Aromatic Compound Degradation in Water Using a Combination of Sonolysis and Ozonolysis

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The combination of sonolysis and ozonolysis as an advanced oxidation process was investigated to gain insight into factors affecting enhancement of the combined system. Sonolysis, ozonolysis, and a combination of the two were used to facilitate the degradation of three known organic contaminants, nitrobenzene (NB), 4-nitrophenol (4-NP), and 4-chlorophenol (4-CP), in water. Experiments were performed at frequencies of 20 and 500 kHz. At 20 kHz, there appeared to be an enhancement due to sonolytic ozonation, while at 500 kHz, an apparent retardation was seen. The catalytic effects of NB, 4-NP, and 4-CP degradation at 20 kHz increased with decreasing kO3 of the compounds, whereas retardation at 500 kHz was correlated with increasing kO3. The correlation of apparent rate enhancement at 20 kHz and retardation at 500 kHz with kO3 is consistent with a pathway involving the thermolytic destruction of ozone to form atomic oxygen. Atomic oxygen then reacts with water vapor in cavitation bubbles, yielding gas-phase hydroxyl radical. Enhancement in loss of total organic carbon (TOC) by sonolytic ozonation was considerable at both 20 and 500 kHz with all three compounds. In addition, intermediate product formation was observed.

Introduction

Ultrasonic irradiation of aqueous solutions has been shown to be effective for the in situ destruction of a variety of organic and inorganic contaminants (1–10). Sonication produces cavitation bubbles which yield high temperatures and pressures upon their implosion (11, 12). The center of a cavitation bubble contains water vapor, gas, and volatile compounds. Destruction of organic compounds occurs in the cavitation bubble itself, or its interfacial sheath due to direct pyrolysis or hydroxylation resulting from the gas-phase pyrolysis of H2O2. Reactions are also possible in the bulk aqueous phase by oxidation with hydrogen peroxide which has been observed to form in sonolytic systems. Sonication has been shown to be particularly effective with volatile and hydrophobic compounds since they can partition to the bubble or interfacial sheath rapidly (1, 7).

A variety of advanced oxidation processes (AOPs) employing ozone at high pH, ozone combined with hydrogen peroxide, or ozone combined with ultraviolet irradiation have been explored. In these systems, O3 decomposes via a free radical chain reaction to generate hydroxyl radical (13–17). Even though ozone is a strong oxidant (E° = 2.07 V), it is selective in terms of its reactions. For example, O3 preferentially reacts with alkenes and sites with high electronic density. In contrast, hydroxyl radical is nonselective in its reactions, allowing it to react with organic compounds by either H-atom abstraction, direct electron transfer, or insertion.

The coupling of ultrasonic irradiation with ozonation provides another possible AOP. Like that for other AOPs using ozone, OH+ is generated from the decomposition of ozone. However, by sonolysis, ozone is decomposed thermolytically in the vapor phase of a cavitation bubble as follows (18, 19):

\[
O_3 \rightarrow O_2 + O(3P) \quad (1)
\]

The initiation reaction yields atomic oxygen which reacts with water to form hydroxyl radical:

\[
O(3P) + H_2O \rightarrow 2OH^+ \quad (2)
\]

The reaction sequence of eqs 1 and 2 occurs in the vapor phase of the cavitation bubbles. The products then migrate to the interfacial sheath of the bubble where they are transferred into the aqueous phase. The combination of O3 and ultrasound may be an effective oxidation system since two OH+ molecules are formed per O3 molecule consumed. However, O3 may also react with atomic oxygen

\[
O_3 + O(3P) \rightarrow 2O_2 \quad (3)
\]

or other reactive species in or near the bubble, thus, reducing the efficiency of OH+ production. Hydrogen peroxide accumulation in the aqueous phase provides an indirect measure of OH+ production in the vapor phase and in the interfacial region. Previous studies have measured increased H2O2 production by sonolytic ozonation over sonolysis of oxygen (18, 20). In addition, ultrasonic irradiation has been demonstrated to increase the mass transfer of ozone to solution, allowing more ozone to enter solution than in a nonirradiated system (21–23).

