Optimization of Ultrasonic Irradiation as an Advanced Oxidation Technology

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The optimization of ultrasonic irradiation as an advanced oxidation technology can be achieved by adjusting the ultrasonic frequency and saturating gas during sonolysis. The sonolytic production of hydrogen peroxide (H₂O₂) and hydroxyl radical (·OH) has been investigated at the ultrasonic frequencies of 20, 40, 80, and 500 kHz, respectively, in the presence of four different saturating gases (i.e., Kr, Ar, He, O₂) at each frequency. H₂O₂ was measured with a KI dosimeter, and the formation of ·OH was monitored by trapping with terephthalic acid. Both the applied frequency and the physicochemical properties of the saturating gases influence the sonochemical rates of production of ·OH and H₂O₂. At 20 kHz, the rate constants for the production of H₂O₂ vary over an order of magnitude as a function of the nature of the dissolved gas (0.0508 and 1.31 µM min⁻¹). Similar trends are observed for the production of ·OH at the same frequencies and under an identical set of saturating gases. The highest rates of production of H₂O₂ (pH 7, 2.94 µM min⁻¹) and ·OH (pH 11, 0.391 µM min⁻¹) are observed during sonolysis of Kr-saturated solutions at 500 kHz. Sonolysis of He-saturated solutions at 20 kHz results in the lowest rates of production of H₂O₂ (0.0508 µM min⁻¹) and ·OH (0.0310 µM min⁻¹). Decreasing differences among the saturating gases at higher frequencies are attributed to changes in bubble dynamics and thermodynamics as the resonant bubble radius decreases from 177 µm at 20 kHz to 7 µm at 500 kHz.

Introduction

During the last 20 years, various legislative acts have mandated the reduction and elimination of water and land pollution. In order to fulfill these mandates, effective control and remediation methods must be developed and implemented. The need for new technology is further driven by the large number of polluted sites across the country; approximately 14 900 sites are in progress within the Department of Defense (DOD) and more than 1200 Superfund sites are on the National Priorities List (NPL). The exploration of alternative technologies is needed in order to supersede conventional destructive techniques. In 1994, approximately 20% of the Environmental Protection Agency’s (EPA) cleanup decisions at Superfund sites involved the use of innovative technologies (1). The creation of the Superfund Innovative Technology Evaluation (SITE) program by the EPA also indicates a willingness to explore and scale up emerging technologies.

The development of novel treatment methods encompasses investigations of advanced oxidation processes (AOPs), which are characterized by production of the hydroxyl radical (·OH) as a primary oxidant. Examples of AOPs include the use of hydrogen peroxide with ultraviolet light (H₂O₂/UV) to treat hazardous compounds (2), semiconductor photocatalysis (4), ozonolysis (5, 6), and ultrasonic irradiation (sonolysis) (7–15). Sequential or parallel process combinations include ozone/radiolysis (16) or ozone/sonolysis (17).

Ultrasonic irradiation of aqueous solutions induces acoustic cavitation: the cyclical growth and collapse of gas bubbles. As a result of cavitation, extreme temperatures and pressures are generated at the center of the collapsed bubble. These conditions often lead to enhanced chemical reactivity (18–20). In particular, the production of the hydroxyl radical (·OH), hydrogen peroxide (H₂O₂), and other oxidants has been exploited during the application of ultrasonic irradiation as an AOP. Previous investigations of sonolysis have demonstrated its effectiveness; however, optimization with respect to solution conditions and reactor configurations is still necessary. In particular, optimization of ·OH and H₂O₂ production is crucial to the successful application of sonolysis to realistic treatment situations.

The influence of sound frequency on the formation of chemical oxidants during treatment with power ultrasound is just beginning to emerge (21–28). Recent reports indicate that irradiation at higher frequencies (e.g., ≥100 kHz) leads to greater enhancements in reaction rates than irradiation at lower frequencies (≤20 kHz). For example, the oxidation of I⁻ to I₃⁻ was reported to be faster at 900 kHz than at 20 kHz (21), while the degradation of phenol (13) was determined to be approximately six times higher at 487 kHz than at 20 kHz. Sonoluminescence, which is the emission of light from acoustically cavitating bubbles, is also affected by variations in ultrasonic frequency. Both the intensity and the emission spectra of sonoluminescence are altered when cavitation is induced at different ultrasonic frequencies (29–32).

