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DEGRADATION OF BENZOTHIOPHENE BY ULTRASONIC IRRADIATION : INTERMEDIATES AND PARAMETERS

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Abstract : Benzothiophene (BT) is decomposed rapidly following a pseudo-first-order kinetics upon ultrasonic irradiation in aqueous solutions. The rate constant increases with temperature, and pH and decreases with increasing initial benzothiophene concentration. Hydroxybenzothiophenes, dihydroxybenzothiophenes, and benzothiophene-dione were identified as intermediates. The evolution of carbon dioxide and sulfite was also observed during sonochemical reaction. The intermediate study suggests that the degradation of benzothiophene via OH radical addition is one of the most important degradation mechanism.

Key Words : advanced oxidation process, benzothiophene, hydroxyl radical, polycyclic aromatic sulfur hydrocarbons (PASHs), sonochemical, ultrasound

INTRODUCTION

Polycyclic aromatic sulfur hydrocarbons (PASHs) are the group of toxic and/or mutagenic compounds[1-3] which are abundant in petroleum and coal tars. Therefore, these compounds can be present in the wastewaters from petroleum and coal liquefaction industries.[4] PASHs can bioconcentrate at magnitude much significant than sulfur-free polycyclic aromatic compounds.[5,6] PASHs have been shown to readily accumulate in sediments,[7] plants and animal tissues.[8] The conventional activated sludge process can not effectively degrade these toxic compounds.[9] PASHs are among the most refractory residues at contaminated sites.[7,10,11] The low biodegradability of PASHs suggests that physical-chemical methods are needed for effective degradation of PASHs in wastewaters.

In recent years, there has been an increasing interest in the use of ultrasound to treat organic contaminants in aqueous solutions.[12-27] Ultrasonic decomposition of organic pollutants is brought by the formation and collapse of high-energy cavitation bubbles. Upon collapse, the solvent vapor is subjected to the enormous increases in both temperature (up to 5,000 °K) and pressure (up to several thousand atm).[28] Under such extreme conditions the solvent molecules undergo homolytic bond breakage to generate radicals. When water is sonicated, $H^{\cdot}$ and $^{\cdot}OH$ radicals are

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produced,[29] the latter being a strong oxidizing agent (E_H^0= 2.33 V) can react with many organic pollutants. Additionally, organic compounds in the vicinity of a collapsing bubble may undergo pyrolytic decomposition due to the high local temperature and pressure.[30]

Much research has been conducted to study the ultrasonic destruction of aromatic compounds in water. Petrier et al.[31] proposed that the ultrasonic degradation of 4-chlorophenol would be characterized as a stepwise reaction involving a number of intermediates including hydroquinone and 4-chlorocatecol. First reaction step leads to the formation of hydroxyl radicals in the cavitation bubbles. Hydroxyl radicals are then dispersed and react with 4-chlorophenol in the liquid layer surrounding the cavity. Kotronarou et al.[15] reported that p-nitrophenol was degraded primarily by denitration yielding NO_2^-, NO_3^-, benzoquinone, 4-nitrocatechol, formate, and oxalate. These reaction products are caused by a mechanism involving high-temperature reactions in the interfacial region of cavitation bubbles due to the thermal instability of p-nitrophenol. Nagata et al.[32] showed that 95% of hydroxybenzoic acids were decomposed within an hour and proposed that the decomposition of hydroxybenzoic acids occurred mainly via reaction with ·OH radicals.

Despite the large body of work conducted, little information is available regarding the mechanisms through which sulfur-containing aromatic compounds degrade during sonication. Specifically, the reaction pathway and the intermediates and products involved remain unknown. In addition, the effect of medium conditions and reaction parameters on the ultrasonic degradation rate of PASHs have not been investigated.

The objectives of this study are to evaluate an ultrasonic process for the treatment of PASHs in water and to elucidate the reaction pathway and mechanism of ultrasonic degradation of PASHs exemplified by benzothiophene (BT). Benzothiophene was selected for the study because it has the basic structural unit of most PASHs and is relatively soluble in water. Several reaction intermediates were identified.

