

## Acoustic Cavitation-assisted Decomposition of 4-Nonylphenol in Water

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Acoustic cavitation-assisted decomposition of 4-nonylphenol in water takes place through OH radical-attack and pyrolysis at the cavitation bubble interface and in the bulk solution. The cavitation-induced physical and chemical effects by addition of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  play an important role in the enhancement of 4-nonylphenol decomposition.

The cavitation phenomenon, which accompanies a series of processes such as the formation, growth, and collapse of micro bubbles, results from ultrasonic irradiation in a liquid. In acoustic cavitation chemistry, the three different reaction sites, such as the gas phase inside the cavitation bubbles, the gas-liquid phase of the cavitation bubble interface, and the bulk solution, exist during ultrasonic irradiation.<sup>1</sup> The formation of the OH radical via the sonolysis of water molecule and the pyrolysis of volatile organic compounds occur inside cavitation bubbles, which present high temperatures (several 1000 K) and pressures (several 100 atm). Pyrolysis of nonvolatile hydrophobic compounds occurs at the cavitation bubble interface. The oxidation of nonvolatile hydrophilic compounds via the attack of the OH radicals takes place in the bulk solution.<sup>2,3</sup> OH radicals are relatively strong non-specific oxidants, which react with most organic compounds, and play an important role in the acoustic cavitation-assisted decomposition of environmental contaminants in water.

4-Nonylphenol (4-NP) is the biological decomposition product of nonylphenol ethoxylates (a group of non-ionic surfactants), which are widely used in industrial processes because of the efficiency in cost and use, in natural environments and in conventional waste water treatment plants. 4-NP is also used by some industries as an antioxidant in plastics and a stabilizer of polyvinyl chloride. It seems likely that 4-NP is suspected to have a hormone mimic property and potential effects as an endocrine disruptor<sup>4</sup> and is more toxic than the parent compound (nonylphenol ethoxylates) in many organisms.<sup>5</sup> In the present study, we report the results of the acoustic cavitation-assisted decomposition of 4-NP in water, and also discuss the effects of added soluble metal ions and insoluble particles in order to raise the efficiency on the acoustic cavitation-assisted decomposition of 4-NP.

Reagent grade chemicals were purchased from Wako and used without further purification. All the water used for the experiment was prepared using a Millipore-Q system. The 4-NP aqueous solution was prepared by bubbling a high purity argon gas before ultrasonic irradiation, and the pH of solution was not adjusted. The determination of 4-NP and the gaseous products were carried out with a gas chromatograph. Hydrogen peroxide was spectrophotometrically determined from the amount of  $\text{I}_3^-$  ( $\epsilon$  of  $\text{I}_3^- = 26000 \text{ M}^{-1} \text{ cm}^{-1}$  at 352 nm). The organic acids were determined by an ion chromatography. The experimental procedure for the ultrasonic irradiation was almost the same as that previously reported.<sup>6</sup> An ultrasonic generator and a barium

titanate oscillator with ultrasonic waves (frequency = 200 kHz, input power = 200 W) were used in this study.

In order to investigate the acoustic cavitation-assisted decomposition mechanism of 4-NP, the decomposition of 4-NP was carried out in a *tert*-butyl alcohol aqueous solution under argon. The *tert*-butyl alcohol, which is well known to be an effective radical scavenger<sup>3</sup> would capture the OH radicals produced from the sonolysis of water, and the decomposition of organic compounds via OH radical-attack may be depressed. During ultrasonic irradiation, the changes in the concentration of 4-NP in water and in a *tert*-butyl alcohol aqueous solution are shown in Figure 1. The decomposition of 4-NP was depressed with the increasing concentration of *tert*-butyl alcohol. It appears that the OH radicals did not accumulate at the cavitation bubble interface and in the bulk solution due to the radical scavenging effect of *tert*-butyl alcohol, and the decomposition rates of 4-NP via the OH radical-attack would be significantly influenced. However, even at 10 mM *tert*-butyl alcohol (about 300 times the molar concentration of 4-NP), the decomposition of 4-NP was not perfectly suppressed. Also the pyrolysis products such as  $\text{CO}$ ,  $\text{CH}_4$ , and  $\text{H}_2$  under argon were detected as shown Figure 2. These results suggest that the acoustic cavitation-assisted decomposition of 4-NP proceeds via pyrolysis as well as OH radical-attack at the cavitation bubble interface,<sup>7</sup> although the contribution of pyrolysis to the decomposition of 4-NP was smaller than that via the OH radical-attack. The acoustic cavitation-assisted decomposition of 4-NP via OH radical-attack would lead to an opening reaction of the aromatic ring. The short-chain organic acids as final products would be finally formed. In this study, the formic acid, acetic acid, and propionic acid as the products of the decomposition of 4-NP were also detected (see Figure 2). It is expected that further mineralization to carbon dioxide and water would be achieved with the effective application of OH radicals during the acoustic cavitation-assisted process.

