Sonochemical Efficiency during Single-Bubble Cavitation in Water

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We investigated nitrite and nitrate ion formation during single-bubble cavitation by realizing stable light emission for more than 30 h. Production yields of nitrite and nitrate ions in water were obtained as a function of irradiation time. The concentrations of nitrate and nitrite ions increased linearly with irradiation time within experimental error, and the molar ratio of nitrate to nitrite ions was about 1:1. The formation rate for these two ions was 3.8×10^{-10} mol·dm^{-3}·min^{-1}, and the number of nitrite or nitrate ions per cycle was estimated as 7.1×10^{6}.

1. Introduction

Large numbers of both chemists and physicists are engaged in studies of acoustic cavitation, which results in interesting chemical and physical effects. Under normal experimental conditions, large numbers of bubbles are generated in liquids and solutions by propagation of high-intensity sound waves. The sonochemical effects[1−4] are caused by the high pressure and temperature fields induced by growth and collapse of bubbles in liquids and solutions under an ultrasonic field. Shock waves and the local shear field are generated simultaneously around bubbles. Light emission from acoustic cavitation bubbles, a phenomenon termed sonoluminescence (SL), has also been observed.

Sonoluminescence from multibubble cavitation has been investigated by many workers, and their results have been summarized in a number of books.[3,4] The behavior of multibubble cavitation is complex, and it is still not possible to determine the number and size distribution of bubbles accurately. This has led to difficulty in elucidating the sonochemical and sonophysical effects induced by acoustic cavitation. Gaitan et al. first reported single-bubble sonoluminescence (SBSL) as light emission from a single bubble in liquids driven by an acoustic wave.[5] Subsequently, many workers turned their attention to SBSL, and their results have been reviewed in the recent literature.[6−8] Most workers are concerned with single-bubble dynamics and the intensity and spectra of sonoluminescence.[5−12] Time dependences of bubble size and light intensity have been elucidated experimentally, and theoretical studies on SBSL have been performed.[13−18] There have also been several studies of the chemical effects caused by single-bubble cavitation.[19−23] It is important to determine the sonochemical effects caused by a single bubble to elucidate the mechanism of acoustic cavitation and the chemical effects.

Winiarczyk and Musioł investigated the effect of salt on the intensity of light emitted from a single bubble.[19] Ashokkumar et al. reported the effects of aliphatic alcohols, alkylamines, carboxylic acids, and surfactants on the intensity of SBSL.[8,20] Hayashi and Hayashi examined SBSL in chlorine-doped water.[21] These studies clarified the changes in light intensity of SBSL by addition of solutes to water. Recently, two other groups investigated the chemical reactions in water or aqueous solution. Lepoint et al. reported the formation of I_3^- in 1 M NaI solution containing starch and CCl_4.[22] Didenko and Suslick reported the energy efficiency of photons, radicals, and ions during single-bubble cavitation.[23] The levels of OH radicals and nitrite ions were evaluated by fluorescence measurement as on the order of 10^6 per cycle. Strictly, they measured the yields in solution containing a small amount of the fluorescence reagent, not in water. As the amounts of chemical species produced in water during single-bubble cavitation are very small, it is not easy to investigate the yields of chemical species formed by single-bubble cavitation.

Here, we report the chemical efficiency during single-bubble cavitation in water by realizing stable SBSL. Sonolysis of water under various atmospheres with multibubble cavitation has been investigated in detail by many workers, and the results have indicated the formation of hydrogen peroxide, nitrite ions, and nitrate ions in water.[24−31] We examined the rates of formation of nitrate and nitrite ions in water as indicators of the sonochemical reaction from single-bubble cavitation and compared them with those from multibubble cavitation.

2. Experimental Methods

Figure 1 shows the experimental setup used here. A Langevin-type transducer was driven with a power amplifier (EMI, 1140AL) and a function generator (NF Wave Factory 1942) with a driving frequency of 32.6 kHz. A cylindrical cell measuring 42 mm in diameter and 100 mm in height made of acrylate resin was used. In all experiments, the volume of deionized and degassed water used was 60 cm^3. The cell was set in a constant-temperature air bath. The bath was regulated to 12.0 ± 0.2 °C, but the temperature of the water increased with sonication, and after 30 h, the temperature reached about 14 ± 0.2 °C. Paraffin film measuring almost the internal diameter of the cell was placed on the surface of the water. In addition, the top of the cell was also covered with paraffin film.