Materials and Methods

Benzothiophene (99%) and 4-oxo-4,5,6,7-tetrahydrobenzothiophene (97%) were obtained from the Aldrich Chemical Company (Milwaukee, WI). Benzothiophene-sulfur dioxide (98%) was obtained from Lancaster Chemical Company (Lancaster, PA). Stock solution of BT was prepared by dissolving an excess amount of benzothiophene in deionized water in a stirred flask sealed with Teflon-lined rubber stopper. At different elapsed times, the solution was filtered (0.45 μm, Cole-Parmer, Vernon Hills, IL), extracted with hexane, and analyzed with a gas chromatograph (Model 5890 GC Series II, Hewlett-Packard, San Fernando, CA) equipped with a mass selective detector (5972 MSD, Hewlett-Packard). The concentration of the solution was determined based on external BT standards in hexane. The aqueous concentration of BT reached an equilibrium value of 0.21 mM in about 2 days.

Experiments were conducted using a 40 mL glass reactor (Ace Glass, Vineland, NJ) and an ultrasonic generator (20 kHz, ultrasonic homogenizer 4710, Cole-Parmer, Vernon Hills, IL) equipped with a titanium probe transducer (Model CV 17, Cole Parmer). The reactor was filled with 40 mL of BT solution, leaving no headspace, and sealed with a Teflon-lined rubber stopper. The reactor was immersed in a water bath (Frigomix 1495 Water Circulation and Temperature Control System, Braun Biotech International, Goettingen, Germany) to maintain a constant temperature. An automatic pH controller (model pH-22, New Brunswick Scientific Co., Edison, NJ) with 0.1 N NaOH and 0.1 N HClO4 was used to keep the pH at a constant value. Experiments were run twice in the following conditions: (1) temperature (20, 30, 40, 50, and 65°C), (2) pH (3, 5, 7, and 9) and (3) initial concentration of benzothiophene (0.01, 0.04, 0.1, and 0.21 mM)

At different elapsed times, 0.5 mL aqueous samples were withdrawn and extracted with 1mL hexane. Two μL of the extract was analyzed by GC/MS, while the remaining extract was analyzed using an UV-visible spectrophotometer

(HP 8452A Diode-array, Hewlett-Packard).

For GC/MS identification of intermediates, a 40-mL aqueous sample was transferred to a glass tube and gently evaporated to dryness using a stream of nitrogen. The residue was re-dissolved in 0.5 mL hexane. GC/MS analysis was performed using a 30 m HP-5MS capillary column. The injection port temperature was 250°C. The column temperature was held constant at 50°C for 2 min and then increased to 250°C at a ramp rate of 8°C/min. The GC/MS interface line was maintained at 300°C. The range of ion mass scanned was from m/z 50 to 550. The mass spectra were produced by electron impact (70 eV).

Concentration of sulfite and sulfate ions were measured using an ion chromatograph (BioLC, Dionex, Marlton, NJ) equipped with a Dionex pulsed electrochemical detector and a Dionex AS-11 metal-free anion column. The eluent was a mixture of 87% deionized water, 10% 0.2 N NaOH, and 3% acetonitrile. The flowrate was 1 mL/min and the volume of the injection loop was 50 μL. Concentration of sulfide ion was measured by adding sulfide reagents (Hach Company, Loveland, CO) into a 2 mL aliquot, diluting to 25 mL with distilled water and analyzed by a visible spectrophotometer (Hach DR/2000, Loveland, CO) at a wavelength of 665 nm. Concentration of carbon dioxide was measured by the flow injection analysis method.[33]

RESULTS AND DISCUSSION

Decomposition of Benzothiophene

The concentration of benzothiophene decreases exponentially with reaction time, where little decomposition was observed in the controls. The degradation rate can be expressed by the following equation:

$$-\frac{d[C]}{dt} = k[C] \quad (1)$$

where C is the concentration of BT at time t, k is the pseudo-first- order rate constant and t is the sonication time.

