

The Rate Control of Sonochemical Reaction by Additives

溶存気体濃度または添加物によるソノケミカル反応速度制御

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1. Introduction

In recent years, sonochemical system has attracted the much attention of a good deal of researchers and engineers from the standpoint of variety of interests. In many cases, however, reaction rate is not attained the necessary level for requirements.

To solve the problem, I proposed some trials; those were selection of atmospheric gas and addition of chemicals into the solution. The former trial involves not only pure gases but also mix gases. It is known that acoustic cavitation, which results from ultrasonic irradiation, is dominated by dissolved gas. The dissolved gas is thought to be corresponding to the atmospheric gas. Under polyatomic gases, for example, chemical reaction can hardly proceed. In previous papers [1][2], it was reported that CO₂ prevented sonochemical action in solution because of low temperature for cavitation. Under monoatomic gases, on the other hand, strong ultrasonic power is observed.

Interestingly, in the case of Ar atmosphere, the rate of sonochemical oxidation had the maximum value with introducing a little amount of CO₂ and this value was three times as high as one without CO₂ [3].

In this presentation, CO₂ was introduced in the system for the rate control of sonochemical reaction. In addition, not only gaseous CO₂ but also solid CO₂ (dry ice) and sodium hydrogen carbonate (NaHCO₃), which provides CO₂ in an aqueous solution under ultrasonic irradiation were used as adding agents.

2. Experimental

Ultrasonic irradiation was performed using an ultrasonic atomizer (Honda Electric HM-303N, 2.4 MHz, 24 W) or an ultrasonic bath (Honda Electric 200 kHz, 15 W, or KAIJO 200 kHz, 50 W) from the bottom surface of the

reactor. In the former examination, similar atomization behavior was observed in all cases.

The rate of sonochemical oxidation was mainly evaluated by potassium iodide (KI) dosimetry [4] at 355 nm using UV-Vis spectrophotometer (JASCO V-650).

The reactor was filled with atmospheric gases. As atmospheric gas, in most experiments argon (Ar) was used as matrix gas. After gas introducing, an additive was added into the solution. Then, the reactor was sealed and ultrasonic irradiation was started. Temperature was stabilized by flowing tap water between 24°C and 26°C.

3. Results and discussion

Dissolved gas is the key for the sonochemical process. For example, the highest intensity of sonoluminescence (SL) is in an Ar atmosphere, as shown in Fig. 1 [2]. Namely, polyatomic gases are less effective than monoatomic gases. [5] The oxidation rate of KI is in the following order: Ar >> CO₂ and the rate falls down sharply by introducing over 0.3 molar fraction of CO₂ in a matrix. Then, the rate becomes nearly zero in CO₂ atmosphere.

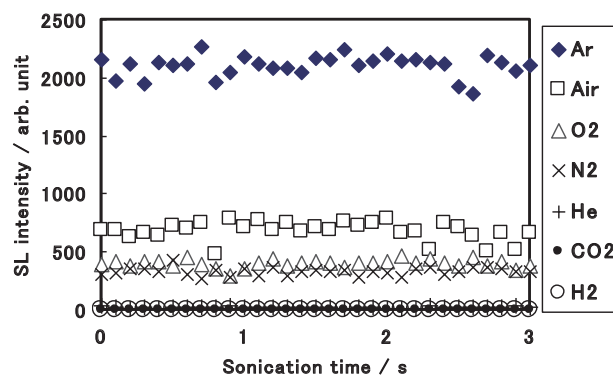


Fig. 1 Effect of various gas on the intensity of SL in water. [2]

Incidentally, it is known that CO₂ has high solubility in water and free radical scavenger. Because of the former reason, estimated concentration of CO₂ in the solution is higher than that in the atmosphere. Because of another (the latter) reason, CO₂ would play the role of scavenger of H radicals from the solvent (H₂O). Thus, more OH radicals or H₂O₂ remained by consuming H radicals and oxidation of KI would be accelerated. As shown in Fig. 2, the rate of oxidation increased by introducing a small amount of CO₂ in some matrix gases except for air.