The OH radicals produced from the sonolysis of water should be recombined to  $\text{H}_2\text{O}_2$  at the cavitation bubble interface, if a scavenger does not exist. The formed  $\text{H}_2\text{O}_2$  would migrate to the bulk solution. For the purpose of the more effective utilization of the recombined  $\text{H}_2\text{O}_2$ , the decomposition of 4-NP in the presence

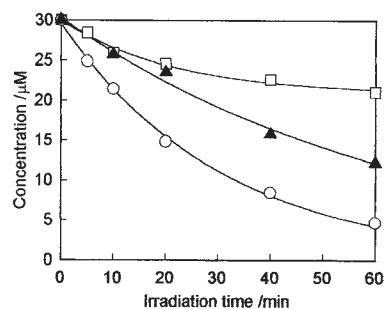
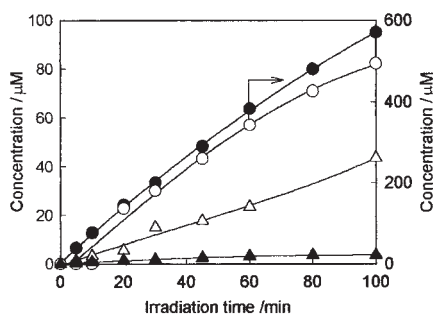
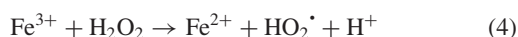
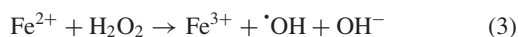


Figure 1. Effect of the *tert*-butyl alcohol on the decomposition of 4-NP under argon. (○) 0 mM *tert*-butyl alcohol, (▲) 3 mM, (□) 10 mM.

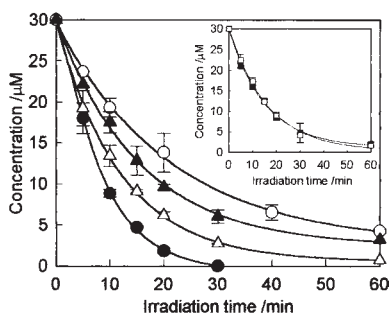


**Figure 2.** Pyrolysis products and organic acids formed from the acoustic cavitation-assisted decomposition of 4-NP in water. (●) H<sub>2</sub>, (○) CO, (▲) CH<sub>4</sub>, (△) organic acids (sum of formic acid, acetic acid, and propionic acid).

of Fe<sup>2+</sup> and Fe<sup>3+</sup> during ultrasonic irradiation was carried out and these results are graphically illustrated in Figure 3. The reactive radical species such as <sup>•</sup>OH and HO<sub>2</sub><sup>•</sup> are derived from the reaction of H<sub>2</sub>O<sub>2</sub> with Fe<sup>2+</sup> and Fe<sup>3+</sup> as follows:



As shown in Figure 3, the decomposition rates of 4-NP increased with the addition of Fe<sup>2+</sup> and Fe<sup>3+</sup>, due to the regeneration of the OH radicals. In particular, in the presence of oxygen, the acoustic cavitation-assisted decomposition rate of 4-NP by the addition of Fe<sup>2+</sup> and Fe<sup>3+</sup> remarkably increased. This result suggests that the increase of H<sub>2</sub>O<sub>2</sub> formation under oxygen would lead to the enhancement of acoustic cavitation-assisted decomposition in the presence of Fe<sup>2+</sup>.<sup>8</sup> However, the decomposition rate at the concentration of 200 μM Fe<sup>2+</sup> decreased compared to that at 100 μM Fe<sup>2+</sup>. It appears that the decrease in the decomposition rate of 4-NP was due to the OH radical scavenging effect induced by an excessive quantity of Fe<sup>2+</sup> (equation (5)). In the case of Fe<sup>3+</sup>, the difference in the decomposition rates at the concentrations of 100 and 200 μM Fe<sup>3+</sup> did not appear (Figure 3 inset). On the other hand, as shown in Table 1, the decomposition of 4-NP was not significantly enhanced by the presence of soluble metal ions such as Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, and Zn<sup>2+</sup>, except for Fe<sup>2+</sup> and Fe<sup>3+</sup>. It appears likely that the catalytic effect of these metal ions on the decomposition of H<sub>2</sub>O<sub>2</sub> existing in the bulk solution is lower than that of Fe<sup>2+</sup> and



**Figure 3.** Decomposition of 4-NP in the presence of Fe<sup>2+</sup> (inset: Fe<sup>3+</sup>) under argon. (○) only ultrasonic irradiation, (△) 100 μM Fe<sup>2+</sup>, (▲) 200 μM Fe<sup>2+</sup>, (●) 100 μM Fe<sup>2+</sup> under oxygen, inset: (□) 100 μM Fe<sup>3+</sup>, (■) 200 μM Fe<sup>3+</sup>.