In this paper, we examine the production rates of the hydroxyl radical and hydrogen peroxide in aqueous solution during sonolysis as a function of frequency and the nature of the dissolved gases. Our working hypothesis is that both the ultrasonic frequency and the physicochemical properties of the saturating gas determine the optimal production rates of ·OH and H₂O₂ in irradiated water.

Experimental Methods

Ultrapure water was obtained from a MilliQ Plus UV System and had a minimum resistance of 18.2 MΩ. All chemicals [e.g., KOH and NH₄MnO₄ (Mallinckrodt); KI and potassium biphthalate (Baker); NaOH, NaH₂PO₄, and 30% H₂O₂ (EM Science)] were reagent grade and used as received. Terephthalic acid (98%) and 2-bromoterephthalic acid (97%) were obtained commercially (Aldrich Chemical Company), while hydroxyterephthalic acid was synthesized following standard procedures (44, 33). Compressed gases were provided by Air Liquide (Walnut Creek, CA).

Sonolyses were performed with a Undatim Sonoreactor (20, 40, and 80.6 kHz) and an Undatim power generator coupled to a 513-kHz transducer (Undatim Ultrasonics S.A., Louvain-La-Neuve, Belgium). The temperature of the sonicated solutions was maintained at 25–30 °C with a Haake A80 refrigerated bath and circulator (Haake Inc., Saddle Brook, NJ). Replaceable titanium tips on the 20.2, and 39.4-kHz transducers were polished with wetted sandpaper as needed and tightened before each use to prevent solvent intrusion into the cavity. The peizoelectric transducers were maintained at a constant temperature by passing a stream of compressed air through a plastic fitting inserted into the housing. Because of differences in reactor configurations,
sonolyses at 80.6 kHz were in 100 mL of solution, while those at 20.2 and 39.4 kHz were in 200 mL of solution, and those at 513 kHz were in 600 mL of solution. Table 1 contains information about the physical dimensions and characteristics of each transducer while the reactor configurations are shown in Figures 1 and 2. Sonications were performed with four different saturating gases at each of four frequencies. Solutions were sparged for 30 min before sonication at a flow rate of 80 mL min\(^{-1}\) and continuously during sonication. In order to facilitate gas and heat transfer, solutions were stirred during sparging and sonication.

Calorimetry measurements were performed at each of the four applied frequencies (Table 1) and at the given power settings and solution volumes used during sonications. The power output was calculated from the change in temperature as described elsewhere (19). The hydroxyl radical was trapped by the direct addition reaction with terephthalic acid (34). Terephthalic acid solutions (1.5 mM) were prepared in a phosphate buffer (6.8 \(\times\) 10\(^{-4}\) M sodium hydroxide and 4.1 \(\times\) 10\(^{-3}\) M sodium phosphate dibasic) at a pH of 10.9 (0.1. At various time intervals during sonication, 3.0-mL samples were taken and transferred to a quartz fluorescence cell in the fluorimeter. Samples irradiated at the lower frequencies (20 and 39.4 kHz) were filtered with Acrodisc 0.2 mM PFTE syringe filters (Gelman Sciences). Fluorescence measurements were made with a Shimadzu spectrofluorophotometer RF-540 and a Shimadzu data recorder DR-3. The slit width for the excitation and emission beams was 5 and 2 nm, respectively. It should be noted that the fluorescence response factor, and thus the sensitivity of the method, will vary depending on the slit widths chosen. The ordinate multiplier was 4. Aqueous solutions sonicated in the presence of terephthalate were analyzed fluorometrically by excitation at 310 nm with emission measured at 425 nm.