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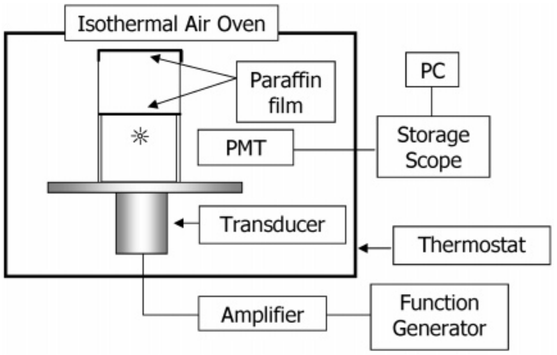

Figure 1. Experimental setup for single-bubble sonoluminescence (SBSL). Paraffin film measuring almost the internal diameter of the cell was placed on the surface of the water. The top of the cell was also covered with paraffin film. In this system, a small amount of air dissolves gradually in water with time from the rim of the paraffin on the surface and the concentration of dissolved oxygen was less than 6 mg·dm^{-3} even after 30 h.

In this system, a small amount of air dissolved gradually in water with time from the rim of the paraffin film on the surface. However, the cell is considered to be in a quasi-closed system. The time dependence of the oxygen dissolution was reproduced within an experimental error of 10%. The sonoluminescence intensity was measured using a photomultiplier tube (R585, Hamamatsu Photonics Co. Ltd.). The oxygen dissolved in the water was measured using a DO-meter (DDK Toa Co., DO-55G). Sonication experiments were carried out at a certain period, and no sampling was done during the sonication. We performed the different period experiments several times for 10, 15, 20, 25, and 30 h. The amount of 1 cm^3 sample was removed from the sonicated water in the cell, and its concentrations of nitrate and nitrite ions were measured by ion chromatography (Japan Dionex, Co. Ltd., IC-20) The calibration curves for nitrite and nitrate ions were obtained using standard nitrite and nitrate solutions. The experiments were repeated several times for all periods. The yields were calculated as the averages of those obtained by the several times experiments. The experimental uncertainty in the yield was within 20%.

3. Results

The light intensity of SBSL is dependent on the temperature, dissolved gas, sound pressure, etc.[9,32] In particular, the stability of SBSL is sensitive to the concentration of dissolved oxygen. In the present study, SBSL disappeared above 6 mg·dm^{-3} dissolved oxygen in water. In cases where no paraffin film was used, the level of dissolved oxygen increased steeply and became saturated at 6 h, making long-term observation of SBSL very difficult. In the quasi-closed system used here, the concentration of dissolved oxygen just before the commencement of sonication was about 3 mg·dm^{-3}; the concentration of dissolved oxygen increased with sonication time and was less than 6 mg·dm^{-3} after 30 h.[35] Figure 2 shows the time dependence of sonoluminescence intensity. Stable light emission continued for over 30 h. The intensity of SBSL fluctuated within 5% of the average value. This enabled us to detect formation of NO_3^- and NO_2^- ions in water by ion chromatography. Figure 3 shows a typical ion chromatogram of water before and after ultrasonic irradiation for 30 h. As is shown in Figure 3, formation of both nitrite and nitrate ions was clearly recognized under sonication.

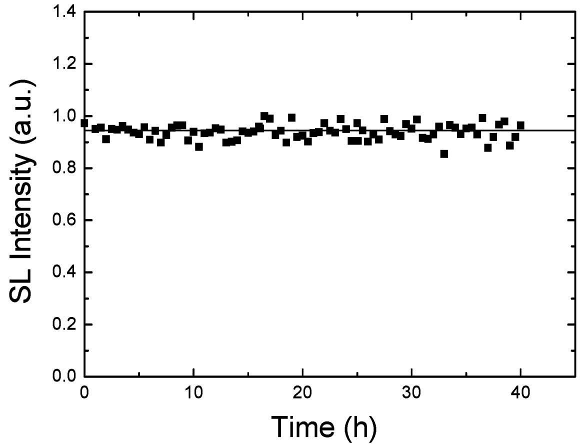

Figure 2. Time dependence of SBSL intensity. Suppression of oxygen dissolution by quasi-closed system illustrated in Figure 1 enabled stable light emission for over 30 h.

