

Sonochemical Degradation of Polychlorinated Biphenyls in Aqueous Solution

Xi Kui WANG*, Guan Hong CHEN, Zhong Yan YAO

College of Chemistry and Environmental Science, University of Jinan, Jinan 250022

Abstract: Polychlorinated biphenyl (PCB) is a kind of persistent and dangerous environmental pollutants. This paper presented the research result of sonochemical degradation of 2-chlorobiphenyl (2-CBP), 4-chlorobiphenyl (4-CBP) and 4,4'-dichlorobiphenyl (4,4'-CBP) in water. The ultrasonic degradation kinetics of 2-CBP, 4-CBP and 4,4'-CBP in water were found to be first-order and the degradation rate coefficients are 3.69×10^{-2} , 3.19×10^{-2} and 2.06×10^{-2} at $25 \pm 1^\circ\text{C}$ for 2-CBP, 4-CBP and 4,4'-CBP respectively. The influence of initial concentrations, reaction temperature on the ultrasonic decomposition of 2-CBP were also investigated.

Keywords: Polychlorinated biphenyl, degradation, sonochemistry, 2-chlorobiphenyl.

Ultrasonic waves in a liquid induce the formation of cavitation bubbles. Submitted to an oscillating pressure field, cavities filled with vapor and dissolved gas pulsate, grow and implode violently when they reach a critical resonant size. According to the 'hot spot' theory, extremely high temperature and pressure are produced during the collapse of cavitation bubbles¹. Under these extreme conditions, the molecules vaporized in the bubbles as well as in the surrounding condensed layer could be decomposed². Over the past years, a great number of studies on the sonochemical degradation of organic compounds of environmental interest have been reported³⁻⁵

Chlorinated hydrocarbons have attracted public attention due to their presence in ground, river and drinking water and their potential hazard to human health. Over the past decade, sonochemical degradation of volatile chlorinated hydrocarbons such as chlorinated methane and ethane^{6,7}, trichloroethylene^{8,9} and chlorobenzene¹⁰⁻¹² have been widely studied. Polychlorinated biphenyl (PCB) is a kind of persistent and dangerous environmental pollutants and widely present in water, soil and atmosphere^{13,14}, however, the sonolysis of these compounds have not been reported. In this paper, a research result of sonochemical degradation of 2-chlorobiphenyl(2CBP), 4-chlorobiphenyl (4-CBP) and 4,4'-dichlorobiphenyl(4,4'-CBP) in water was presented.

*E-mail: xk_wang@x263.net

Experimental

2-CBP, 4-CBP and 4,4'-CBP were purchased from Aldrich Inc. and used without further purification. 2-CBP and 4-CBP were dissolved directly into water with magnetic stirring for 8 h. 4,4'-CBP was dissolved in ethanol and then diluted into water with magnetic stirring for 8 h.

The sonication of 100 mL aqueous solutions of PCB in a 150 mL glass reactor cell were performed with a 20 kHz Model JCS-204 ultrasonic reactor at a power of 50 W (Jining Ultrasonic Instruments Factory). The aqueous solution was saturated with pure air before and during the sonication. The reaction temperature was controlled with the help of condensation water surrounding the reactor cell. The quantifications of PCB were carried out with a Model 244 HPLC equipped with a model 163 variable wavelength ultra-violet detector (Beckman, USA) on a Dupont Zorbax-ODS C₁₈ column (15 cm × 4.6 mm ID).

Result and Discussion

The air saturated aqueous solutions of 2-CBP, 4-CBP and 4,4'-CBP were sonicated for 60 min. During the sonication, the concentrations of above PCBs were determined every 10 min. The kinetics of PCBs degradation during sonication were showed in **Figure 1** and **Figure 2**. It was found that the concentrations of PCBs in aqueous solutions decreased exponentially with sonication time, indicating first-order kinetics. Regression on the experiment data delivered the first-order reaction rate coefficients (k_1) are 3.69×10^{-2} ($r=0.996$, $n=6$), 3.19×10^{-2} ($r=0.998$, $n=6$) and 2.06×10^{-2} ($r=0.995$, $n=6$) at $25 \pm 1^\circ\text{C}$ for 2-CBP, 4-CBP and 4,4'-CBP respectively. The result showed that mono-substituted PCB decomposed faster than dichlorobiphenyl. During sonication the solution can be divided into three different zones². In the collapsing cavitation bubbles, solvent vapor and volatile solutes are pyrolyzed, producing radicals that undergo further reactions. In the interfacial region, pyrolysis as well as radical degradation reaction occur. The third region is the bulk solution at ambient temperature. Here, solutes

Figure 1 Concentration vs. sonication time profiles of PCB at 25°C (initial concentrations: 2 mg L⁻¹)

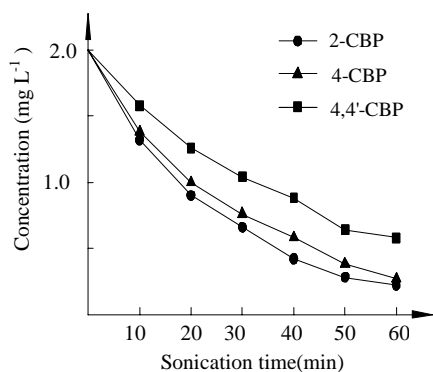


Figure 2 Sonochemical degradation kinetics of PCB at 25°C (2 mg L⁻¹)