Hydrogen peroxide was detected by the method of Kormann et al. (35). Sonications were carried out at pH 7 in the presence of a phosphate buffer (4.8 \(\times\) 10\(^{-3}\) M NaOH and 8.3 \(\times\) 10\(^{-3}\) M KH\(_2\)PO\(_4\)) at each frequency. At regular time intervals during sonication, 2.0-mL sample aliquots were withdrawn, filtered, and mixed in a quartz cuvette with 1.0 mL of 0.1 M potassium biphthalate and 0.75 mL of a solution containing 0.4 M potassium iodide, 0.06 M sodium hydroxide, and \(\sim\)2 \(\times\) 10\(^{-4}\) M ammonium molybdate. The mixed solutions (total volume = 3.75 mL) were allowed to stand for 2 min before the absorbance was measured. Absorbance measurements were made at 298 K with a Hewlett-Packard 8452a diode array spectrophotometer and a 89090A temperature controller.

### Aqueous Cavitation Chemistry

#### Sonolytic Production of H\(_2\)O\(_2\) and \(\cdot\)OH

The generation of oxidizing species during sonolysis of aqueous solutions is initiated by the thermolysis of water (eq 1) as follows:

\[
\text{H}_2\text{O} \xrightarrow{\Delta} \cdot\text{OH} + \cdot\text{H}
\] (1)

The production of \(\cdot\)OH and \(\text{H}\) during sonolysis under a variety of physical and chemical conditions has been directly determined using electron spin resonance (36, 37). The presence of \(\cdot\)OH is also indicated by the hydroxylation of aqueous benzoic acid (38) and terephthalic acid (28, 39) during sonication. The G-value (molecules produced per 100 eV or 1.6 \(\times\) 10\(^{-17}\) J) for the formation of \(\cdot\)OH during sonolysis has been estimated to be 0.35 by using the Fricke dosimeter (40).

After the initial splitting of H\(_2\)O, further reactions depend on other species present in the gas phase. A total of 80% of
the formed ‘OH and ‘H has been estimated to recombine (41). However, ‘OH can self-react to form hydrogen peroxide:

\[ 2\text{‘OH} \rightarrow \text{H}_2\text{O}_2 \]  

(2)

Recombination of ‘OH to form H₂O₂ most likely occurs at the collapsing bubble interface (42). The recombination rate constant measured in water under ambient conditions is \( 5.5 \times 10^9 \text{L mol}^{-1} \text{s}^{-1} \) (43). The rate constant for the self-reaction at the interface should be at least as large. ‘H does not appear to accumulate outside the cavitation bubble (44).

If O₂ is present in the vapor phase of the bubble, it can also undergo thermolysis as follows:

\[ \text{O}_2 \rightarrow 2\text{‘O}^\bullet \]  

(3)

Cleavage of the O–O bond during sonolysis has been demonstrated by isotopic exchange experiments (41). Because the dissociative bond energies in the gas phase for water and oxygen are both 119 kcal mol⁻¹ (45), thermolysis of these molecules within the cavitation bubbles is an important process during sonication of O₂-saturated solutions. Since H₂ is not detected during sonolysis of an O₂-saturated solution (46), it appears that O₂ efficiently scavenges ‘H according to the following standard reaction:

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

(4)

An alternate pathway for production of ‘OH in an O₂-saturated solution is as follows (41):

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

(5)

Both H₂O₂ and ‘OH are strong oxidants and have aqueous reduction potentials at pH 7 of 1.35 and 2.31 V, respectively (E°, V vs NHE) (47). The kinetics of ‘OH reactions with organic compounds have been studied extensively both in the gas phase (48) and in aqueous solution (43).

The production rates of ‘OH and H₂O₂ during sonolysis will be affected by the final collapse temperature (\( T_{\text{max}} \)) and pressure (\( P_{\text{max}} \)) within the cavitation bubbles. These quantities can be estimated from an approximate solution to the Rayleigh–Plesset equation, assuming adiabatic bubble collapse, as follows (18):

\[ T_{\text{max}} = T_o \left\{ \frac{P_m(K-1)}{P} \right\} \]  

(6)

\[ P_{\text{max}} = P \left( \frac{P_m(K-1)}{P} \right)^{\frac{(K-1)}{K}} \]  

(7)

where \( P_m \) is the pressure in the liquid at the time of collapse, \( P \) is the pressure in the bubble at its maximum size, and \( K = C_p/C_v \) is the ratio of specific heats. The polytropic index, \( K \), is correlated to the heat released upon compression of a gas. Also important are the thermal conductivity and solubility of a gas. The influence of \( K \) and the thermal conductivity on the sonochemical production of free radicals has been demonstrated experimentally (49). In addition, sonoluminescence is influenced by the thermal conductivity of the background gas (50). Various physicochemical properties of the four gases used in this investigation are listed in Table 2.