Previous studies of the combined process involving ultrasound and ozone have shown faster degradation rates for humic and fulvic acids, 4-nitrophenol, trinitrotoluene, and phenol than either system alone as well as very rapid decomposition of ozone due to an ultrasonic field (18–27). However, there have been no comprehensive studies demonstrating the relative importance of ozone decomposition and enhanced mass transfer mechanisms in enhancing degradation rates of substrates.

The primary objective of this study was to examine the degradation kinetics of three similar aromatic compounds, nitrobenzene (NB), 4-nitrophenol (4-NP), and 4-chlorophenol (4-CP), by ultrasound (at frequencies of 20 and 500 kHz), by ozone, and by the combination of ultrasound and ozone. These compounds have a range of reaction rate constants with ozone as shown in Table 1 (28–32). The relative effect of thermolytic ozone decomposition compared to that of ultrasonically enhanced mass transfer may be observed by looking at differences in rates of the combined system and comparing it to rates obtained in separate sonication and ozonation experiments. The objective of this study was to
TABLE 1. Selected Properties and Rate Constants of Compounds

<table>
<thead>
<tr>
<th>compound</th>
<th>pKa ( a )</th>
<th>( H^r ) ( \left( \text{Pa m}^3\text{mol}^{-1}\text{K}^{-1} \right) )</th>
<th>( \log k_b ) ( (29, 30) )</th>
<th>( k_{sw} ) ( (29, 30) )</th>
<th>( k_{sw} ) ( (28) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>ozone</td>
<td>1.08 \times 10^4</td>
<td>1.1 \times 10^4 ( R ) 12.2 M cm² s⁻¹</td>
<td>1.2 \times 10⁻²</td>
<td>1.2 \times 10⁻¹</td>
<td>1.2 \times 10⁻⁵</td>
</tr>
<tr>
<td>nitrobenzene</td>
<td>1.3</td>
<td>( &gt; 10^6 ) ( \text{bar} \text{mm}^{-1} \text{cm}^{-2} \text{mol}^{-1} \text{K}^{-1} )</td>
<td>9.38</td>
<td>0.0567</td>
<td>2.16 \times 10⁶</td>
</tr>
</tbody>
</table>

*Values from ref 31 except for those for ozone which are from 32.

Experimental Methods
Materials and Reagents. 4-Nitrophenol (Aldrich, >99%), 4-chlorophenol (Aldrich, >99%), phosphoric acid (EM Science, 85%), sodium phosphate monobasic (Mallinckrodt), sodium hydroxide (Mallinckrodt), and sodium thiosulfate (Mallinckrodt) were used as received. All solutions were prepared with water purified by a Millipore Milli-Q UV Plus system (R = 18.2 MΩ-cm).

Sonochemical Experiments. The experimental setup consisted of a glass chamber reactor surrounded by a self-contained water jacket, a constant gas flow, and a source of ultrasound. The temperature of the solution was kept constant at 25 ± 1 °C by a 20 °C water bath (Haake Co., model A81) flowing through the surrounding water jacket.

Ozone gas was filtered through a Drierite and molecular sieve system purifier (Alltech) followed by an activated charcoal hydrocarbon trap (Alltech) before flowing through an OREC Ozonator (model O3V10-O) at 0.6 atm and 4.5 L min⁻¹. In both reactors, the gas flowed out of a coarse fritted-glass diffuser at 10 mL min⁻¹. The O₃ gas phase concentration was determined to be approximately 1.0% w/w by oxidation of indigo trisulfonic acid, corresponding to an O₃ dose of 0.01 g h⁻¹ (33).

