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Effect of operational conditions on sonoluminescence and kinetics of H_2O_2 formation during the sonolysis of water in the presence of Ar/O_2 gas mixture

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ABSTRACT

Ultrasonic frequency is a key parameter determining multibubble sonoluminescence (MBSL) spectra of water saturated with Ar/O_2 gas mixtures. At 20 kHz, the MBSL is quenched by oxygen. By contrast, at high-frequency ultrasound the maximal MBSL intensity is observed in the presence of $Ar/20\%O_2$ gas mixture. Nevertheless, oxygen has no influence on the shape of MBSL spectra. The effect of oxygen on MBSL is explained by oxygen dissociation inside the collapsing bubble which is much more effective at high ultrasonic frequency compared to 20 kHz ultrasound. In contrast to MBSL, a higher yield of H_2O_2 is observed in $Ar/20\%O_2$ gas mixture whatever the ultrasonic frequency. At 20 °C and 20% of oxygen the maximal yield of H_2O_2 is observed at 204–362 kHz. The maximal yield of H_2O_2 is shifted to 613 kHz when the bulk temperature is raised up to 40 °C. Coupling of high-frequency ultrasound with mechanical stirring and intensive Ar/O_2 bubbling improves H_2O_2 production. Comparison of MBSL and sonochemistry allowed to conclude that H_2O_2 is formed from non-excited $OH^{\cdot}$ ($X^2\Pi$) and $HO_2^{\cdot}$ radicals. Finally, it was shown that at the studied conditions the efficiency of ultrasonic degassing is hardly influenced by frequency.

1. Introduction

Over the past few decades, sonochemistry in aqueous solutions has been extensively studied as an advanced oxidation process (AOP) potentially suitable for waste water treatment [1–9]. The sonochemical AOP is based on the generation of oxidative species during acoustic cavitation in water, particularly $OH^{\cdot}$ and $HO_2^{\cdot}$ radicals and hydrogen peroxide H_2O_2 formed as a secondary product of radical recombination. The efficiency of oxidizing species production is affected by a number of factors including ultrasonic frequency, acoustic power, sparge gas, external pressure and solution temperature. Several authors have reported higher H_2O_2 formation rate in argon-saturated water at high-frequency ultrasound (>100 kHz) compared to low-frequency 20 kHz ultrasound [10–14]. The yield of H_2O_2 ($G_{H_2O_2}$) is strongly increased in the presence of oxygen, which was attributed to much more significant generation of both $OH^{\cdot}$ and $HO_2^{\cdot}$ radicals [5,10,12,15]. With a gas mixture of 80–70% argon and 20–30% oxygen, the $G_{H_2O_2}$ value was found to be drastically higher than for water sonication under pure argon or pure oxygen whatever the ultrasonic frequency [15]. At higher oxygen concentration $G_{H_2O_2}$ decreases, which has been attributed to the drop of intrabubble temperature in the presence of a polyatomic gas presuming adiabatic heating during bubble collapse [15,16]. However, the influence of ultrasonic frequency on the sonochemical reactions with oxygen is as yet poorly understood. For example, Henglein et al. [16] have shown that at high ultrasonic frequency (300 kHz) oxygen molecules may dissociate inside the cavitation bubble. By contrast, these processes have never been reported for low-frequency ultrasound. Recent studies revealed that the variation of ultrasonic frequency, in particular between low and high frequencies, could lead not only to a change in reaction kinetics but also to significant modifications of reaction mechanisms [13].

Spectroscopic studies of sonoluminescence provide a powerful tool to better understand sonochemical mechanisms. However, the relationship between sonochemical activity and sonoluminescence has just begun to emerge. Usually, the sonochemical activity is compared with the total intensity of sonoluminescence or with the intensity of chemiluminescence produced in sonicated solutions of luminol [12,17]. It should be emphasized that the multibubble sonoluminescence (MBSL) spectra in water are quite complex and contain emission lines attributed to different electronic and vibrational excited states of $OH^{\cdot}$ radicals and H_2O molecules [18,19]. The variation of the experimental parameters could generate the redistribution of relative line intensities and

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not only a change in total emission intensity. Therefore, a thorough spectroscopic analysis of MBSL spectra is required to elucidate the impact of experimental conditions on reaction mechanism. This paper describes a comparative study of H_2O_2 formation rate and MBSL spectra in water saturated with Ar/O_2 gas mixtures at different ultrasonic frequencies.

2. Materials and methods

2.1. Materials

Deionized water (Milli-Q 18.2 MΩ cm) was used to prepare all aqueous solutions. Argon and oxygen at 99.999% purity and $20\%O_2/Ar$ gas mixture were provided by Air Liquide. Reagents and chemicals used in the various procedures were all of analytical grade and were purchased from Sigma–Aldrich.

