Free radical formation from sonolysis of water in the presence of different gases

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In the present study by applying electron spin resonance-spin trapping method, when high frequency (1650 kHz) ultrasound was irradiated to water dissolved with different gas molecules (O₂, N₂, Ar, Ne, He, and H₂) at 25°C of water bulk temperature, free radical generation pattern differed dependently on the dissolved gas molecules. Only ‘OH was detected in the O₂-dissolved water sample, and the amount of the radical was much greater than that determined in any of other gas-dissolved water samples. One of the possible reasons to explain why the ‘H radical was not detected in the O₂-dissolved water is that the ‘H reacts with O₂ to form ‘OOH. However, no electron spin resonance signals related to the adduct of not only 5,5-dimethyl-1-pyrroline-N-oxide but 5-(2,2-Dimethyl-1,3-proproxy cyclophosphoryl)-5-methyl-1-pyrroline N-oxide and ‘OOH were observed. In the H₂-dissolved water, only ‘H was detected, suggesting that H₂ reduces or neutralizes ‘OH. In the N₂-dissolved water, both ‘OH and ‘H were detected at comparable level. In the water samples dissolved with rare gases (Ar, Ne, and He), the amount of ‘H was almost double as compared with that of ‘OH, and both ‘OH and ‘H yields increased in the order Ar > Ne > He.

Key Words: water sonolysis, radical formation, electron spin resonance

Ultrasound has been widely applied for clinical diagnosis, dental care and therapeutic tools.¹⁻⁷ Especially diagnostic devices are commonly used for tomography or distance measurement in internal medicine or obstetrics, by using ultrasound energy in the high frequency range at low intensity. In the field of ophthalmology for example, cataract surgeries are widely performed by using phacoemulsification and aspiration, which utilizes high-intensity ultrasound energy for the fragmentation and emulsification of the cataractous lens.⁸

Free radical formation by sonolysis of water has been considered to be generated by cavitation especially when ultrasound was irradiated with low frequency (from a few dozens to several hundred kHz).⁹⁻¹⁰ Cavitation is a phenomenon which refers to the formation, growth, and collapse of small bubbles formed in liquids. During the process of cavitation, the extremely high temperature (several thousand degrees K) and high pressure (hundreds of atmospheres) of imploding cavitation bubbles lead to the thermal dissociation of water molecule, which in turn results in generation of ‘OH and ‘H.¹¹⁻¹³

As reported in previous papers,¹⁰⁻¹² ‘OH yield produced by low-frequency (47 kHz) ultrasound was inversely proportional to the thermal conductivity of the dissolved rare gases. Furthermore, it was reported that when ‘OH yields were compared between 47 kHz and 400 kHz ultrasound in the presence of different rare gases, the amount of ‘OH produced by 400 kHz ultrasound was less inversely proportional to the thermal conductivity of the dissolved gas than that of ‘OH produced by 47 kHz,¹⁹ suggesting that the temperature of the cavitation bubbles and ‘OH yield by ultrasound are strongly correlated. That is, the size of the cavitation bubbles produced by 400 kHz ultrasound is smaller than that by 47 kHz, and final temperature of the collapse by 400 kHz becomes relatively low, so that the difference of the final temperature induced by the differences of the thermal conductivities of rare gases decreases. In contrast, the formation mechanism of ‘OH by high frequency ultrasound (more than 1 MHz) has not been fully understood.

We have applied a free radical generation system in which ultrasound was irradiated at 1650 kHz to pure water to the basic studies such as a kinetic study of 5,5-dimethyl-1-pyrroline-N-oxide (DMPO)-‘OH, a spin adduct of DMPO and ‘OH, and an antimicrobial study.¹¹⁻¹⁵ In these studies, we could detect neither ‘H nor O₂ by applying an electron spin resonance (ESR)-spin trapping technique. In the present study, to elucidate the underlying mechanism of free radical formation by sonolysis with a high frequency (1650 kHz), we analyzed the free radicals (O₂⁻, ‘OH, and ‘H) generated by ultrasound irradiation to pure water containing a dissolved gas (O₂, N₂, Ar, Ne, He, or H₂) by applying the ESR-spin trapping technique.