This data, observe that Kr is the least heat conducting and most soluble of the gases; thus, collapse of a bubble containing Kr is expected to yield the most extreme transient temperatures.

The ultrasonic frequency will affect the reaction environment by determining the resonant bubble radius (51):

\[ \rho_o \omega^2 R_r^2 = 3K P_o \]  

(8)

\[ \begin{array}{|c|c|c|c|}
\hline
\text{gas} & \text{polytropic index} & \text{thermal conductivity} & \text{water solubility} \\
& & (\text{mW m}^{-1} \text{K}^{-1}) & (\text{m}^{-1} \text{m}^3) \\
\hline
\text{Kr} & 1.66 & 17.1 & 5.94 \times 10^{-2} \\
\text{Ar} & 1.66 & 30.6 & 3.37 \times 10^{-2} \\
\text{He} & 1.63 & 0.0252 & 8.60 \times 10^{-4} \\
\text{O}_2 & 1.41 & 48.1 & 3.05 \times 10^{-4} \\
\hline
\end{array} \]

TABLE 2. Physical Properties of Saturating Gases

FIGURE 3. Zero-order rate of production of H₂O₂ at 20.2 kHz in Kr, Ar, O₂, or He-saturated solutions at pH 7 and 25 °C.

where \( \rho \) is the density of water, \( \nu_r \) is the resonant frequency, \( R_r \) is the resonant radius, \( P_o \) is the pressure in the liquid, usually taken to be 1 atm, and \( K \) is the polytropic index, as defined before. This expression is valid when surface tension effects are small. Differences in bubble radii will result in variable bubble collapse times as well as surface area to volume ratios. The data in Tables 3 and 4 illustrate these differences. Although the radius is slightly influenced by the nature of the saturating gas, the most significant influence is the frequency. The resonant radius ranges from ~7 µm at 513 kHz to ~170 µm at 20.2 kHz. However, it should be noted that the cavitating solution will contain a bubble population with a distribution of radii.

Results and Discussion

**Influence of Saturating Gas on Cavitation Chemistry.** The kinetic data illustrating the effects of different saturating gases at selected frequencies are shown in Figures 3–7. The slopes of the linear regression lines yield the uncorrected (observed) formation rates for production of ‘OH and H₂O₂. In order to determine the effect of frequency on the reaction rates, the formation rates are normalized by correcting for the differences in the acoustic power output. The complete set of normalized rate constants is tabulated in Table 5.

H₂O₂ production during sonication at 20.2 kHz as a function of the saturating gases is illustrated in Figure 3. The apparent kinetics are zero-order, with the observed rates ranging from \( 5.08 \times 10^{-2} \mu \text{M min}^{-1} \) for He to 1.31 µM min⁻¹ for Kr. The differences in rates in Kr-saturated solutions versus Ar-saturated solutions can be inversely correlated with the difference in thermal conductivity and solubility of each gas.
TABLE 3. Compression Half-Cycle Length, Bubble Collapse Times, and Resonant Bubble Radii for Ar and Kr as Saturating Gases

<table>
<thead>
<tr>
<th>frequency (kHz)</th>
<th>half-cycle length (µs)</th>
<th>collapse time (µs)</th>
<th>resonant radius (µm)</th>
<th>surface area (µm²)</th>
<th>volume (nL)</th>
<th>resonant radius, He (µm)</th>
<th>surface area, He (µm²)</th>
<th>volume, He (nL)</th>
<th>A₀V, He (µm⁻¹)</th>
<th>A₀V, He (µm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.2</td>
<td>25.0</td>
<td>16.20</td>
<td>178</td>
<td>3.96 x 10⁶</td>
<td>23.4</td>
<td>6.34 x 10²</td>
<td>6.34 x 10²</td>
<td>0.0015</td>
<td>4.22 x 10⁻¹</td>
<td></td>
</tr>
<tr>
<td>39.4</td>
<td>12.5</td>
<td>8.10</td>
<td>88.8</td>
<td>9.91 x 10⁴</td>
<td>2.930</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>80.6</td>
<td>6.8</td>
<td>4.10</td>
<td>44.4</td>
<td>2.48 x 10⁴</td>
<td>0.366</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>513</td>
<td>1.0</td>
<td>0.65</td>
<td>7.1</td>
<td>6.34 x 10²</td>
<td>4.22 x 10⁻¹</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* For a bubble of resonant radius; assumed to be an ‘empty void’ with pressure in the liquid at 1 atm.