**Table 1.** Acoustic cavitation-assisted decomposition of 4-NP in the presence of the soluble metal ion and the insoluble particle under argon

Additive	Concentration / μM	d[4-NP]/dt / μM min <sup>-1</sup>
Ultrasound	—	1.11
Fe <sup>2+</sup>	100	2.15
	200	1.60
Fe <sup>2+a</sup>	100	2.40
Fe <sup>3+</sup>	100	1.73
	200	1.52
Co <sup>2+</sup>	100	1.49
Ni <sup>2+</sup>	100	1.55
Cu <sup>2+</sup>	100	1.16
Zn <sup>2+</sup>	100	1.29
SiO <sub>2</sub>	100 <sup>b</sup>	1.45
Al <sub>2</sub> O <sub>3</sub>	100 <sup>b</sup>	2.04

<sup>a</sup>Under oxygen atmosphere. <sup>b</sup>Unit: mg l<sup>-1</sup>.

Fe<sup>3+</sup> during ultrasonic irradiation.

Fe<sup>3+</sup> formed from the oxidation of Fe<sup>2+</sup> by H<sub>2</sub>O<sub>2</sub> (equation (3)) in natural pH may be present as a hydroxide (e.g., Fe(OH)<sub>3</sub>). The existence of these solid particles would result in a micro-mixing effect in solution and then the decomposition reaction would be enhanced. In order to investigate the effect of solid particles during ultrasonic irradiation, the decomposition of 4-NP was carried out in the presence of insoluble particles such as SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> and these results are also shown in Table 1. The decomposition rates were faster than that with only ultrasound. This result suggests that insoluble particles play a significant role in the acoustic cavitation-assisted decomposition due to cavitation induced micro-mixing effects and shock waves on the surface of the particles, although no remarkable increase in the formation rate of the OH radical by its addition was observed.

In conclusion, the acoustic cavitation-assisted decomposition of 4-NP occurred by OH radical-attack and pyrolysis at the cavitation bubble interface and in the bulk solution. The addition of Fe<sup>2+</sup> and Fe<sup>3+</sup> on the decomposition results in the regeneration of OH radicals and the cavitation-induced physical effects and eventually leads to the enhancement of acoustic cavitation-assisted decomposition.

#### References and Notes

- 1 a) A. A. Atchely and L. A. Crum, in "Ultrasound: its chemical, physical, and biological effects," ed. by K. S. Suslick, VHC Pub. Inc., Weinheim (1988), p 1. b) T. J. Mason and J. P. Lorimer, "Sonochemistry: theory, application and uses of ultrasound in chemistry," Ellis Horwood, West Sussex (1988).
- 2 a) E. B. Flint and K. S. Suslick, *Science*, **253**, 1397 (1991). b) W. B. McNamara, III, Y. T. Didenko, and K. S. Suslick, *Nature*, **401**, 772 (1999).
- 3 A. Henglein and C. Kormann, *Int. J. Radiat. Biol.*, **48**, 251 (1985).
- 4 a) K. S. Korach, *Endocrin.*, **132**, 2277 (1993). b) R. White, S. Jobling, S. A. Hare, J. P. Sumpter, and M. G. Parker *Endocrin.*, **135**, 175 (1994).
- 5 a) R. Ekelnd, A. Bergman, A. Granmo, and M. Berggren, *Environ. Pollut.*, **64**, 107 (1990). b) M. Ahel, J. McEnvoy, and W. Giger, *Environ. Pollut.*, **79**, 243 (1993).
- 6 a) B. Yim, Y. Nagata, and Y. Maeda, *J. Phys. Chem. A*, **106**, 104 (2002). b) H. Okuno, B. Yim, Y. Mizukoshi, Y. Nagata, and Y. Maeda, *Ultrason. Sonochem.*, **7**, 261 (2000).
- 7 It seems likely that 4-NP is concentrated at the cavitation bubble interface because of its physicochemical properties, such as solubility in water (0.007 g L<sup>-1</sup>), vapor pressure (0.817 × 10<sup>-3</sup> mmHg), and octanol-water distribution (Log P = 5.76).
- 8 The formation rates of H<sub>2</sub>O<sub>2</sub> by ultrasonic irradiation under argon and oxygen were 9 μM min<sup>-1</sup> and 14 μM min<sup>-1</sup>, respectively.