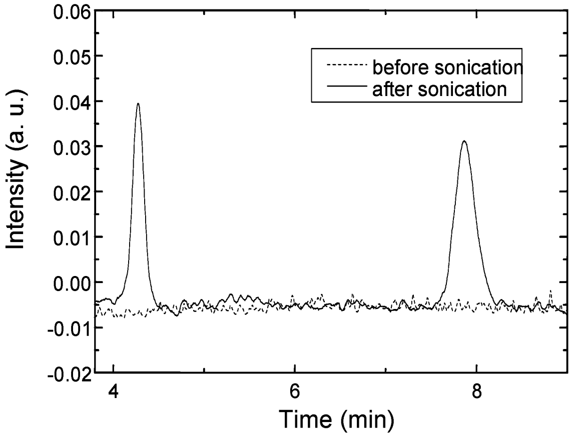

Figure 3. Ion chromatography of water after 30 h. Dotted and solid curves indicate the chromatographs before and after sonication, respectively. A peak centered at 4.27 min was due to nitrite ions, and that at 7.88 min was due to nitrate ions. Peaks for nitrite and nitrate ions were clearly recognized after sonication.

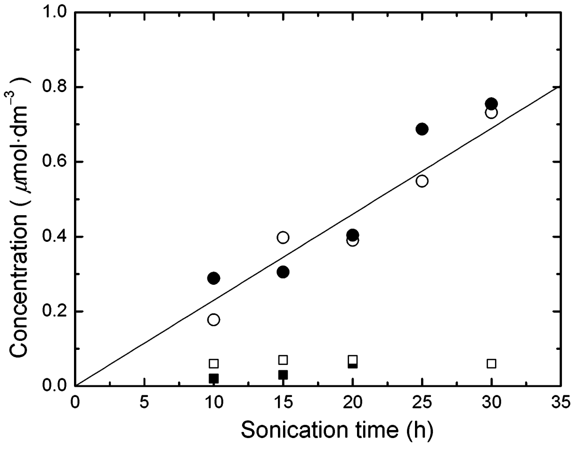

Figure 4. Sonication time dependence of concentrations of nitrite (open circles) and nitrate ions (closed circles) during single-bubble cavitation. The concentrations of nitrite and nitrate ions increased with time. Small amounts of nitrite (open squares) and nitrate ions (closed squares) were detected even without sonication.

The averaged yields are plotted against sonication time in Figure 4. Small amounts of nitrite and nitrate ions were detected even without sonication, and these are also plotted as square symbols in Figure 4. They increased slightly with time. The source background nitrate and nitrite ions may come from contamination from air in the headspace. Although the origin has not been clarified, the background levels were within the limits of experimental uncertainty. The yields of nitrate ions were nearly equal to those of nitrite ions within experimental

TABLE 1: Formation Rate of Nitrite and Nitrate Ions and Total Formation Yield per Energy in Water for Single-Bubble and Multibubble Cavitation

	formation rate/mol·dm^{-3}·min^{-1}				ultrasonic power density/W·dm^{-3}	formation yield per energy/mol·J^{-1}	freq/kHz	atmosphere
	HNO_2	HNO_3	total	HNO_2:HNO_3				
Virtnen et al. (1952)	7.1×10^{-6}				1400		300	air
Mead et al. (1976)	22×10^{-6}	6.0×10^{-6}	28×10^{-6}	3:1	1000	4.6×10^{-10}	447	air
Hart et al. (1986)	10×10^{-5}	6×10^{-5}	16×10^{-5}	2:1			300	$2N_2O + 8Ar$
Margulis (1993)	6×10^{-5}	2×10^{-5}		3:1				N_2
Venault et al. (1996)	4.1×10^{-7}				63		20	air
Wakefold et al. (1999)	2.5×10^{-7}	9×10^{-8}		3:1			35	air
Tiehm (1999)	7.1×10^{-7}	8.5×10^{-6}	9.2×10^{-6}	1:10	200	7.6×10^{-10}	360	air
Supeno et al. (2000)	3×10^{-6}	1.5×10^{-6}	4.5×10^{-6}	2:1	270	2.8×10^{-10}	900	air
this study	4×10^{-10}	4×10^{-10}	8×10^{-10}	1:1	10	1.3×10^{-11}	32.6	SBSL