TABLE 4. Influence of Frequency and Saturating Gases, O₂ and He, on Bubble Resonant Radius

<table>
<thead>
<tr>
<th>frequency (kHz)</th>
<th>resonant radius, He (µm)</th>
<th>surface area, He (µm²)</th>
<th>vol, He (nL)</th>
<th>A₀V, He (µm⁻¹)</th>
<th>resonant radius, O₂ (µm)</th>
<th>surface area, O₂ (µm²)</th>
<th>volume, O₂ (nL)</th>
<th>A₀V, O₂ (µm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.2</td>
<td>176</td>
<td>3.89 x 10⁶</td>
<td>22.8</td>
<td>1.70 x 10⁻²</td>
<td>163</td>
<td>3.38 x 10⁵</td>
<td>18.4</td>
<td>1.84 x 10⁻²</td>
</tr>
<tr>
<td>39.4</td>
<td>87.9</td>
<td>9.73 x 10⁴</td>
<td>2.85</td>
<td>3.40 x 10⁻²</td>
<td>81.9</td>
<td>8.84 x 10⁴</td>
<td>2.30</td>
<td>3.66 x 10⁻²</td>
</tr>
<tr>
<td>80.6</td>
<td>43.9</td>
<td>2.43 x 10⁴</td>
<td>0.356</td>
<td>6.81 x 10⁻²</td>
<td>40.9</td>
<td>2.11 x 10⁴</td>
<td>0.288</td>
<td>7.33 x 10⁻²</td>
</tr>
<tr>
<td>513</td>
<td>7.0</td>
<td>6.23 x 10⁻⁷</td>
<td>0.00146</td>
<td>4.26 x 10⁻¹</td>
<td>6.5</td>
<td>5.40 x 10⁻²</td>
<td>0.00118</td>
<td>4.61 x 10⁻¹</td>
</tr>
</tbody>
</table>

TABLE 5. Rate Constants (µM min⁻¹) for Hydrogen Peroxide and Hydroxyl Radical Production at 20.2, 39.4, 80.6, and 513 kHz

<table>
<thead>
<tr>
<th>frequency (kHz)</th>
<th>Kr (H₂O₂)</th>
<th>Ar (H₂O₂)</th>
<th>O₂ (H₂O₂)</th>
<th>He (·OH)</th>
<th>Kr (·OH)</th>
<th>Ar (·OH)</th>
<th>O₂ (·OH)</th>
<th>He (·OH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.2</td>
<td>1.31</td>
<td>0.717</td>
<td>0.204</td>
<td>0.0508</td>
<td>0.146</td>
<td>0.103</td>
<td>0.0699</td>
<td>0.0310</td>
</tr>
<tr>
<td>39.4</td>
<td>1.35</td>
<td>0.756</td>
<td>0.233</td>
<td>0.902</td>
<td>0.128</td>
<td>0.0981</td>
<td>0.0600</td>
<td>0.0185</td>
</tr>
<tr>
<td>80.6</td>
<td>2.76</td>
<td>3.01</td>
<td>1.48</td>
<td>0.939</td>
<td>0.480</td>
<td>0.489</td>
<td>0.350</td>
<td>0.100</td>
</tr>
<tr>
<td>513</td>
<td>23.8</td>
<td>15.6</td>
<td>13.3</td>
<td>2.33</td>
<td>3.17</td>
<td>2.90</td>
<td>2.68</td>
<td>0.580</td>
</tr>
</tbody>
</table>

* Corrected for differences in total acoustic power at each frequency.

