicals, which are produced from solvent by sonication. In that case, ·OH radicals survive in the reaction field. Thus, number of ·OH radicals is the main factor of sono-oxidation. Because of rapid decay, however, detection of ·OH radicals is hard work.

In this presentation, we confirm the role of CO₂ for acceleration of sono-oxidation through Fricke reaction and ESR measurement. Because number of ·OH radicals is the main factor of sono-oxidation.

The Fricke reaction was also performed as the oxidation reaction by the ·OH radical. We confirmed the reaction rate improving by addition of CO₂.

2. Experimental

Sonolysis of pure water was performed with 2.4 MHz (15 W, Honda Electric, HM 303N) transducer under various atmospheric gases. Experiments were conducted with ultrasonic irradiation time of 5min and reactant solution volume of 5 mL. One mM DMPO (5,5-dimethyl-1-pyrroline-N-oxide) was used for ·OH radical detection as a spin trap reagent. The amount of ·OH radicals produced was estimated by peak height of ESR spectrum.

In the Fricke reaction, ultrasonic waves were irradiated on the Fricke solution. Fricke solution was prepared with Fe(NH₄)₂(SO₄)₂·6H₂O (1 mM), H₂SO₄ (0.4 M), and NaCl (1 M). Ions of Fe²⁺ in the solution were oxidized to Fe³⁺ ions by ·OH radicals. The analysis of Fe³⁺ ions was carried out by a UV spectrophotometer (λ max=304 nm).

Fe²⁺+·OH→Fe³⁺+OH⁻

The procedure of sonication was the same as ESR measurement.

3. Results and Discussion

In sono-oxidation, ·OH radicals generated from water play an important role because of their strong oxidation power. Thus, the more amount of ·OH radicals, the more rate of oxidation. As shown in Fig. 1, the amount of ·OH radicals in Ar was larger than that in Air. Because high cavitation power in expected in Ar.

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radicals were expected to participate oxidation process. In the case of under CO2-Ar atmosphere, a certain amount of \( \cdot \text{H} \) radicals are scavenged by CO2. As the result, a certain amount of \( \cdot \text{OH} \) radicals are expected to remain in the reaction field.

\[
\text{Sonolysis of water,}\quad \text{H}_2\text{O} + \text{ultrasound} \rightarrow \cdot \text{H} + \cdot \text{OH}
\]

Under Ar,
\[
\cdot \text{H} + \cdot \text{OH} \rightarrow \text{H}_2\text{O}
\]
\[
(2 \cdot \text{H} \rightarrow \text{H}_2, \quad 2 \cdot \text{OH} \rightarrow \text{H}_2\text{O}_2)
\]

Under CO2-Ar atmosphere,
\[
2 \cdot \text{H} + \text{CO}_2 \rightarrow \text{CO} + \text{H}_2\text{O}
\]

On the other hand, when CO2 added to Air system, the amount of \( \cdot \text{OH} \) radicals decreased. Because Air is mixed gas and most portion of it is two atoms molecule. Of course Air contains CO2. Thus, weak acoustic cavitation would be in prospect.

Figure 2 shows addition effects of CO2 on Improvement indexes of chemical reactions and ESR measurement. Increasing in ESR peak was observed and Improvement index also increased with increasing CO2. Chemical reactions were also increased when 0.0223 mol of CO2 was added to the system. Thus, they behaved themselves similar trend about addition of CO2.

On another viewpoint, the dependence of Improvement index on CO2 amount. The rates of chemical reactions decreased with increasing CO2. It is known that acoustic cavitation power falls down with addition of CO2. Thus, total amounts of radicals in the system would reduce. Naturally, the amount of active radicals for oxidation would decrease.

Due to ESR measurement, however, the amount of \( \cdot \text{OH} \) radicals survived in the system although total amount of radicals produced decreased. We supposed higher rate of \( \cdot \text{H} \) radical scavenging occurred in the system. Because the rate for scavenging \( \cdot \text{H} \) radicals was higher, most portion of \( \cdot \text{OH} \) radicals would remain even in the case of relatively small amount of radical production. Above results, decrease in the rate of chemical reactions and more \( \cdot \text{OH} \) radicals survived, were contradictory. We considered that unknown conditions played important rote for sono-oxidation and their contribution would be large. We would like to consider that matter on another opportunity.

**References**