Materials and Methods

Reagents were purchased from the following sources: 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) from Labotec (Tokyo, Japan); hydrogen peroxide (H₂O₂) from Santoku Chemical Industries (Tokyo, Japan); 4-hydroxy-2,2,6,6-tetramethylpiperidine (TEMPOL) from Sigma Aldrich (St. Louis, MO). 5-(2,2-Dimethyl-1,3-proproxy cyclophosphoryl)-5-methyl-1-pyrroline N-oxide (CYPMO) was synthesized according to the protocol described in the previous report.¹⁰ All other reagents used were of analytical grade. O₂, H₂, and N₂ gases were purchased from Japan Fine Products Co., Ltd. (Kawasaki, Japan), Ar and Ne gases from Japan Air Gases Co., Ltd. (Tokyo, Japan), and He gas from Union Helium Co., Ltd. (Kawasaki, Japan). The purities of these gases were 99.5–99.999%. An experimental device which generates 1650 ± 50 kHz ultrasound with an acoustic intensity of 50 W/cm² was kindly supplied by Nimo Corporation (Nagoya, Japan). A glass tube (16 mm in diameter and 125 mm long) containing 400 µl of 445 mM DMPO dissolved in ultrapure water was placed in the device. Subsequently, each of six different gases was bubbled for 3 min, followed by ultrasound irradiation for 10 to 120 sec. In an experiment using water sample dissolved with O₂, 27 mM CYPMO was used as a spin trap alternative to DMPO. The temperature of the water was controlled by a thermo-regulated
water bath. After ultrasound irradiation, the DMPO aqueous solution was transferred to a quartz cell for ESR spectrometry, and then an ESR spectrum was immediately recorded on an X-band ESR spectrometer (JES-FX-100, JEOL, Tokyo, Japan). The measurement conditions for ESR were as follows; field sweep, 330.50–340.50 mT; field modulation frequency, 100 kHz; field modulation width, 0.1 mT; amplitude, 20; sweep time, 2 min; time constant, 0.03 sec; microwave frequency, 9.421 GHz; microwave power, 4 mW. To calculate the concentrations of DMPO-H and DMPO-OH, 20 μM of TEMPO was used as a standard sample for quantitative analysis, and the ESR spectrum of manganese (Mn²⁺) which was equipped in the ESR cavity was used as an internal standard. The concentrations of ‘H and ‘OH were determined using Digital Data Processing (JEOL, Tokyo, Japan) and the concentrations of DMPO-H and DMPO-OH were expressed in μM.

Dissolved O₂ concentration was determined as in the following way. A beaker containing 100 ml of ultrapure water was placed in a homo-isothermal bath and the ultrapure water was bubbled with O₂ gas. When the temperature of the ultrapure water stabilized, the dissolved O₂ concentration was measured by a diaphragm electrode method using a Dissolved Oxygen Meter YSI-5100 (YSI Inf; Yellow Spring, OH).