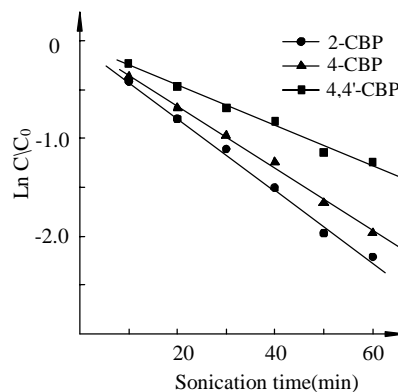


Figure 3 Degradation kinetics of 2-CBP for different initial concentrations at 25°C

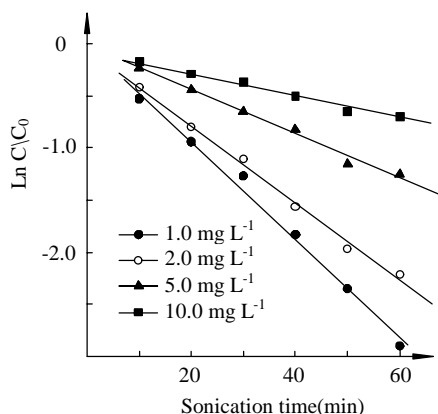
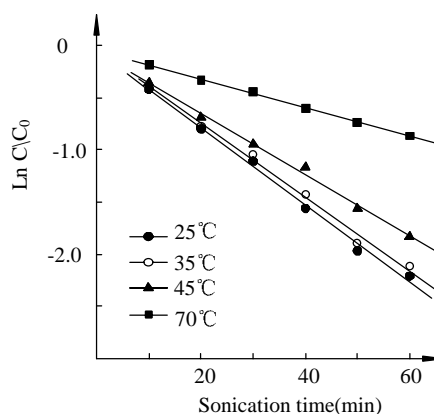


Figure 4 Degradation kinetics of 2-CBP for different temperature (2 mg L⁻¹)



react with radicals that have not yet recombined. Consequently, apolar compounds of high vapor pressure degraded faster than non-volatile compounds. Here the vapor pressure of 4-CBP (<1.4 Pa at 25°C) is lower than that of 2-CBP (<1.8 Pa at 25°C) and 4,4'-CBP is of lowest vapor pressure. So 2-CBP was degraded slightly faster than 4-CBP, and 4,4'-CBP appears to decompose more slowly than 2-CBP and 4-CBP under the same solution conditions.

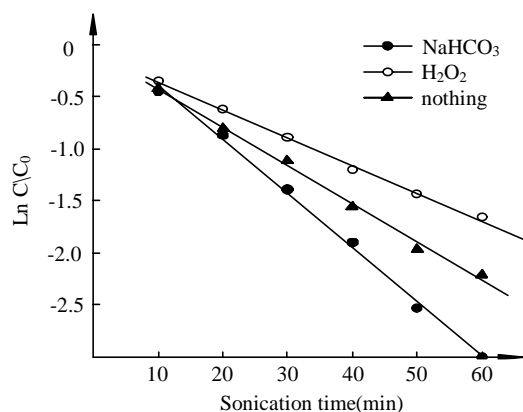
It was found that the ultrasonic degradation rates of PCB varied at different initial concentrations. **Figure 3** showed the degradation kinetics of 2-CBP for different initial concentrations at 25°C. It was observed that with increasing the initial concentration, the degradation rate coefficients was decreased. The ultrasonic degradation rate coefficients (k_1) of 2-CBP were 4.70×10^{-2} ($r=0.998$, $n=6$), 3.69×10^{-2} ($r=0.997$, $n=6$), 2.15×10^{-2} ($r=0.994$, $n=6$) and 1.12×10^{-2} ($r=0.994$, $n=6$) min^{-1} at initial concentrations 1.0, 2.0, 5.0 and 10.0 mg L^{-1} respectively.

The influence of the reaction temperature on the ultrasonic degradation of 2-PCB (2.0 mg L^{-1} in water) was also investigated and the results were showed in **Figure 4**. The ultrasonic degradation rate coefficients (k_1) of 2-CBP were 3.69×10^{-2} ($r=0.996$, $n=6$), 3.55×10^{-2} ($r=0.997$, $n=6$), 2.92×10^{-2} ($r=0.997$, $n=6$), and $0.0136 \times 10^{-2} \text{ min}^{-1}$ ($r=0.999$, $n=6$) at temperature $25 \pm 1^\circ\text{C}$, $35 \pm 1^\circ\text{C}$, $45 \pm 1^\circ\text{C}$ and $70 \pm 2^\circ\text{C}$ respectively. The result showed that with increasing the reaction temperature, the rate of degradation was decreased in the range of temperature in this study. As the bulk temperature of water increased, the vapor pressure of water and volatile solutes inside the cavitation bubbles is increased. The collapse of cavity is thus cushioned more than that at a lower bulk temperature, this results in more moderate conditions and a lower sonochemical degradation rate.

The experimental results showed that H_2O_2 can accelerate the ultrasonic degradation of PCB, and the presence of sodium bicarbonate as a free-radical scavenger could hinder the decomposition. **Figure 5** showed the degradation kinetics of 2-PCB aqueous solution (2 mg L^{-1}) at 25°C in the presence of H_2O_2 and NaHCO_3 separately. The ultrasonic degradation rate coefficients (k_1) of 2-CBP were found to be 5.22×10^{-2} ($r=0.997$,

n=6) when 100 mg L⁻¹ of H₂O₂ was present, and 2.67×10^{-2} (r=0.998, n=6) when 100 mg L⁻¹ of sodium bicarbonate was present.

Figure 5 Degradation kinetics Of 2-PCB in water (2 mg L⁻¹) at 25°C in the presence of H₂O₂ and NaHCO₃ separately



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