(a factor of ∼2). The observed production rate in the presence of He is slower than would be predicted solely by its low water solubility, but faster than predicted by its high thermal conductivity. Differences in the polytropic index, K, affect the production rate in O₂-saturated solutions. Less heat is released during the implosion of a cavitation bubble in O₂-saturated solutions. The lower collapse temperature decreases the ·OH production rate and leads to a slower formation rate for H₂O₂. However, the lower value of K does not appear to influence the production rate as significantly as the higher thermal conductivity of He.

Differences in thermal conductivity and solubility appear to have a lesser effect on H₂O₂ production during irradiation at 39.4, although the kinetic curves follow similar trends as those observed at 20.2 kHz. At 80.6 kHz (Figure 4), the differences in thermal conductivity and K with respect to the production rate of H₂O₂ are minimal. In this case, all the rate constants are of the same order of magnitude (0.101–0.325 µM min⁻¹). The apparent rate constants differ by 10% in Ar and Kr-saturated solutions (0.325 µM min⁻¹ vs 0.288 µM min⁻¹). Furthermore, the production rate in an O₂-saturated solution (0.160 µM min⁻¹) is only ∼50% less than that observed in Ar- and Kr-saturated solutions, while the rate is 66% less under He (0.101 µM min⁻¹). These results imply that differences in the polytropic index are minimized at 80.6 kHz or that scavenging of ·H by O₂ occurs more readily in smaller bubbles.

The analogous trends during sonication at 513 kHz (Figure 5) are intermediate between those observed at 20 and 39.4 kHz and those observed at 80.6 kHz. The differences in H₂O₂ production rate in solutions saturated with the three noble gases do not correlate very strongly with the corresponding differences in thermal conductivity, with the exception of He. The three highest rate constants are within 50% of each other (kKr = 2.94 µM min⁻¹, kAr = 1.92 µM min⁻¹, kO₂ = 1.65 µM min⁻¹) although there is an order of magnitude difference between the lowest (kHe = 0.288 µM min⁻¹) and the highest rate constant.

The differences in production rate of ·OH at 20.2 kHz are shown in Figure 6. The rate constants range from 0.0310 to 0.146 µM min⁻¹. Even though the production rates with different dissolved gases are correlated with the thermal conductivities of the gases, the correlation is not as strong as that observed for hydrogen peroxide production at this frequency. Sonication at 39.4 kHz yields similar trends to those observed at 20.2 kHz.

During ultrasonic irradiation at 80.6 kHz (Figure 7), the apparent ·OH formation rate constants are all of the same

FIGURE 4. Zero-order rate of production of H₂O₂ at 80.6 kHz in Kr, Ar, O₂, or He-saturated solutions at pH 7 and 25 °C.

FIGURE 5. Zero-order rate of production of H₂O₂ at 80.6 kHz in Kr, Ar, O₂, or He-saturated solutions at pH 7 and 25 °C.
order of magnitude (i.e., $1.08 \times 10^{-2} \mu M \text{ min}^{-1}$ to $5.28 \times 10^{-2} \mu M \text{ min}^{-1}$). The difference between the rates observed in Ar-saturated solutions as compared to Kr-saturated solutions ($5.28 \times 10^{-2} \mu M \text{ min}^{-1}$ vs $5.18 \times 10^{-2} \mu M \text{ min}^{-1}$) is $\sim 10\%$, which is much less than the difference among the various physical properties of the gases. Furthermore, the production rate in O$_2$-saturated solutions ($3.78 \times 10^{-2} \mu M \text{ min}^{-1}$) is $\sim 30\%$ lower than in solutions saturated with either Ar or Kr. The reduced variability of •OH production rates with different saturating gases at 80.6 kHz is very similar to the trends observed at this frequency for H$_2$O$_2$ production.