**Results**

When ultrasound at 1650 kHz was irradiated to ultrapure water samples dissolved with either of six different gases in the presence of 445 mM DMPO at 25 ± 5°C of the water bulk temperature, the ESR signals of DMPO-spin adducts were observed (Fig. 1). In the water samples dissolved with N₂, Ar, Ne and He, the signals consists of quartet segments (intensity ratio, 1:2:2:1) and triplet of triplet segments (intensity ratio, 1:1:2:1:2:1:1) were observed. As shown in the representative ESR spectrum of the Ar-dissolved water irradiated by ultrasound (Fig. 2), the former segments were assigned to DMPO-OH, a spin adduct derived from ‘OH (hyperfine coupling constant, aN = 1.49; aH = 1.49 mT). The latter segments were assigned to DMPO-H, a spin adduct derived from ‘H (hyperfine coupling constant, aN = 1.63; aH = 2.25 mT) as reported in a previous study. In the water samples dissolved with O₂ and H₂, the ESR-signal of only DMPO-OH and that of only DMPO-H were observed, respectively (Fig. 1). Since the formation and decay of the spin adducts would affect the yield of the spin adducts, time course changes in the concentrations of the spin adducts generated for 10 to 120 sec were monitored (Fig. 3). In any of the gas-saturated water samples, both DMPO-OH and DMPO-H increased with time up to certain time points, and a linear relationship with a correlation coefficient of over 0.99 between the concentration of each DMPO-adduct and the irradiation time was observed up to 30 sec. Based on the results shown in Fig. 3, the yields of DMPO-OH and DMPO-H obtained after irradiation for 30 sec were compared among the water samples (Fig. 4). Only ‘OH (as indicated by DMPO-OH) was detected in the O₂-saturated water and the amount of the radical was much greater than that determined in any of the other gas-dissolved water samples, and only ‘H (as indicated by DMPO-H) was detected in the H₂-dissolved water and the amount of the radical was less than that in the N₂-dissolved water. As for ‘H yields in the presence of rare gases, the amount of ‘H was double or more as compared with that of ‘OH. Emphasizing a focus on the effect of dissolved rare gases on the radical formation, both ‘OH and ‘H yields increased in the order Ar > Ne > He (Fig. 4). To further examine whether ‘H was not generated in the water sample saturated with O₂, CYPMPO was used as an alternative spin trapping agent. Fig. 5 shows the representative ESR spectrum of sonolyzed water sample in the presence of O₂ and CYPMPO. The ESR signal was proved to be CYPMPO-OH since the hyperfine coupling constants aN = 1.39; aH = 1.39 mT; ap = 5.04 mT were identical to those reported in a previous study whilst no ESR signals related to the adducts of CYPMPO and ‘OH were observed. Then, to examine the kinetics of ‘H and ‘OH, ESR analysis of the radicals from the water samples sonolyzed for 60 sec in the presence of either Ar or N₂ was performed at different temperatures. As shown in Fig. 6, the yield of ‘OH as indicated by DMPO-OH derived from sonolysis of water in the presence of Ar increased with increasing water bulk temperature, whilst the yield of ‘H as indicated by DMPO-H decreased. The similar phenomenon was observed in the sonolysis of water dissolved with N₂ (data not shown).

To discuss the radical formation mechanism in water sonolysis with the frequency of 1650 kHz in the presence of O₂, relation

![ESR signals of DMPO-spin adducts generated by ultrasound irradiation at 1650 kHz to ultrapure water dissolved with a particular gas for 1 min.](image)

![ESR signals of DMPO-spin adducts generated by ultrasound irradiation at 1650 kHz to water dissolved with Ar gas for 1 min.](image)
among water bulk temperature, dissolved O$_2$, and ‘OH yield was evaluated. As shown in Fig. 7a, increasing the water temperature led to dissolved O$_2$ concentration decreased. Similarly, ‘OH yield as indicated by the amount of DMPO-OH increased with decreasing dissolved O$_2$ concentration (Fig. 7b).

Discussion

In the present study where water was exposed to ultrasound irradiation at 1650 kHz, the pattern of radical formation was different among the dissolved gases. Of the dissolved gases, only ‘OH was detected in the water sample under O$_2$ and the amount of the radical was much greater than that determined in any of the other gas; -dissolved water samples (Figs. 1, 3 and 4). Two possible reasons can be considered to explain why the ‘H radical was not detected in the O$_2$-dissolved water: (i) the formation of ‘H was suppressed and (ii) the ‘H reacted with O$_2$ to form ‘OOH. Regarding the latter case, it was reported that when aqueous DMPO solutions were sonicated during air bubbling or in the presence of air, only the ESR signal due to DMPO-OH adduct, but not that due to DMPO-H, was observed.\(^{18}\) To explain this phenomenon, the authors speculated that O$_2$ scavenges ‘H in the cavitation bubbles. In the present study, however, no ESR signals related to the adducts of the DMPO and ‘OH were observed, suggesting that the formation of ‘H might be suppressed. To further confirm the absence of ‘OOH, an additional experiment with CYPPO as a spin trap, which reacts with O$_2$ with a rate constant that is superior to DMPO, and the half-life of the corresponding spin trapped adduct is considered longer,\(^{16,19}\) was conducted. (Fig. 5). As is the case with DMPO, no ESR signals related to the adduct of CYPPO and ‘OOH were observed. If the formation of ‘H is suppressed under the O$_2$-saturated condition,

