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Effect of ultrasonic frequency on H_2O_2 sonochemical formation rate in aqueous nitric acid solutions in the presence of oxygen



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ABSTRACT

The influence of the ultrasonic frequency (20 kHz, 207 kHz, and 615 kHz) towards the formation kinetics of H_2O_2 under Ar and $Ar/(20 vol.%)O_2$ atmospheres was evaluated in pure water and aqueous nitric solutions. Results obtained at low frequency ultrasound demonstrate that hydrogen peroxide formation is enhanced under an Ar/O_2 gas mixture whatever the sonicated medium. Nevertheless, H_2O_2 yields are higher in aqueous nitric solutions whatever the nature of the saturating gas. These observations are consistent at high frequency ultrasound under Ar gas notwithstanding higher yields for H_2O_2 . Surprisingly, an inverse tendency is observed for high frequency sonolysis carried out under an Ar/O_2 atmosphere: higher yields of H_2O_2 are measured in pure water. Further studies in the presence of pure Ar revealed a more important decomposition of nitric acid under high frequency ultrasound leading to higher yields of both HNO₂ in the liquid phase and NO in the gas phase. In the presence of Ar/O_2 mixture, the intrabuble oxidation of NO causes cavitation bubble depletion in O_2 leading to the drop of H_2O_2 yield. On the other hand, it was found that for $Ar/(20 vol.%)O_2$ mixture there is no influence of oxygen on HNO₂ yield whatever the ultrasonic frequency; this is most likely explained by two processes: (i) HNO₂ formation results from nitrate-ion thermolysis in the liquid reaction zone surrounding the cavitation bubble, and (ii) effective intrabubble oxidation of NO_x species by oxygen to nitrate-ion.

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1. Introduction

Sonochemical reactions in nitric acid solutions have attracted considerable attention as a potentially "reagent-free" route to control the oxidation states of actinide ions during spent nuclear fuel reprocessing mostly due to the *in situ* generation of hydrogen peroxide and nitrous acid [1]. In pure water saturated with noble gases, power ultrasound causes the homolytic splitting of H₂O molecules yielding H^{\cdot} and OH^{\cdot} radicals (reaction (1)) [2–6]. These highly reactive species mostly recombine into H₂O inside the cavitation bubble [5,6]. Some of OH radicals (roughly 20% [6,7]) can nevertheless diffuse to the bubble interface where the temperatures are lower, and recombine into hydrogen peroxide (reaction (2)). Molecular hydrogen H₂ is formed as a recombination product of H⁻ radicals mostly in the gaseous phase of the collapsing bubble (reaction (3)) [5,8]. Several investigations devoted to the kinetics of H₂O₂ sonochemical formation have been reported in the literature [9-12]. It was showed that the H_2O_2 formation rate in pure water under argon can be significantly enhanced when increasing the ultrasound frequency [11-15] or the acoustic power [14,15].

$H_2O \rightarrow))) \rightarrow$	• H. + OH.		(1)
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$$20H^{\bullet} \rightarrow H_2O_2 \tag{2}$$

$$2H \rightarrow H_2$$
 (3)

Sonication of aqueous nitric acid solutions is known to initiate the formation of nitrous acid in solution and NO_x species that can be observed in the gaseous phase (reaction (4)) [16]. In 4 M HNO₃ solution sonicated at 20 kHz under Ar bubbling, HNO₂ production was shown to accumulate linearly versus time during the first 60 min of sonolysis [17]. After 180 min, a HNO₂ steadystate concentration is then observed. This steady-state is related to the sonochemical degradation of HNO₂ and the subsequent release of NO and NO₂ into the outlet gas (reaction (5)) [17,18]. At moderate concentration of HNO₃ (<4 M), HNO₂ is principally formed as a result of NO₃⁻ ion thermolysis at the interfacial bubble/solution region (reaction (6)) [1,19]. In more concentrated solutions, its formation can also result from HNO₃ molecule degradation inside the bubble followed by secondary reactions with NO_x



in the bulk solution (reactions (7)-(9)) [1]. Note that nitrates and nitrites can also be formed in pure water saturated with air or N_2/O_2 gas mixture [15].