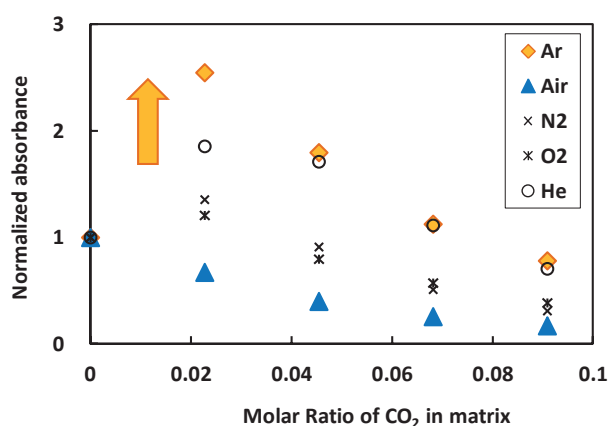


Fig. 2 Acceleration of oxidation rate by introducing CO₂ into matrix gases.

The intensity of SL, on the other hand, did not increase with introducing CO₂ in the range between 0 (0 mL in figure) and 0.02 (4 mL) molar fraction of CO₂, as shown in Fig. 3. Namely, cavitation (ultrasonic) power held or decreased with introducing CO₂.

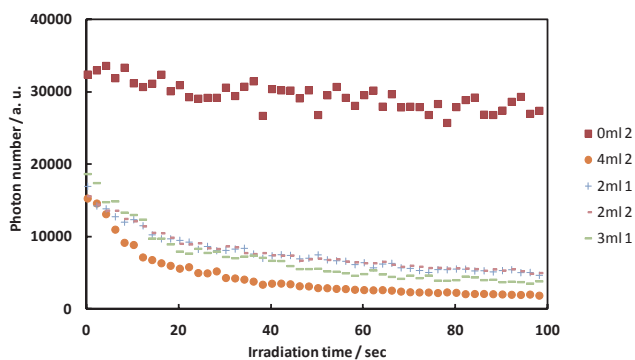


Fig. 3 Addition effect of CO₂ into Ar matrix on the intensity of SL in water.

Similar behavior was obtained when sonochemical degradation of methyl blue was carried out. The degradation rate did not increase by introducing a small amount of CO₂ into Ar atmosphere as shown in Fig. 4. The degradation might proceed without radicals. Further discussion is needed.

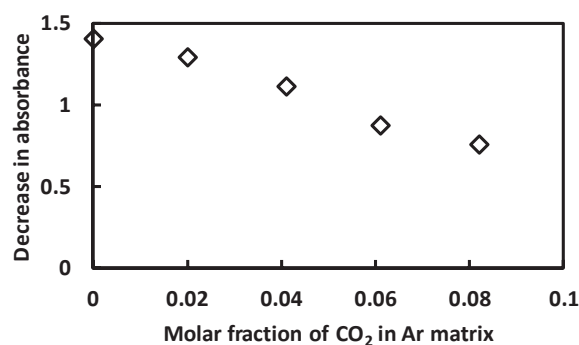


Fig. 4 Addition effect of CO₂ into Ar matrix on the degradation rate of methylene blue.

In addition, adding not only gaseous CO₂ into atmosphere but also solid CO₂, such as dry ice or sodium hydrogen carbonate, into the solution was performed.

References

- [1] H. Harada: *Ultrason. Sonochem.* **5** (1998) 73.
- [2] H. Harada, N. Iwata, K. Shiratori: *Jap. J. Appl. Phys.* (2009), **48** 07GH01-1-4.
- [3] H. Harada, Y. Ono, M. Oda: *AOOS-1* (The 1st meeting of Asia Oceania Sonochemical Society), GS-10.
- [4] S. Koda, T. Kimura, T. Kondo, and H. Mitome: *Ultrason. Sonochem.* **10** (2003) 149.
- [5] L. Broeckaert, T. Caulier, O. Fabre, C. Maerschalk, J. Reisse, J. Vandercammen, and D. H. Yang: *Current Trends in Sonochemistry* (ed. G. J. Price): *Quantitative Homogeneous Sonochemistry: Scope and Limitations*: **8**. (Royal Society of Chemistry, U. K.). **2005**.
- [6] S. Kumari, M. Keswani, S. Singh, M. Beck, E. Liebscher, P. Deymier, and S. Raghavan: *Microelectronic Engineering*, **88** (2011) 3437.