error. That is, the NO_2^-/NO_3^- ratio was about 1:1. The concentrations of nitrite and nitrate ions linearly increase with time. Saturated concentrations of oxygen and nitrogen at 12 °C under air estimated the Henry's constant of oxygen and nitrogen to be 10.4 mg·dm^{-3} (324 μmol·dm^{-3}) and 14.7 mg·dm^{-3} (525 μmol·dm^{-3}), respectively. About 100 μmol·dm^{-3} nitrogen was assumed to be dissolved into the water because 3 mg·dm^{-3} oxygen was dissolved before sonication. The number of moles of nitrogen will be much larger than the production yields of nitrate and nitrite ions, so the conversion ratio is small. This is why the formation rate is constant during the experiments. The formation rate of these two ions was estimated as 2.3×10^{-8} mol·dm^{-3}·h^{-1} or 3.8×10^{-10} mol·dm^{-3}·min^{-1}.

4. Discussion

The number of nitrite and nitrate ions per cycle determined from the yields of nitrite ions at the driving frequency was 7.1×10^6 per cycle, which corresponded to 1.2×10^{-17} mol per cycle. Didenko and Suslick reported that the number of nitrite ions was 3.7×10^6 per cycle at 25 °C.[23] The number determined in the present study was about double this value. This may have been due to differences in cavitation conditions, such as the driving frequency, sample volume, and temperature. However, our results were on the same order of magnitude as those reported by Didenko and Suslick. Lohse and Higenfeldt estimated the amounts of HNO_3 and HNO_2 during SBSL in water as about 3.6×10^6.[14] Recently, Yasui et al. calculated the number of ions per cycle at a frequency of 130 kHz.[18] The value is dependent on the sound pressure and temperature inside a bubble. For example, the numbers of nitrite and nitrate ions per cycle were 4×10^6 and 1.9×10^6 at 4900 K and 2 atm, respectively. In the present study, the sound pressure was 1.4 atm. Our results were on the same order of magnitude as those predicted by Lohse and Higenfeldt and by Yasui et al.

For multibubble cavitation, many investigators reported the formation of nitrite and nitrate ions in water and aqueous solutions. Virtanen and Elifolk reported the formation of nitrite and nitrate ions in aqueous solutions.[24-26] The initial formation rate of HNO_2 was 7.1×10^{-6} mol·dm^{-3}·min^{-1}.[26] Mead et al. reported that the initial rates of formation of HNO_2 and HNO_3 were 2.2×10^{-5} and 6.0×10^{-6} mol·dm^{-3}·min^{-1}, respectively.[27] The typical reaction rates of nitrite and nitrate ions for single-bubble and multibubble cavitations are summarized in Table 1. For multibubble cavitation, the values of product yields reported in the literature were not always consistent with one another and the majority of the reported values were on the order of 10^{-6} mol·dm^{-3}·min^{-1}.[24-31] The sonochemical effects are dependent on the ultrasound frequency, intensity, cell shape, temperature, dissolved gas conditions, etc. In particular, the sonochemical effects caused by multibubble conditions are dependent on the applied frequency.[34,35] Therefore, the formation rates of HNO_2 and HNO_3 reported by different workers may be inconsistent even if all experimental conditions are standardized. We estimated the total concentration of nitrite plus nitrate ions per ultrasonic power density, defined as the power of the ultrasound divided by volume (W·dm^{-3}). The results are also listed in Table 1. The total concentration of nitrite plus nitrate ions per ultrasonic power density for single-bubble cavitation was ca. 1.3×10^{-11} mol·J^{-1}. In the present study, the ultrasonic power determined by calorimetry was 1.0 ± 0.5 W. The total concentrations reported by Mead et al.[27] and Supeno and Kruus[31] were 4.6×10^{-10} and 2.8×10^{-10} mol·J^{-1}, respectively. Didenko and Suslick[23] reported that the yield of OH radicals per ultrasonic intensity (*G*-value) during single-bubble cavitation was comparable to that for multibubble cavitation reported by Mark et al.[34] Our estimation of the yields of nitrite and nitrate ions indicated that the sonochemical efficiency for multibubble cavitation is about 20-fold greater than that for single-bubble cavitation. Mark et al.[34] estimated the *G*-value but did not give a detailed description of the measurement of ultrasonic power. Suslick and Didenko did not report any information about the ultrasonic intensity. For further comparison with these results, it is necessary to know the ultrasonic intensities for the different experiments.