$$2HNO_3 \to))) \to 2NO_2 + H_2O + 1/2O_2 \tag{4}$$

$$2HNO_2 \rightarrow))) \rightarrow NO + NO_2 + H_2O \tag{5}$$

$$H^{+} + NO_{3}^{-} \rightarrow))) \rightarrow HNO_{2} + 1/2O_{2}$$

$$\tag{6}$$

$$2NO + HNO_3 + H_2O \rightarrow 3HNO_2 \tag{7}$$

$$2NO_2 \leftrightarrow N_2O_4 \tag{8}$$

$$N_2O_4 + H_2O \rightarrow HNO_2 + HNO_3 \tag{9}$$

Reactions (4) and (5) may occur inside the bubble, the decomposition of HNO₂ and HNO₃ in such extreme conditions can be rapid. Kinetic for reaction (6) is supposed to be lower and probably depends on the interface temperature. In these conditions, a higher decomposition rate can be assumed at higher ultrasonic frequencies. Presuming a NO steady state in the gas phase, the kinetic constant for reaction (7) is $k_{(7)} = 0.7 \text{ L}^3 \text{ mol}^{-3} \text{ s}^{-1}$ [18]. The kinetic constants for NO₂ dimerization (reaction (8)) and for N₂O₄ disproportionation at 298 K (reaction (9)) are respectively $k_{(8)} = 4.5 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ and $k_{(9)} = 1.7 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ [18].

In sonicated nitric solutions, hydrogen peroxide cannot accumulate due to its rapid reaction with nitrous acid according to the reaction (10) [17]. However, in the presence of anti-nitrous reagents such as hydrazinium nitrate or sulfamic acid which scavenge HNO₂ by the reaction (11) and (12), H₂O₂ can accumulate at a higher rate than that observed in pure water [20,21]. This phenomenon is attributed to the reaction of nitrate ions with OH radicals forming NO₃ radical species, which, after hydrolysis, yield hydrogen peroxide in solution (reactions (13) and (14)). In this mechanism, only one hydroxyl radical is used whereas two are used in pure water to generate one molecule of hydrogen peroxide.

$$HNO_2 + H_2O_2 \rightarrow HNO_3 + H_2O \tag{10}$$

 $N_2H_5^+ + 2HNO_2 \rightarrow N_2O + N_2 + 3H_2O + H^+$ (11)

$$HNO_2 + NH_2SO_3H \rightarrow N_2 + H_2O + H_2SO_4$$
(12)

$$NO_3^- + H^+ + OH^- \rightarrow NO_3^- + H_2O \tag{13}$$

$$NO_3^{\cdot} + H_2O \rightarrow NO_2 + H_2O_2 \tag{14}$$

In water, the sonochemical yield of H_2O_2 can be increased in the presence of oxygen. Several authors have reported higher H_2O_2 yield for $Ar/(20-30 \text{ vol.}%)O_2$ gas mixtures. This was attributed to much more significant generation of both OH⁻ and HO₂ radicals [12,21,22]. According to these observations, one can assume that the sonication of a correctly tuned system combining nitric acid (in the presence of anti-nitrous reagent) and Ar/O_2 atmosphere may enhance H_2O_2 yields. To the best of our knowledge, the study at such condition has never been reported in the literature. Furthermore, the sonolysis of nitric acid has been only studied under low-frequency ultrasound (~20 kHz). The aim of the present work is to investigate the behavior of aqueous nitric solutions in the presence of Ar/O_2 gas mixtures at different ultrasonic frequencies.