The sonication at 500 kHz was performed with an ultrasonic transducer (Undatim Ultrasonic) operating at 515 kHz and 100% power with a reaction volume of 640 mL, while the 20 kHz reactor was a direct immersion probe system (VCX-400 Vibracell, Sonic & Materials) operating at 50% power with a reaction volume of 235 mL. The emitting areas of the transducers were 25.5 and 1.2 cm² for the 500 and 20 kHz reactors, respectively, by sonication, ozonation, and sonolytic ozonation in the 20 kHz reactor. The O₃ gas flow rate was 10 mL min⁻¹. The pH was 2.4 ± 0.2. T = 293 K. The initial NB concentration was 100 µM. The power was 56.1 W.

Analysis. To quantify 4-NP and its intermediate, 4-nitrooctaethylene (4-NC), a Hewlett-Packard HP 8452a diode array spectrophotometer was used. The absorbance was measured at \( \lambda = 400 \text{ nm} \) \( (e = 17,009 \text{ M}^{-1} \text{ cm}^{-1} \text{ for 4-CP}) \) and \( \lambda = 512 \) \( (e = 12,500 \text{ M}^{-1} \text{ cm}^{-1} \text{ for 4-NC}) \). Quantification of NB, 4-CP, and their intermediates was carried out on a Hewlett-Packard Series II 1090 HPLC. A 5 mm, 100 mm × 2.1 mm ODS Hypersil column (Hewlett-Packard) was used for the analysis of 4-CP and intermediates. With this column, a gradient program was used with an eluent mixture consisting of an aqueous phosphate buffer solution (pH 3) and acetonitrile. For NB, a 3 mm, 100 mm × 4 mm Hypersil BDS-C18 column (Hewlett-Packard) was used. The eluent consisted of a 30:70 (water/acetonitrile) isocratic mixture. TOC analysis was performed on a Shimadzu 5000A total organic carbon analyzer operating in the nonpurgeable organic carbon (NPOC) mode.

Results
Figures 1 and 2 show the destruction of NB in the 20 and 500 kHz reactors, respectively, by sonication, ozonation, and sonolytic ozonation. The linearity in the first-order plot by sonication demonstrates that the degradation rate is first-order with respect to NB at both frequencies. Table 2 lists the first-order degradation rate constants of NB, 4-NP, and 4-CP by sonolysis \( (k_{sw}) \), all of which follow first-order kinetics. In the 20 kHz reactor, NB degrades the fastest and 4-NP the slowest, but in the 500 kHz reactor, 4-CP is the fastest while 4-NP is the most resistant to destruction by sonication. Lower-frequency sonication results in a greater degree of vapor-phase pyrolysis due to high temperatures that are achieved during bubble collapse conditions, while higher frequencies favor OH⁻ production (35). The NB results are consistent with these observations since NB has the highest Henry's Law constant and reacts considerably faster in the 20 kHz system than 4-CP or 4-NP. As the Henry's Law constant decreases, other pathways such as OH⁻ attack become increasingly more dominant as observed with 4-CP and 4-NP. In contrast, in the 500 kHz system, 4-CP reacts most rapidly due to its fast reaction rate with OH⁻ and its high \( K_{sw} \) which suggests a greater partitioning to the bubble interface due to its higher hydrophobicity.
3-NP, 3-nitrophenol; 2-NP, 2-nitrophenol; 4-NC, 4-nitrocatechol; and 4-CC, 4-chlorocatechol. In the sonochemical reactor but without ultrasonic irradiation.

The reaction of ozone with these compounds also followed a pseudo-first-order degradation rate law for the loss of substrate over four half-lives due to the continuous bubbling of O3. As expected from the known overall second-order substrate over four half-lives due to the continuous bubbling of O3. As expected from the known overall second-order reaction rate constants in the 20 and 500 kHz experiments, resulting in accumulation of intermediates over the length of the experiment. In general, the concentration of the intermediate species increased initially, and then decreased after reaching a peak concentration. Typical concentrations observed reached levels of ~1 (near the detection limit) to 4 μM. In all cases, the intermediates peaked earlier with sonolytic ozonation than with sonication.