The differences among Ar, Kr, and O$_2$ are smallest when solutions are irradiated at 513 kHz (Figure 8). At this frequency, the three highest rates are within $\pm 8\%$ ($3.31 \times 10^{-1} \mu M \text{ min}^{-1}$ to $3.92 \times 10^{-2} \mu M \text{ min}^{-1}$). However, •OH production in He-saturated solutions ($7.16 \times 10^{-2} \mu M \text{ min}^{-1}$)
is 18% of that observed in the presence of Kr. From these observations we conclude that, at 513 kHz, a large difference in  
thermal conductivity can still influence the production of \( \cdot \text{OH} \) and the subsequent physicochemical conditions during  
cavitational bubble collapse. Furthermore, because the production rates in the presence of \( \text{O}_2 \) (\( K = 1.41 \)) are  
comparable to those observed in the presence of Ar or Kr (\( K = 1.66 \)), the influence of the \( K \) values is minimized.

We note that interpretation of the apparent rate constants for hydroxyl radical production may be complicated by several  
factors. First, terephthalic acid must diffuse to the bubble surface in order to trap the \( \cdot \text{OH} \), which is present at a much  
lower concentration than in the hotter vapor-phase region of the imploded bubbles. Second, hydroxyterephthalic acid  
(HTA), the hydroxyl radical addition product, may react further with \( \cdot \text{OH} \) before it diffuses away from the bubble  
surface. Therefore, quantifying \( \cdot \text{OH} \) production via hydroxyterephthalic acid represents a lower limit for the actual \( \cdot \text{OH} \)  
production rate under a given set of conditions. In all cases, the steady-state production of \( \text{H}_2\text{O}_2 \) is greater than that of  
\( \cdot \text{OH} \).

The rate constants for the production of \( \text{H}_2\text{O}_2 \) and \( \cdot \text{OH} \) at each of the four frequencies in solutions saturated with each  
gas are tabulated in Tables 4 and 5. Because the experiments were carried out at different acoustic power intensities, the  
observed rate constants were normalized according to

\[
\kappa_{\text{norm}, f} = \kappa_{\text{obs}, f} \left( \frac{P_{20}}{P_{r}} \right)^{2.00} \left( \frac{1}{P_{10}} \right) \quad (9)
\]

where \( \kappa_{\text{norm}, f} \) and \( \kappa_{\text{obs}, f} \) are the corrected and the observed rate constants at the irradiation frequency, \( f \), \( I_1 \) and \( P_1 \) are sound intensity and power per unit volume at irradiation frequency, \( f \), \( I_{20} \) and \( P_{20} \) are the sound intensity (10 W cm\(^{-2}\)) and power per unit volume (0.078 W mL\(^{-1}\)) during irradiation at 20.2 kHz.

The fastest production of \( \text{H}_2\text{O}_2 \) occurred during sonolysis at 513 kHz of Kr-saturated solutions, whereas the slowest production rate was observed during sonolysis at 20.2 kHz of He-saturated solutions. Hydrogen peroxide formation occurs most rapidly in Kr-saturated solution at each frequency except at 80.6 kHz. Sonication at 513 kHz yields the fastest production rates, regardless of the saturating gas, except for He-saturated solutions, for which maximum rates were observed at 80.6 kHz. In general, the apparent rate constants tend to increase with increasing frequency and surface area to volume ratios.

A similar trend for the production of \( \cdot \text{OH} \) is seen in the data of Table 5, even though these rates represent a lower  
limit of the true rate of \( \cdot \text{OH} \) production by thermolysis of \( \text{H}_2\text{O} \) that occurs in the gas phase of the bubble. Hydroxyl radical  
production is optimized during sonolysis of Kr-saturated solutions at 513 kHz, and it occurs most slowly during  
sonication at 20.2 kHz in He-saturated solutions, respectively. In addition, Kr-saturated solutions yield the highest rates of \( \cdot \text{OH} \) production regardless of the irradiation frequency, and irradiations at 513 kHz appear to maximize the \( \cdot \text{OH} \) production rate, regardless of the nature of the dissolved gas. \( \cdot \text{OH} \) production rates are comparable at 20.2 and 39.4 kHz, but increase sharply at 80.6 kHz.

The larger observed rate constants at higher frequencies may indicate both a higher production rate for \( \cdot \text{OH} \) and a  
higher trapping efficiency of the terephthalic acid at the bubble interface. Petrier et al. (26) have suggested that, at  
higher frequencies, hydroxyl radicals are ejected out of the bubble before they can recombine in the gas phase because  
the collapse time at higher frequencies is shorter.