Figure 1(a) shows a decrease in decomposition efficiency over 65°C. This is because the

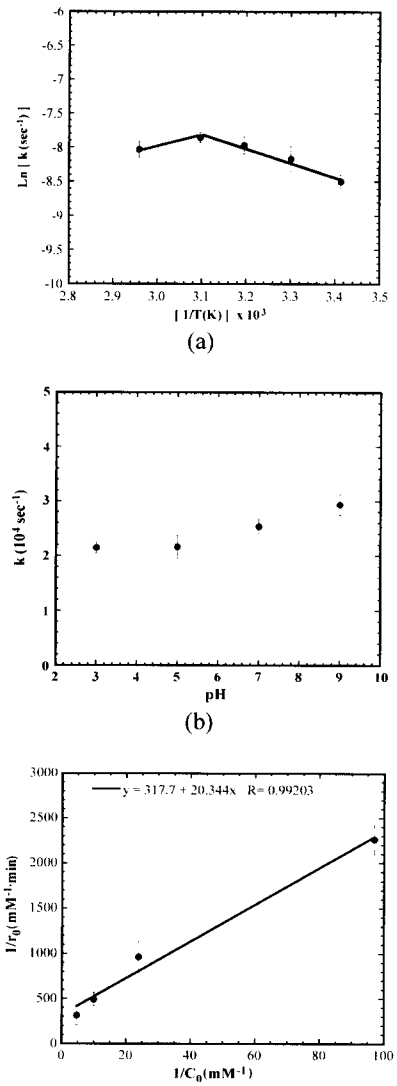

Figure 1. Factors controlling the rate of BT decomposition. (a) temperature (20, 30, 40, 50, and 65°C) (b) pH (3, 5, 7, and 9) (c) the reciprocals of the initial rates vs. the reciprocals of the initial benzothiophene concentrations (0.01, 0.04, 0.1, and 0.21 mM). Experimental conditions: total volume = 40 mL, ionic strength = 0.05 M $NaClO_4$, energy intensity = 300 watts/cm^2, temperature = 25 °C (except b), pH = 5 (except c), initial concentration = 0.12 mM (except d).