2. Experimentals

2.1. Materials

Reagents used in this study were all of analytical grade and were purchased from Sigma Aldrich and VWR. To prepare aqueous solutions for experiments, purified ultrapure water having a resistivity higher than 18.2 M Ω cm at 25 °C was used. The experiments were performed under pure Ar (purity >99.9%) or with an Ar/O₂ (20 vol.% of O₂) mixture provided by Air Liquide. For several experiments, hydrazinium nitrate [N₂H₅NO₃] (NH) or sulfamic acid NH₂SO₃H were used as anti-nitrous reagent. NH was prepared by careful neutralization of hydrazine hydrate with HNO₃.

2.2. Sonochemical experiments

Experiments at low frequency ultrasound (20 kHz) were performed with a 1 cm² titanium horn fitted on top of a 50 mL homemade reactor. The power supply was provided by a 750 W generator (sonics & materials vibracell VCX 750). High frequency studies (207 and 615 kHz) were performed in a 250 mL cylindrical reactor mounted on top of a 25 cm² high-frequency transducer (L3 communications ELAC Nautik) connected to a 125 W generator (LVG 60 RF-generator). For high frequency experiments, the solution was stirred in the meantime at ~240 rpm to obtain a homogeneous system. Both reactors are tight and are supplied with several connections dedicated to temperature control, solution sampling, gas bubbling, and a connection to a mass spectrometer. In order to compare accurately the experimental results, the acoustic power P(W) delivered to the solution was determined by the calorimetric method (reaction (15)). This was then used to determine the specific acoustic power P_{ac} expressed in W mL⁻¹ (reaction (16)).

$$P_{\rm (W)} = mC_{\rm p} \left(\frac{dT}{dt}\right)_0 \tag{15}$$

$$P_{\rm ac} = \frac{P_{\rm (W)}}{V_{\rm (mL)}} \tag{16}$$

where, *m* is the mass of water (kg), $C_{\rm p}$, is the calorific capacity of the water at room temperature and atmospheric pressure (4.18 kJ kg⁻¹ K⁻¹), $(dT/dt)_{0}$, is the initial rate of water heating during sonication, and *V* is the volume of the sonicated solution (mL).

During sonication, the temperature was maintained at 21 ± 1 °C with a Huber CC1 cryostat and was controlled with a thermocouple immersed in the reactor. Various treated solutions were sparged with gas (constant rate flow: 100 mL min⁻¹) 15 min before starting ultrasound which was then maintained into the solution during the whole experiments. All materials constituting the sonoreactor (horn, tube for gas bubbling, thermocouple) were placed reproducibly in the solution to avoid artefacts.

2.3. UV–Vis spectroscopy

During sonolysis, aliquots of solutions (1 mL) were sampled with a syringe through a septum and filtered with 0.2 µm PTFE filters. Then, samples were diluted with appropriate solutions before analysis with UV–Vis absorption spectrophotometry (Thermo Evolution 220). Absorption spectra were recorded from 300 to 750 nm. The formation of H₂O₂ was followed by mixing the sampled solution (1:1) with 1.2×10^{-2} M TiOSO₄ (0.330 g TiOSO₄ dissolved in 100 mL of pure water under stirring and previously gently heated in 3.5 mL of 18 M H₂SO₄) to form a colorimetric complex absorbing at 410 nm (ε = 698 cm⁻¹ M⁻¹). A calibration curve was previously prepared with a standard H₂O₂ solution.

The formation of HNO₂ during sonolysis of aqueous nitric solutions was followed by UV–Vis absorption spectrophotometry using the Griess method, which consists to the measurement of a colorimetric complex formed by the reaction of NO₂⁻ with sulfanilic acid and α -naphtylamine (λ = 535 nm, ε = 41,500 cm⁻¹ M⁻¹). The procedure consists of mixing filtered solution aliquots (0.1–1 mL) with 2 M NaOH (1 mL), sulfanilic acid (3.45 × 10⁻² M, 0.6 g sulfanilic

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