The combination of ultrasound and ozone also follows apparent pseudo-first-order kinetics. As observed in the ozonation of the compounds, degradation is greater at 20 kHz. As shown in Figures 1 and 2 and Table 2, ozonolysis is observed to be slower than sonolysis combined with ozonolysis and sonolysis is slowest for all the compounds at both frequencies. At 20 kHz, degradation of compounds in an ultrasonic field is considerably slower than reactions with ozone or ultrasound combined with ozone. However, at 500 kHz, results from all three types of experiments for each compound were within a factor of 2.

Intermediate degradation products at 20 and 500 kHz are shown in Figure 3. During a 3.5 h sonolysis experiment at 20 kHz, intermediates were produced throughout the run, while in the 500 kHz reactor, the intermediate concentrations grew and then began to degrade. Reaction rate constants were much smaller for 20 kHz sonolysis experiments, resulting in accumulation of intermediates over the length of the experiment. In general, the concentration of the intermediate species increased initially, and then decreased after reaching a peak concentration. Typical concentrations observed reached levels of ~1 (near the detection limit) to 4 μM. In all cases, the intermediates peaked earlier with sonolytic ozonation than with sonication.

**TABLE 2. Pseudo-First-Order Rate Constants for Degradation of NB, 4-CP, and 4-NP under Various Conditions**

<table>
<thead>
<tr>
<th>experiment</th>
<th>k_{US} (min^{-1})</th>
<th>k_{O3} (min^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>nitrobenzene</td>
<td>3.2 × 10^{-3} ± 8.4 × 10^{-5}</td>
<td>1.3 × 10^{-2} ± 1.1 × 10^{-4}</td>
</tr>
<tr>
<td>ozonation,</td>
<td>3.9 × 10^{-2} ± 1.1 × 10^{-3}</td>
<td>1.6 × 10^{-2} ± 6.1 × 10^{-4}</td>
</tr>
<tr>
<td>ozonation,</td>
<td>8.8 × 10^{-2} ± 3.9 × 10^{-3}</td>
<td>2.5 × 10^{-2} ± 6.5 × 10^{-4}</td>
</tr>
<tr>
<td>ozonation,</td>
<td>4.6 × 10^{-2} ± 4.1 × 10^{-3}</td>
<td>-4.2 × 10^{-3} ± 8.9 × 10^{-4}</td>
</tr>
<tr>
<td>sonication with O3, k_{US}</td>
<td>1.7 × 10^{-3} ± 3.6 × 10^{-5}</td>
<td>1.2 × 10^{-2} ± 9.3 × 10^{-5}</td>
</tr>
<tr>
<td>sonication with O3, k_{O3}</td>
<td>4.5 × 10^{-2} ± 2.0 × 10^{-3}</td>
<td>1.8 × 10^{-2} ± 7.7 × 10^{-4}</td>
</tr>
<tr>
<td>sonication with O3, k_{total}</td>
<td>7.8 × 10^{-2} ± 4.7 × 10^{-3}</td>
<td>2.1 × 10^{-2} ± 8.2 × 10^{-4}</td>
</tr>
<tr>
<td>residual kinetic effect, k_{US/O3}</td>
<td>3.2 × 10^{-2} ± 5.1 × 10^{-3}</td>
<td>-9.0 × 10^{-3} ± 1.1 × 10^{-2}</td>
</tr>
</tbody>
</table>

In the sonochemical reactor but without ultrasonic irradiation.