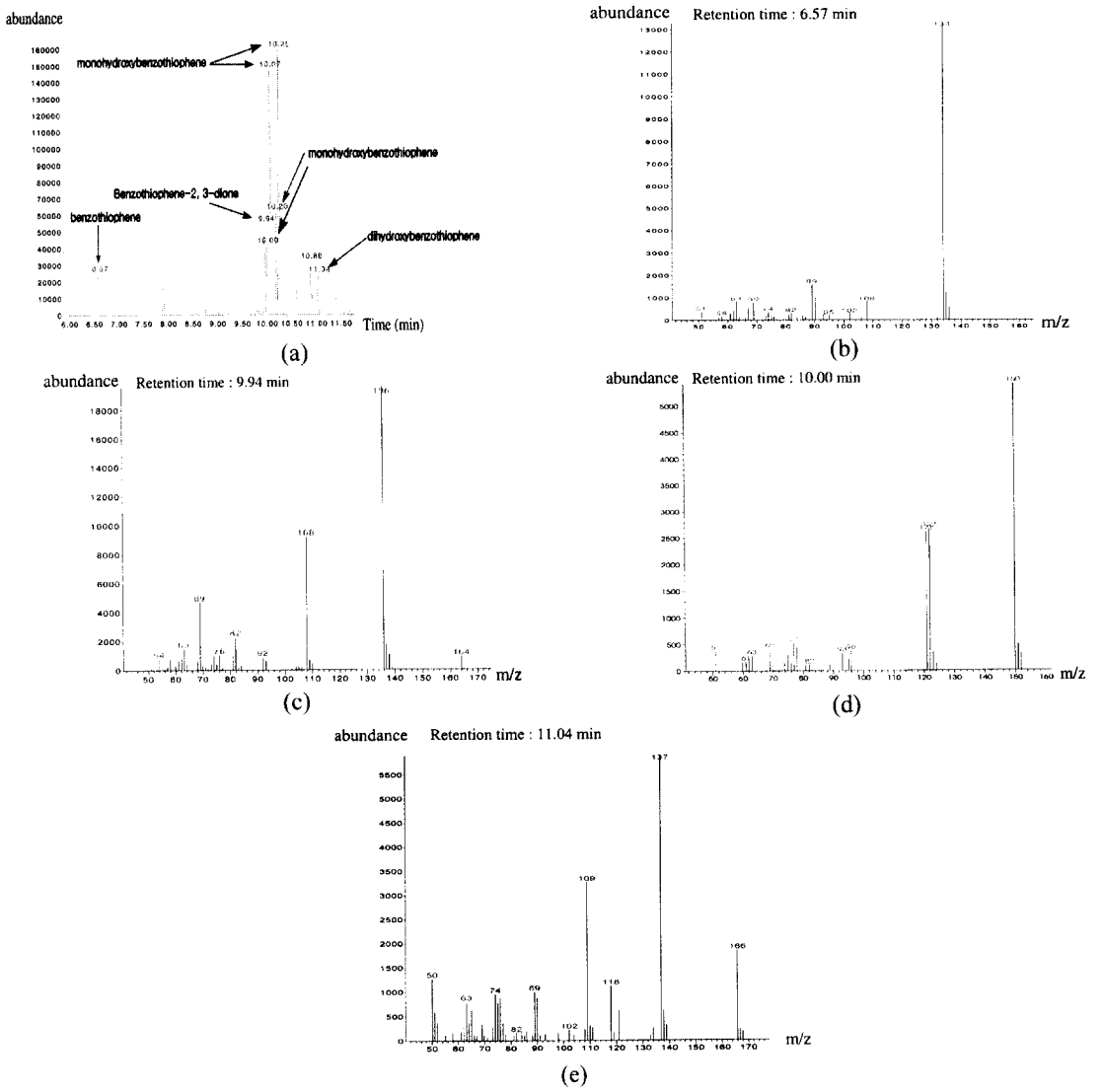

Figure 2. Identification of sonochemical reaction intermediates.
(a) total ion chromatogram of BT (b) mass spectrum of BT (c) mass spectrum of Benzothiophene-2,3-dione (d) mass spectrum of hydroxylbenzothiophene (e) mass spectrum of 2,3-dihydroxylbenzothiophene. Experimental conditions: reaction time = 120 min, energy intensity = 300 watts/cm^2, pH = 5, initial concentration = 0.2 mM, temperature = 25°C, ionic strength = 0.05 M $NaClO_4$.

rarefaction cycle causes boiling of the solution (as a result of the reduced pressure generated) and any cavitation bubbles formed would fill almost instantaneously with water vapor. Collapse of these vapor-filled bubbles during the compression cycle would be cushioned thereby reducing the extremes of temperature and pressure generated.[34] Over a rather narrow temperature range between 20 and 50°C, an increasing reaction rate was observed as the solution temperature increased. Because this reaction is mass-transfer limited and the cushion effect did not occur over the narrow temperature range studied. The effect of temperature on the ultrasonic decomposition of organic compounds has been reported. Gondrexon et al.[12] studied

the decomposition of the chlorophenol in the range of 25 to 50°C and found that the higher temperature the larger was the reaction rate. It seems that the collision frequency of chlorophenol molecules in solution increased as the solution temperature increased from 25 to 50°C. Koszalka[35] reported high removal efficiency at 85% in the temperature range of 25 to 35°C for tetrachloromethane and an efficiency of 48% between 85 and 95°C. Much lower decomposition efficiency of tetrachloromethane between 85 and 95°C appears to be caused by cushion effect in high solution temperature. In the temperature range of 20 to 50°C, results indicated that the Arrhenius equation has the following expression:

$$\ln k = \ln A \frac{-E_a / R}{T} = -1.57 + \left(\frac{-2020}{T}\right) \quad \left(r^2 = 0.96\right) \quad (2)$$

where k is the rate constant (sec^{-1}), T is the absolute temperature (K), A is the frequency factor (sec^{-1}), Ea is the activation energy (kJ/mole), and R is the gas constant (kJ/mole·K). Arrhenius equation has been used to describe the effect of temperature on reaction rates in heterogeneous systems with good degree of satisfaction.[36~42] Generally, a heterogeneous reaction such as the one studied here, is mass-transfer limited if the activation energy is low (< 42 kJ/mole) and reaction-controlled if the activation energy is high (> 42 kJ/mole).[43]