2.2. Reactor setup and MBSL measurements

The multifrequency ultrasonic device consisted of a thermostated glass-made batch reactor mounted on top of the high-frequency piezoelectric transducer (ELAC Nautik, 25 cm^2) providing 204–1057 kHz power ultrasound connected to a high-frequency generator with a maximum electrical power of 125 W (T & C Power Conversion, Inc.). Ultrasonic irradiation with low frequency ultrasound of 20 kHz was performed with 1 cm^2 titanium probe (750 W Sonics). The probe was placed reproducibly on top of the reactor opposite the high-frequency transducer using a tight Teflon ring. A new probe tip was used in each experiment to avoid the drop of SL due to the tip cavitation erosion. The absorbed acoustic power, P_{ac}, was measured by the conventional thermal probe method. At high ultrasonic frequency many experiments (not MBSL measurements) have been performed under additional mechanical stirring to provide a homogeneous temperature inside the reactor during the ultrasonic treatment. A glass-made three-bladed propeller agitator was then placed instead of the 20 kHz ultrasonic probe. Table 1 summarizes the values of acoustic power, P_{ac}, measured as a function of amplitude or electric load power, LP, for low- and high-frequency ultrasound.

For all experiments, 250 mL of the solutions were sparged with gas (Ar, O_2 or $20\%O_2/Ar$) about 30 min before sonication and during the ultrasonic treatment at a controlled rate of typically 80 mL min^{-1}. Gas flow rates were measured with a volumetric flowmeter with stainless steel float (Aalborg). The calibration chart provided by the manufacturer was validated against a numerical mass flowmeter (Aalborg GFM17). The temperature in the reactor during sonolysis was maintained with a Huber Unistat Tango thermo-cryostat and measured by a thermocouple immersed approximately 2 cm below the surface of the solution.

The light emission spectra were collected through a flat quartz window using parabolic Al-coated mirrors and recorded in the spectral range from 230 nm up to 600 nm using a SP 2356i Roper Scientific spectrometer (gratings 300blz300 and 150blz500, slit width 0.25 mm) coupled to a charge-coupled CCD camera with UV coating (SPEC10-100BR Roper Scientific) cooled by liquid-nitrogen. A high-pass filter was used when necessary to avoid second order light. Spectral calibration was performed using a Hg(Ar) pen-ray lamp (model LSP035, LOT-Oriel). The spectra acquisition was started after reaching a steady-state temperature. For each experiment, at least three 300 s spectra were averaged and corrected for background noise and for the quantum efficiencies of grating and CCD. The SL spectra were collected at the focusing point providing the highest light emission intensity without mechanical agitation.

Table 1
Values of acoustic power, P_{ac}, measured by thermal probe method for 20 kHz (a) and high-frequency ultrasound (b).

Amplitude, %[a]	Acoustic power, P_{ac} (W)	
(a)		
30	17	
40	24	
50	32	
60	40	
Frequency, kHz	Acoustic power, P_{ac} (W)	
	LP = 55 W[b]	LP = 73 W[b]
(b)		
204	32	41
362	43	57
613	43	57
1057	42	56

[a] Amplitude of the generator.
[b] Load electric power of the generator.

2.3. Analytical procedures

The concentration of dissolved oxygen was measured with Orion 3 Star meter (Thermo Scientific) after establishment of the steady state which was typically about 20 min. Hydrogen peroxide was monitored by absorption spectrophotometry with Ti(IV) in 0.5 M H_2SO_4 ($\lambda = 411$ nm, $\varepsilon = 707$ cm^{-1} M^{-1}). The statistical error for H_2O_2 formation rate was estimated to be 10%. Hydrogen in the outlet gas was analyzed using a Thermo Scientific VG Prolab Benchtop quadrupole mass spectrometer. The concentration of H_2 was followed with the multiple ion monitoring (MIM) provided by the software. The water vapor in the outlet gas was trapped using molecular sieves (Sigma–Aldrich, 3 Å) prior to mass spectrometric analysis.

3. Results and discussion

3.1. Effect of ultrasound on the concentration of dissolved oxygen

The steady-state concentration of dissolved oxygen, $[O_2]$, is one of the critical parameters determining the sonoluminescence and the sonochemical activity at the studied conditions. Fig. 1 shows that $[O_2]$ drops as the temperature increases. Under silent conditions the measured $[O_2]$ values fit well with published data at atmospheric pressure [20]. In the presence of ultrasound the

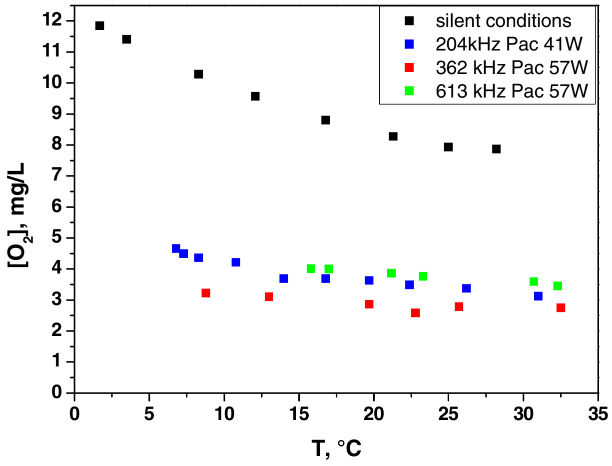

Fig. 1. Effect of temperature on the concentration of dissolved oxygen under silent conditions (◆) and at 204 kHz ($P_{ac} = 41$ W), 362 and 613 kHz ($P_{ac} = 57$ W) ultrasound (■). Bubbling of $Ar/20\%O_2$ mixture at 80 mL min^{-1}, no mechanical stirring. The uncertainty on $[O_2]$ measurements is of 5%.