**TABLE 3. Aromatic Intermediates Observed in the Degradation of NB, 4-NP, and 4-CP at 20 and 500 KHz by Sonolysis, Ozonolysis, and Sonolytic Ozonation**

<table>
<thead>
<tr>
<th>experiment</th>
<th>20 kHz</th>
<th>500 kHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>nitrobenzene</td>
<td>4-NP (1.3), 3-NP (2.8), 4-NC (7.8)</td>
<td>4-NP (0.9), 3-NP (2.1), 2-NP (3.2), 4-NC (3.8)</td>
</tr>
<tr>
<td>ozonation</td>
<td>4-NP (1.2), 3-NP (0.3)</td>
<td>4-NP (1.3), 3-NP (1.1), 2-NP (2.1), 4-NP (0.3)</td>
</tr>
<tr>
<td>ozonation</td>
<td>4-NP (2.9), 3-NP (2.1), 4-NC (1.0)</td>
<td>4-NP (2.2), 3-NP (2.3), 2-NP (1.9), 4-NC (2.9)</td>
</tr>
<tr>
<td>4-nitrophenol</td>
<td>4-NC (3.0)</td>
<td>4-NC (7.6)</td>
</tr>
<tr>
<td>ozonation</td>
<td>4-NC (1.2)</td>
<td>none detected</td>
</tr>
<tr>
<td>ozonation</td>
<td>4-NC (1.2)</td>
<td>none detected</td>
</tr>
<tr>
<td>4-chlorophenol</td>
<td>4-CC (10.3)</td>
<td>4-CC (13.7)</td>
</tr>
<tr>
<td>ozonation</td>
<td>none detected</td>
<td>4-CC (16.4)</td>
</tr>
<tr>
<td>ozonation</td>
<td>none detected</td>
<td>none detected</td>
</tr>
</tbody>
</table>

Values in parentheses represent maximum micromolar concentrations observed during an experiment. Abbreviations: 4-NP, 4-nitrophenol; 3-NP, 3-nitrophenol; 2-NP, 2-nitrophenol; 4-NC, 4-nitrocatechol; and 4-CC, 4-chlorocatechol. In the sonochemical reactor but without ultrasonic irradiation.
or ozonation alone, indicating more rapid degradation of the parent compound than with the separate systems. NB intermediates, 4-NP and 3-NP, in the combined system, had higher peak concentrations than they did in the separate processes. More significant accumulation of 4-NP in the combined system demonstrates that 4-NP is less reactive by sonolytic ozonation than NB, as shown in Table 2.

Initial pseudo-first-order degradation rate constants for the loss of TOC associated with NB, 4-NP, and 4-CP are given in Table 4. The rate constant, \( k_{\text{US/TOC}} \), is approximately 10% of the \( k_{\text{obs}} \) of the parent compound. This is expected since the degradation products will contribute to TOC until the carbon species are oxidized completely to CO2. Similar to what was observed with the destruction of the parent compounds, sonication with O2 yielded the slowest reaction rate with TOC. Although ozonation showed rapid initial destruction over the first 3 h, the rates decreased as intermediates resistant to destruction by ozone were formed. Degradation rates of TOC by sonolytic ozonation were faster than those with sonication or ozonation alone and followed first-order kinetics over four half-lives. First-order kinetics in the combined system resulted from \( \text{OH} \) formed from sonolytic decomposition of ozone reacting with intermediates resistant to destruction by ozone. Examples of ozone-resistant intermediates likely in these systems include oxalate and acetate. The rapid reaction rate with sonolytic ozonation resulted in mineralization in 3 h with the 20 kHz probe and 6 h in the 500 kHz reactor.

**Discussion**

The overall rate of substrate (S) disappearance in the sonolytic ozonation process can be represented by a linear combination of contributing terms similar to that proposed by Peyton et al. for O3 combined with ultraviolet irradiation (17):

\[
-\frac{dS}{dt} = k_{\text{US}}[S] + k_{\text{O3}}[S] + k_{\text{US/O3}}[S]
\]

where \( k_{\text{US}}, k_{\text{O3}}, \) and \( k_{\text{US/O3}} \) are, respectively, the first-order degradation rate constants for sonolysis, ozonolysis, and the residual kinetic effect upon combining the two systems. A term for gas stripping of compounds may be added, but was not expected to be significant over the time period of degradation. If terms are combined, eq 4 can be expressed as

\[
-\frac{dS}{dt} = k_{\text{total}}[S] = \sum k_i[S]
\]