The low apparent activation energy (Ea) of 16.8 kJ/mole suggests that the ultrasonic decomposition of benzothiophene is controlled by mass transfer process, e.g., diffusion.[43,44] Most likely, the apparent rate reflects the rate at which benzothiophene molecules diffuse from the bulk solution to the reaction zone; i.e., the solution-bubble interfacial regions where temperature and OH radical concentrations are high. In a related study, ultrasonic degradation of chlorophenol was also found to be controlled by diffusion.[13]

Figure 1(b) shows that the reaction rate is approximately constant in the pH range of 3 to 6 and increases as pH becomes greater than 6. Kotronarou et al.[15] found that the reaction rate of p-nitrophenol decreased with increasing initial pH from 3 to 10, whereas Wu et al.[45] showed that the reaction rate of carbon tetrachloride increased with increasing initial pH from 3 to 9. Kim et al.[14] reported that the sonochemcial oxidation rate of dibenzothiophene slightly increased with increasing pH. The conflicting observations may be explained by the solubility of the parent compounds and their intermediates at different pH. Assuming most of the reaction takes place at the bubble-liquid interface,[46] compounds that become ionized (and hence more soluble) at higher pH (e.g., nitrophenol) would partition less to the interface and hence exhibit lower reaction rates at higher pH. On the other hand, intermediates that dissociate at higher pH may become ionized and become partitioned into the aqueous phase at higher pH, providing more access of the non-ionized parent compound (e.g. carbon tetrachloride and benzothiophene) to the interface.

Figure 1(c) shows the relationship between the initial reaction rate (r_0) and the initial benzothiophene concentration (C_0). When the reciprocals of the initial rates are plotted against the reciprocals of the initial benzothiophene concentrations using the Langmuir- Hinshelwood equation (equation 3), a linear relationship is obtained with r^2 = 0.99:

$$\frac{1}{r_0} = \frac{1}{k} + \frac{1}{kKC_0} \quad \left(r^2 = 0.99\right) \quad (3)$$

where k is the rate constant (mM/min) and K is the adsorption coefficient (mM^{-1}). From Figure 1(c), the k and K values are 3.15×10^{-3} mM-min^{-1} and 15.6 mM, respectively. The good fit with Langmuir-Hinshelwood relationship indicates that the decomposition of benzothiophene is likely to occurred at the limited interfacial area of cavitation bubbles. A proportional relationship between the reciprocals of initial rates and the initial benzothiophene concentrations were also observed from a reaction of an organic pollutant on limited surface area of TiO_2 thin film.[47]

Identification of Benzothiophene Intermediates

The chromatogram of BT and intermediates is shown in supporting information, Figure 2(a). The mass spectra of BT and its intermediates are shown in Figure 2(b) to (e). The mass spectra were compared with the computer database of the National Institute of Science and Technology (NIST) mass spectral library and the published mass spectra of BT intermediates.[48,49]

The mass spectra of peaks at 6.57, 10.00, and 11.04 min have a near 100 : 4.4 ratio based on the isotope ion peaks at m/z values of M^+ and $(M+2)^+$. This ratio indicates the presence of a sulfur atom (Figure 2(b) to (e)).

The m/z value of the molecular ion of the peak at 9.94 min (Figure 2(c)) differs from that of peak at 11.04 min (Figure 2(e)) by 2. This difference indicates that the reaction intermediate at 9.94 min has two less hydrogen atoms than the intermediate at 11.04 min has.

The peak at 9.94 min has major ions at m/z (percentage of intensity, proposed composition of ions) 164 (5, $[M]^+$), 136 (100, $[M-CO]^+$), and 108 (45, $[M-CO-CO]^+$). This mass spectrum is identical to that obtained from an authentic standard, benzothiophene-2,3-dione.[48]

The m/z value of the molecular ion of the peak at 11.04 min (Figure 2(e)) differs from that of peak of benzothiophene (Figure 2(b)) by 32. This difference indicates that the reaction intermediate at 11.04 min has two more oxygen atoms than benzothiophene.

The peak at 11.04 min has major ions at m/z 166 (36, $[M]^+$), 137 (100, $[M-COH]^+$), 109 (59, $[M-COH-CO]^+$), and 76 (15, $[M-COH-COH-S]^+$). Its spectrum is similar to that of dihydroxylbenzothiophene.