In addition, the increased efficiency of \( \text{H}_2\text{O}_2 \) and \( \cdot \text{OH} \) production at higher irradiation frequencies may also be due to  
variations in the acoustic pressure amplitude and in the surface tension. The acoustic pressure amplitude ranges from  
4.9 atm at 20.2 kHz to 5.7 atm at 80.6 kHz, while at 513 kHz the pressure amplitude is 2.1 atm. This implies that a bubble  
may not collapse as completely at 513 kHz. Instead, at 513 kHz, a stable bubble will oscillate a greater number of times  
per second and will produce a greater flux of \( \cdot \text{OH} \). The surface tension, which is inversely correlated with bubble radius,  
provides a collapsing force on the bubble. For a bubble in the absence of an acoustic field, the pressure varies as follows:

\[
P = P_h + \left( \frac{2 \sigma}{R} \right) (10)
\]

where \( P \) is the pressure that the bubble must maintain, \( P_h \) is the hydrostatic pressure, \( \sigma \) is the surface tension,  
and \( R \) is the bubble radius. A 44-\( \mu \text{m} \) (80.6 kHz) bubble will experience a surface tension that is approximately 4-fold  
larger than a 177-\( \mu \text{m} \) (20.2 kHz) bubble, regardless of the acoustic pressure. Thus, at a given acoustic pressure (e.g.,  
sound intensity), the total implosive force on a bubble at the resonant radius may be larger at higher frequencies, resulting  
in a more complete collapse and more extreme temperatures.

The cyclic growth and collapse of bubble clouds can also be altered as a function of frequency. Acoustic cavitation is  
induced by the excitation of a population of bubble nuclei to a resonant radius, at which point the bubbles efficiently absorb energy from the sound waves. The bubbles grow by the process of rectified diffusion (52). When the bubble expands during a rarefaction half-cycle, the gas within the bubble expands, and there is an influx of gas from the surrounding liquid into the bubble. During the compression half-cycle, the gas is compressed and results in an outward flux of gas into the bulk liquid. Because the surface area of the bubble during the expansion cycle is larger than during the compression cycle, there is a net increase of gas within the bubble at the end of each acoustic cycle. At higher frequencies, the resonant radius is calculated to be smaller, and therefore, fewer acoustic cycles are required before the bubble reaches resonant size. With a greater number of acoustic cycles per unit time at higher frequencies, rectified diffusion occurs more rapidly. Thus, a greater number of nuclei can reach resonance more quickly than at lower frequencies. The net effect is to produce a greater enhancement of sonochemical reactions.

Optimal application of ultrasonic irradiation as an advanced oxidation technology is achieved by selecting the  
correct physical and chemical parameters. The sonolytic production of \( \text{H}_2\text{O}_2 \) at \( \text{pH} \) 7 and of \( \cdot \text{OH} \) is strongly  
influenced by the nature of the dissolved gases and the applied ultrasonic frequencies. A maximum production rate of \( \text{H}_2\text{O}_2 \)  
and \( \cdot \text{OH} \) occurs at frequencies where the resonant radius may be larger at higher frequencies, resulting  
in a more complete collapse and more extreme temperatures. Thus, sonochemical destruction of compounds may occur more quickly at higher frequencies.

Even though the \( \text{H}_2\text{O}_2 \) and \( \cdot \text{OH} \) production rates at each frequency differ according to the nature of the background  
gas, the variability is less at higher frequencies. In addition, the surface area to volume ratio of the bubbles appears to play a role in the production efficiency of \( \text{H}_2\text{O}_2 \). The effect of the different gases reaches a maximum for each species, except in the case of \( \text{O}_2 \)-saturated solutions. The sonolytic production rates of both \( \text{H}_2\text{O}_2 \) and \( \cdot \text{OH} \) in \( \text{O}_2 \)-saturated solutions relative to \( \text{Ar} \)-saturated solutions increase monotonically with increasing frequency.

The absolute production rates are also higher at each frequency: \( k_{\text{Ar}0} > k_{\text{Ar}1} > k_{\text{Ar}2} > k_{\text{Ar}3} \) for most saturating gases. There are several reasons for enhanced sonochemistry at
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