Fig. 3. Time course changes in the concentrations of the spin adducts generated by ultrasound irradiation to ultrapure water in the presence of different dissolved gases at 25°C. Each value represents the mean of duplicate determinations. Solid circle (●) and open circle (○) indicate DMPO-OH and DMPO-H, respectively.
the reaction between ‘H and ‘OH to form H$_2$O is also suppressed because of ‘H depletion, which in turn makes the concentration of ‘OH increase. Meanwhile, in another point view in which the ‘OH yield was much greater under O$_2$ than that determined under any of the other gases, following reactions can be considered as proposed by Uddin et al. (20):

\[
\text{H}_2\text{O} \rightarrow \text{‘H} + \text{‘OH} \\
\text{‘H} + \text{O}_2 \rightarrow \text{‘OH} + \text{O} \\
\text{O} + \text{‘OH} \rightarrow \text{OOH}
\]

In this case, O$_2$ reacts with ‘H to form ‘OH, indicating that the presence of dissolved O$_2$ in water sonolysis gives additional amount of ‘OH. However, a question is still remained as described above. That is, no ESR signals related to the adduct of DMPO and ‘OH were observed. In addition, the results of the experiments, in which the relation among water bulk temperature, dissolved O$_2$, and ‘OH yield was evaluated (Fig. 7 a and b), revealed that the ‘OH yield decreases with increasing dissolved O$_2$ concentration, suggesting that the reaction “‘H + O$_2$ → ‘OH + O” seems to be controversial. Of the effects of different gases, the ‘OH yield in the water sonolysis under N$_2$ was almost equal to that under Ar (Figs. 3 and 4). In a study where 50 kHz ultrasound-induced ubiquinol formation in aqueous solutions of ubiquinone was studied in the presence of different gases, (21) the yield of ubiquinone ring radical, which was formed by addition of ‘OH (or ‘H) to the...
5,6 double bond of ubiquinone, decreased when aqueous solution of ubiquinone was saturated with N₂; instead of Ar. In this case, it is assumed that the temperature of collapsing cavitation bubbles is much lower in N₂- than in Ar-saturated solution.\(^{(1,2)}\) In the present study, 'OH yields from N₂- and Ar-dissolved water samples were almost the same (Figs. 3 and 4), suggesting that collapsing cavitation bubbles might not be implicated in the phenomenon. As for H₂-dissolved water sample, since it was reported that H₂; reduces or neutralizes 'OH,\(^{(22,23)}\) it seems to be natural that DMPO-OH was not detected in the water sonolysis under H₂ (Figs. 3 and 4). Fukuda et al.\(^{(9)}\) reported that the amount of 'OH formed by sonication of water at either 47 kHz or 400 kHz was inverse order of the thermal conductivity of rare gases. That is, 'OH yield increased in the order Ar > Ne > He (Fig. 4). Fukuda et al.\(^{(9)}\) reported that the amount of 'OH formed by sonication of water at either 47 kHz or 400 kHz was inverse order of the thermal conductivity of rare gases. That is, 'OH yield increased in the order Ar > Ne > He, which was in agreement with not only our results but the previous study.\(^{(1,2)}\) Thus, the result of the present study might also be dependent on the cavitation phenomenon, in which the lower the thermal conductivity is, the higher the temperature of cavitation collapse is. In a point of view that the ratios of 'H and 'OH were near 2:1 under any of Ar, Ne, and He atmosphere, the result is hard to be interpreted by the cavitation phenomenon where 'H and 'OH are assumed to be formed at a ratio of 1:1 via thermal dissociation of water led by the extremely high temperature and high pressure of imploding cavitation bubbles. Regarding the point that DMPO-H detected was more than twice of DMPO-OH in the water samples in the presence of rare gasses, one of the possibilities is that hydrated electron (e\(_{\text{aq}}\)) increases the level of 'H. It was postulated that in the core of a cavitation bubble, the concentration of electrons upon electric breakdown can be high enough and, thus, can lead to the formation of e\(_{\text{aq}}\).\(^{(1,2,6)}\) Then, the resultant e\(_{\text{aq}}\) could increase the level of 'H via following reaction.

\[
e_{\text{aq}} + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H} \text{ or } e_{\text{aq}} + \text{H} \rightarrow \text{H}_2.
\]

However, Gutierrez and Henglein\(^{(15)}\) proposed that e\(_{\text{aq}}\) is generated in strongly alkaline solutions as the pK value of the equilibrium ‘‘H + OH\(^-\) ↔ H\(_2\)O + e\(_{\text{aq}}\)’’ is 9.8, so that the reaction does not seem to contribute significantly at neutral pH as in the present study. At present, since we could not reach the firm conclusion, further study is required to elucidate the fundamental mechanism by which the DMPO-H detected is more than twice of DMPO-OH in water saturated with rare gases.

