Sonolysis of Aqueous Solutions in CO₂-Ar Atmosphere. ESR study of Various in Number of OH Radicals with Concentration of CO₂.

CO₂-Ar 雰囲気中における水溶液の超音波反応。CO₂ 濃度と OH ラジカル量の ESR 研究。

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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[1]. As the acceleration mechanism, we assumed that CO₂ scavanges ・H radicals, which are produced from solvent by sonication. In that case, ・OH radicals survive in the reaction field. Thus, number of ・OHradicals 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[2] and ESR measurement .Because number of ・OH radicals is the main factor of sono-oxidation.

The Fricke reaction was also performmed 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 $Fe(NH_4)_2(SO_4)_2 6H_2O$ (1 mM), H_2SO_4 (0.4 M), and NaCl (1 M). Ions of Fe^{2+} in the solution were oxidized to Fe^{3+} ions by ・OH radicals. The analysis of Fe^{3+} ions was carried out by a UV spectrophotometer (λ_{max}=304 nm).

$$Fe^{2+} + ・OH \rightarrow Fe^{3+} + OH^-$$

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.

A=Air B=Ar C=Ar+CO₂ 0.0223 mmol
D=Ar+CO₂ 0.0446 mmol
E=Air+CO₂ 0.0223 mmol
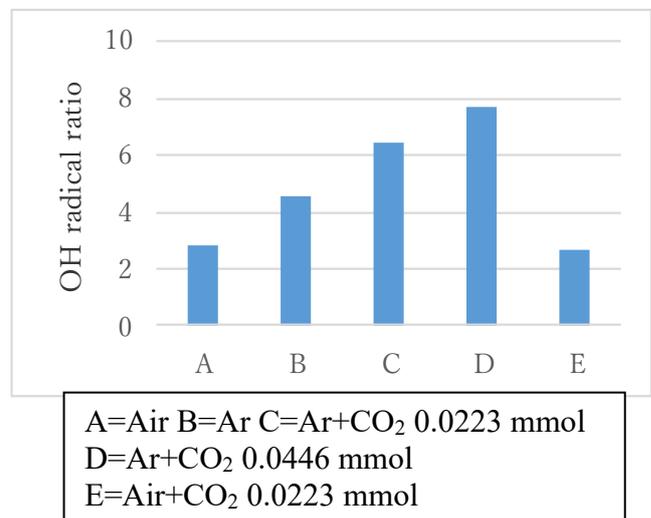
Fig.1 Comparison of amount of ・OH radicals among various atmospheres. ・OH radical ratio means the value of first ・OH radical peak divided base peak measured ESR.

More amount of the radicals was obtained in Ar - CO₂ atmosphere and increased with the amount of CO₂ introduction. Our assumed processes are below. Some amount of ・H radicals and ・OH radicals are produced by sonolysis of water. Some of them are converted back to water. Survived ・OH

radicals were expected to participate oxidation process. In the case of under CO_2-Ar atmosphere, a certain amount of $\cdot$H radicals are scavenged by CO_2. As the result, a certain amount of $\cdot$OH radicals are expected to remain in the reaction field.

Sonolysis of water,
$H_2O + ultrasound \rightarrow \cdot H + \cdot OH$

Under Ar,
$\cdot H + \cdot OH \rightarrow H_2O$
$(2 \cdot H \rightarrow H_2, \quad 2 \cdot OH \rightarrow H_2O_2)$

Under CO_2-Ar atmosphere,
$2 \cdot H + CO_2 \rightarrow CO + H_2O$
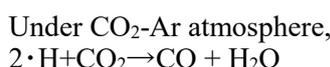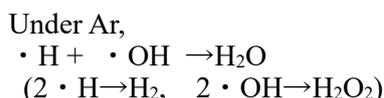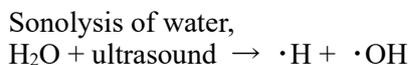
On the other hand, when CO_2 added to Air system, the amount of $\cdot$OH radicals decreased. Because Air is mixed gas and most portion of it is two atoms molecule. Of course Air contains CO_2. Thus, weak acoustic cavitation would be in prospect.

Figure 2 shows addition effects of CO_2 on Improvement indexes of chemical reactions and ESR measurement. Increasing in ESR peak was observed and Improvement index also increased with increasing CO_2. Chemical reactions were also increased when 0.0223 mol of CO_2 was added to the system. Thus, they behaved themselves similar trend about addition of CO_2
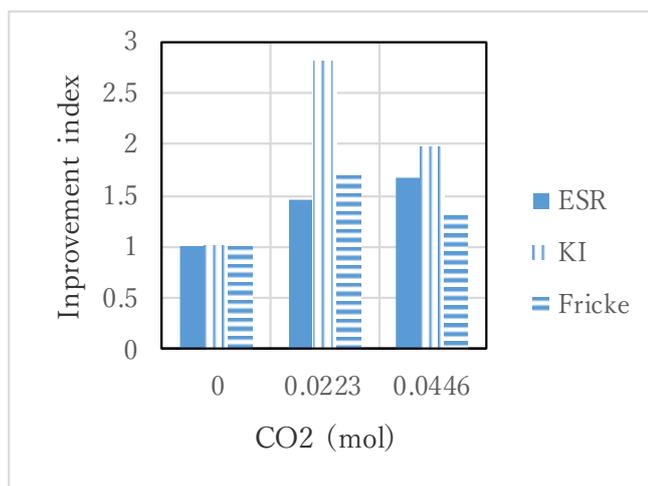

Fig.2 Addition effects of CO_2 on Improvement index for amount of $\cdot$OH radicals and rate of chemical reactions. Improvement index means the value with addition of CO_2 divided by the value without CO_2.

On another viewpoint, the value of Improvement index of chemical reactions exceeded that of ESR, in particular, acceleration of the rate of KI oxidation was remarkable. Because of short lifetime of $\cdot$OH radicals and destruction of the spin adducts produced from DMPO and $\cdot$OH radicals, lower value of Improvement index might be observed in the case of ESR measurement. In the cases of chemical reactions, on the other hand, we also considered that some radicals for oxidation other than $\cdot$OH radicals might be generated during sonolysis. Furthermore, changing pH in the solution also would contribute the acceleration in the case of KI oxidation.

By the way, mentioned above, the value of Improvement index of KI was higher than that of Fricke reaction in the presence of CO_2 in the system. We suppose that active chemical species other than $\cdot$OH radicals and/or reaction environment contribute the reaction. We think it is very interesting. We will consider on another opportunity about the peculiar case of sono-oxidation of KI solution.

Figure 2 also shows the dependence of Improvement index on CO_2 amount. The rates of chemical reactions decreased with increasing CO_2. It is known that acoustic cavitation power falls down with addition of CO_2. 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 $\cdot$OH radicals increased continuously with increasing CO_2. As the result, more $\cdot$OH radicals survived in the system although total amount of radicals produced decreased. We supposed higher rate of $\cdot$H radical scavenging occurred in the system. Because the rate for scavenging $\cdot$H radicals was higher, most portion of $\cdot$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 $\cdot$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
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