where \( k_{\text{total}} \) is the overall pseudo-first-order reaction rate
constant in the combined system. Values of $k_{US}$ and $k_{O3}$ were determined from separate experiments involving only sonication or ozonation. The $k_{US}[S]$ term combines all pyrolysis and OH radical reactions with the substrates observed in the plain sonication experiments. In addition, due to the nature in which $k_{O3}$ was evaluated, the term $k_{O3}[S]$ includes both direct O$_3$ reactions and secondary reactions from O$_3$ auto-decomposition that occur in the nonirradiated experiments. After the terms $k_{US}$ and $k_{O3}$ were determined, the remaining residual kinetic effect in the combined process over the individual processes was attributed to sonochemical ozonation. Table 2 lists the rate constants for all three substrates in both individual processes was attributed to sonolytic ozonation.

FIGURE 4. Enhancement of the combined system compared to the linear combination of separate sonolysis and ozonolysis experiments at 20 and 500 kHz vs reported second-order rate constants.

the combined system than for the linear combination of separate experiments. However, in the 500 kHz system, the model consistently overpredicts the degradation rates (i.e., $k_{US/O3} < 0$) by 15, 30, and 35% for NB, 4-NP, and 4-CP, respectively. Therefore, at 20 kHz, synergism is observed, while at 500 kHz, antagonism is seen.

Initial first-order rate constants for TOC loss corresponding to NB, 4-NP, or 4-CP solutions as well as the residual kinetic effect, $k_{US/O3}$, are listed in Table 4. The model underpredicted the rate constant at both frequencies for the mineralization of the compounds (i.e., $k_{US/O3} > 0$). At 20 kHz, the enhancements were 411, 227, and 315% for NB, 4-NP, and 4-CP, respectively. The enhancements were not as significant at 500 kHz but followed the same general trend of NB (137%) > 4-CP (64%) > 4-NP (35%).

A conceptual diagram of possible pathways of substrate degradation and interactions of sonolysis and ozonolysis is shown in Figure 5. Pathways 1 and 2 indicate ozonolysis reactions with the substrate in the absence of sonication.

FIGURE 5. Conceptual diagram of possible pathways of substrate degradation and interactions of sonolysis and ozonolysis.
This includes mass transfer of ozone from the gas phase to solution (pathway 1) and bulk solution reactions of the substrate with ozone or radicals from O$_3$ auto-decomposition, which occur in the absence of sonolysis (pathway 2). Pathways 6 and 7 occur by sonolysis of the substrate in the absence of ozone by direct pyrolysis of the substrate (pathway 6) or pyrolysis of H$_2$O in a cavitation bubble producing OH$^\cdot$ (pathway 7). However, in the combined system, pathways 2, 6, and 7 may be altered by the addition of other pathways which only occur by the direct interaction of sonolysis and ozonolysis. For example, the decomposition of O$_3$ by pathway 4 may be the major pathway of O$_3$ sonication which only occur by the direct interaction of sonolysis and ozonolysis. For example, the decomposition of O$_3$ by pathway 4 may be the major pathway of O$_3$ sonication which only occur by the direct interaction of sonolysis and ozonolysis. For example, the decomposition of O$_3$ by pathway 4 may be the major pathway of O$_3$ sonication which only occur by the direct interaction of sonolysis and ozonolysis. For example, the decomposition of O$_3$ by pathway 4 may be the major pathway of O$_3$ sonication which only occur by the direct interaction of sonolysis and ozonolysis. For example, the decomposition of O$_3$ by pathway 4 may be the major pathway of O$_3$ sonication which only occur by the direct interaction of sonolysis and ozonolysis. For example, the decomposition of O$_3$ by pathway 4 may be the major pathway of O$_3$ sonication which only occur by the direct interaction of sonolysis and ozonolysis. For example, the decomposition of O$_3$ by pathway 4 may be the major pathway of O$_3$ sonication which only occur by the direct interaction of sonolysis and ozonolysis. For example, the decomposition of O$_3$ by pathway 4 may be the major pathway of O$_3$ sonication which only occur by the direct interaction of sonolysis and ozonolysis.