If radical formation observed in the present study is mediated by cavitation, the yield of 'H was supposed to increase as did 'OH, because sonolysis of water to 'H and 'OH caused by cavitation is an endothermic reaction. However, the yield of 'OH from the water sonolysis under either Ar or N₂ increased with water bulk temperature, whilst the yield of 'H decreased (Fig. 6). To explain this phenomenon, the following reactions are considered to proceed dependently on the water bulk temperature.

\[
'\text{H} + '\text{OH} \rightarrow '\text{H}_2\text{O}.
\]

Regarding the reaction, Rassokhin et al.\(^{(26)}\) reported that H\(_2\) formation rate increased with increasing water bulk temperature from 5 to 50°C when water was irradiated by ultrasound (724 kHz, 50 W) under an Ar atmosphere. Meanwhile, it seems natural that 'OH yield increases with water bulk temperature. Indeed, Uddin et al.\(^{(20)}\) assumed that 'OH yield increases from sonolysis of water with increasing water bulk temperature. In their study where sonolysis of bisphenol A, a representative endocrine disrupting chemical, was studied at different temperatures (5 to 60°C) in aqueous solutions under various gases at 489 kHz, the degradation rate increased with water bulk temperature under O\(_2\) and air up to 50 and 40°C, respectively. Under Ar and N₂, the degradation rate also increased slightly with the temperature up to 40°C. Since the increase in degradation rate was cancelled by adding tert-butyl alcohol, a 'OH scavenger, they assumed that 'OH is responsible for temperature effects on sonolysis of bisphenol A. As for the relation among the water bulk temperature, dissolved O\(_2\) concentration and DMPO-OH yield (Fig. 7), decreasing the dissolved O\(_2\) concentration increased the DMPO-OH yield. Thus, a question, for instance, is raised that why the concentration of DMPO-OH was low in N₂-saturated water which was an extreme case of low O\(_2\) condition. As described above, if 'H formation is suppressed under O\(_2\)-saturated condition, 'OH fails to react with 'H, resulting in an elevated level of 'OH. In this case, it seems to be natural that the 'OH yield under O\(_2\) is higher than that under N₂; even though N₂-saturated water is an extreme case of low O\(_2\) condition. From the viewpoint of N\(_2\), one of the possibilities is the following reactions by which N\(_2\) is supposed to react with 'OH, resulting in a reduced level of 'OH.

\[
\text{H}_2\text{O} \rightarrow '\text{OH} + '\text{H}.
\]

Thus, the result was reported to take place when sonication is carried out during air injection.\(^{(27,28)}\)

Results obtained in the present study suggest that free radical generation pattern induced by 1650 kHz ultrasound in the presence of different gases gives informative findings on the sonolysis of water. It is well known that sonolysis of water by a low frequency ultrasound results in 'H and 'OH formation via thermal dissociation of water led by the extremely high temperature (several thousand degrees K) and high pressure (hundreds of atmospheres) of imploding cavitation bubbles.\(^{(11–13)}\) In the present study applying sonolysis of water induced by a high frequency ultrasound, some results are hard to be interpreted by cavitation phenomenon. To elucidate the underlying mechanism of radical formation in the sonolysis of water, a comparative study between sonolysis of water by 1650 kHz ultrasound and that by a low frequency ultrasound will be conducted.

### Abbreviations

- CUMPPO: 5-(2,2-Dimethyl-1,3-proxpo cyclophosphoryl)-5-methyl-1-pyroline N-oxide
- DMPO: 5,5-dimethyl-1-pyroline-N-oxide
- ESR: electron spin resonance
- TEMPOL: 4-hydroxy-2,2,6,6-tetramethylpiperidine

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