Our results indicated that the sonochemical efficiency for multibubble cavitation is greater than that for single-bubble cavitation. The number of bubbles and the temperature in the bubbles may be responsible for the observed differences in the formation rates of ions between single-bubble and multibubble cavitation. Although the temperature is considered to be higher in a single bubble than in multiple bubbles, the number of bubbles in multibubble cavitation is greater than that in single-bubble cavitation. The chemical efficiency is determined by both the number of bubbles and the temperature in the bubbles. The effect of the number of bubbles may overwhelm the temperature effect because, as expected, large numbers of bubbles are generated in multibubble cavitation. However, we have no information regarding the number of bubbles in multibubble cavitation.

The ratio of formation of nitrite to nitrate ions is useful information for understanding the mechanism of water sonolysis. We showed that the ratio for a single bubble is 1/1 in air. For multibubble cavitation, Mead et al.[27] obtained an HNO_2/HNO_3 ratio of 3/1 and the ratio decreased with sonication time. The nitrite ion concentration decreased with sonication for long periods, and a part of the nitrite was oxidized to nitrate in solution. Hart and Henglein[28] investigated the production of NO_2^- and NO_3^- under an atmosphere consisting of a mixture of Ar and NO_2. The HNO_2/HNO_3 ratio was 2/1 in a mixture of 20% NO_2 and 80% N_2. Margulis[3] reported a 3/1 ratio under a N_2 atmosphere. There have also been many reports of the formation ratio of nitrite and nitrate ions, and the results are listed in Table 1.[24−31] There are several reasons for the differences in the HNO_2/HNO_3 ratio. However, there has been no satisfactory discussion of the formation rate ratio. We note that the ratio of nitrite to nitrate ranges from 2 to 3, while the ratio for single-bubble cavitation is ca. 1.

The formation mechanism of nitrite and nitrate ions for multibubble cavitation has been discussed by many workers.[24−31] OH radicals are formed after decomposition of water, and NO and NO_2 are formed in bubbles by the following reactions:

$$O + N_2 \rightarrow NO + N \tag{1}$$

$$N + O_2 \rightarrow NO + O \tag{2}$$

$$NO + O_2 \rightarrow NO_2 \tag{3}$$

$$2NO + O_2 \rightarrow 2NO_2 \tag{4}$$

The main mechanism of the formation of nitrite and nitrate ions inside bubbles is the reaction of NO or NO_2 species with OH radicals:

$$HO + NO \rightarrow HNO_2 \tag{5}$$

$$HO + NO_2 \rightarrow HNO_3 \tag{6}$$

We cannot exclude the possibility that other intermediates, such as N_2O_3 or N_2O_4, may contribute to the formation of nitrite and nitrate ions inside bubbles. Supeno and Kruss suggested that the levels of NO_2 are much less than those of NO in multibubble cavitation with increasing temperature in the bubbles. Yasui et al. reported that the concentration of NO is 10-fold greater than that of NO_2 for single-bubble cavitation.[18] These results suggest that in single-bubble cavitation NO would be more abundant than NO_2 at higher temperatures. The reaction rate constants are given by the Arrhenius equation, and their thermodynamic data are given in the literature. However, these data are unavailable at high pressure and temperature during single-bubble cavitation as the thermodynamic data are only available for temperatures below 2000 K.

A portion of the NO_2 formed in a bubble diffuses to the interface between the bubble and the surrounding solution. In the solution, nitrite and nitrate are formed according to the reaction

$$2NO_2 + H_2O \rightarrow HNO_2 + HNO_3 \tag{7}$$

Using the EPR method, Mišík and Riesz reported that 45% of nitrite was formed in the solution.[29] Mead et al. suggested that a part of the nitrite is oxidized to nitrate in solution by sonication for long periods.[27] Although we cannot make any definitive conclusions regarding the detailed mechanism of the formation of nitrite and nitrate ions, our observations indicate that the molar ratio of nitrite and nitrate ions is responsible for the high-temperature field in single-bubble cavitation. Our results are important for clarification of the reaction mechanism during single-bubble cavitation. Further studies are required to clarify the mechanism in detail.

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