\[ k_{US} + k_{O3} > k_{US} + k_{O3} + k_{US/O3} \]  

(9)

The US/O$_3$ rate constants, $k_{US}$ and $d/ or k_{O3}$ are smaller than $k_{US}$ and $k_{O3}$ from the separate sonolysis and ozonolysis experiments at 500 kHz. The addition of pathways 3 and/or pathway 5 at 500 kHz does not compensate for the reductions in pathways 7 and/or pathway 2 in the combined system compared to the individual systems. Furthermore, formation of O$_2$ by pathway 4 may be the major pathway of O$_2$ sonication at 500 kHz. In the 20 kHz reactor and for TOC destruction in both reactors, the opposite condition exists:

\[ k_{US} + k_{O3} < k_{US} + k_{O3} + k_{US/O3} \]  

(10)

Pathways 3 and 5 more than compensate for reductions in pathways 2 and 7 in relation to the separate ultrasound and ozonolysis systems. In addition, the formation of O$_2$ from sonication of O$_3$ does not overwhelm the formation of OH$^\cdot$ by pathway 4. However, it is impossible to determine the values of $k_{US}$, $k_{O3}$, and $k_{US/O3}$ from the experiments performed.

The predominance of ultrasonically enhanced mass transfer as the mechanism for enhancement will result in an increase in pathway 2 of Figure 5:

\[ -\frac{dS}{dt} = k_{US}[S] + k_{O3}[O_3][S] + k_{O3}[O_2][S] \]  

(11)

where $k_{O3}$ is written as a second order rate constant in eq 11 and $[O_3]$ is the additional O$_3$ due to enhanced mass transfer ($k_{US/O3}[S] = k_{O3}[O_3][S]$). This mechanism results in a similar increase in enhancement with NB, 4-NP, and 4-CP. On the other hand, the predominance of sonolytic decomposition of O$_3$ as the major mechanism of enhancement depends on $k_{O3}$. Compounds with a smaller $k_{O3}$ will exhibit the most enhancement if O$_3$ is converted to OH$^\cdot$, assuming S has a high $k_{OH}$. In the extreme case where $k_{US}$ is zero, any OH$^\cdot$ that is formed at the expense of O$_3$ will increase the destruction of the substrate. As $k_{O3}$ increases, this benefit is reduced as pathway 2 of Figure 5 becomes more important.

Therefore, the degradation of NB, 4-NP, and 4-CP by sonication, ozonation, and sonolytic ozonation at 20 and 500 kHz supports a thermal decomposition mechanism as the major enhancement mechanism of the combined system compared to the separate sonication or ozonation systems. Figure 4 shows the expected trend that a thermal decomposition mechanism predicts. At 20 kHz, the degradation rate is enhanced substantially as $k_{O3}$ decreases. On the other hand, antagonism increases with increasing $k_{O3}$ at 500 kHz. Although the 500 kHz system does not give benefits over ozonation or sonication with oxygen for the destruction of the parent compounds, the antagonism does follow the trend we expect for thermolytic ozone destruction in a cavitation bubble. The negative factors affecting the observed rate constants appear to be greater than the effect of increased radical production occurring in the combined system. In addition, in a separate study in which the mass transfer effects of ultrasound were investigated, increased O$_3$ to solution was minimal (36). Despite the complexity of the combined treatment system, our results support the mechanism of OH radical formation from O$_3$ decomposition as the main mechanism for sonolytic ozonation.

Acknowledgments

Financial support provided by Defense Advanced Research Projects Agency (DARPA), the Office of Naval Research (ONR), the Electric Power Research Institute (EPRI), and the Department of Energy (DOE) is gratefully acknowledged.

Literature Cited


Received for review July 31, 1997. Revised manuscript received June 16, 1998. Accepted June 20, 1998.
ES970675A