The m/z values of the molecular ions of the peaks at 10.00, 10.07, 10.20, and 10.25 min (Figure 2(d)) differ from that of benzothiophene (Figure 2(b)) by 16. These differences indicate that the reaction intermediates at 10.00, 10.07, 10.20, and 10.25 min have one more oxygen atom than benzothiophene.

The peaks at 10.00 min has major ions at m/z 150 (94, $[M]^+$), 122 (74, $[M-CO]^+$), and 121 (100, $[M-CHO]^+$). The peaks at 10.07, 10.20, and 10.25 min have mass spectra similar to that obtained from hydroxybenzothiophene as shown in Figure 2(d).[48] The mass spectra correspond potentially to the isomers 2-, 3-, 4-, 5-, 6-, or 7-hydroxybenzothiophene. Among them, the peaks at 10.07 and 10.25 min appear to be 2-hydroxy-benzothiophene and 3-hydroxybenzothiophene. It has been reported that the major reaction products retaining the intact benzene ring such as sulfobenzoic acid were obtained from all radical reactions for benzothiophene and methyl-benzothiophenes.[50,51] The thiophene ring with smaller resonance energy (29 kcal/mole) appears to be more reactive than the benzene ring with the resonance energy (36 kcal/mole).[52,53]

Reaction Mechanism

Based on the hydroxylated intermediates identified above, it is possible to propose a reaction pathway for the ultrasonic decomposition of benzothiophene in aqueous solution. The reaction begins with the generation of OH radicals mainly from sonolytic decomposition of water. The radicals can either directly react with the organic species at the bubble-water interface or diffuse into the bulk solution and react with the organic compounds in the solution. In both cases, reactions lead to formation of hydroxylated products such as hydroxybenzothiophene and dihydroxy-benzothiophene. Eventually, these intermediates will be mineralized to end products such as carbon dioxide and inorganic sulfur species.

The first step of the reaction is the OH radical addition, which yields the 3-hydroxy-2,3-dihydrobenzothiophene. The thiophene ring moiety is more susceptible to the hydroxyl radicals than the benzene moiety[50,51] because thiophene ring with a resonance energy of 29 kcal/mole appears to be more reactive than benzene ring with a resonance energy of 36 kcal/mole.[52,53] After the addition of the first OH radical, 3-hydroxy-2,3-dihydrobenzothiophene can be

transformed to 3-hydroxybenzothiophene by the elimination of a proton to recover the aromatic resonance stability at the thiophene ring moiety. The electron-releasing effect of OH through resonance increases the susceptibility of thiophene ring moiety to the electrophilic attack of OH radical.[51] Then further reaction with OH radical generates 2,3-dihydroxybenzothiophene as a main intermediate product. The 2,3-dihydroxybenzothiophene undergoes further radical reaction to yield the benzothiophene-2,3-dione. Andersson and Bobinger[50,51] reported the formation of sulfobenzoic acid and quinone during photochemical degradation of benzothiophene. Subsequent cleavage of the quinone would result in the formation of organic acids, as has also been observed in Fentons reaction.[54] Carbon dioxide and sulfite were detected as reaction products.

CONCLUSION

Benzothiophene (BT) is decomposed rapidly following a pseudo-first-order kinetics upon ultrasonic irradiation in aqueous solutions. The rate constant increases with temperature, and pH and decreases with increasing initial benzothiophene concentration. Hydroxybenzothiophenes, dihydroxy-benzothiophenes, and benzothiophene-dione were identified as intermediates. The intermediate study suggests that major portion of the benzothiophene decomposition occurs via OH radical addition. The first step of the reaction is the OH radical addition, which yields the 3-hydroxy-2,3-dihydrobenzothiophene. After the addition of the first OH radical, 3-hydroxy-2,3-dihydrobenzothiophene can be transformed to 3-hydroxybenzothiophene. Then further reaction with OH radical generates 2,3-dihydroxybenzothiophene as an intermediate product. The 2,3-dihydroxybenzothiophene undergoes further radical reaction to yield the benzothiophene-2,3-dione. Subsequent cleavage of the benzothiophene-2,3-dione would result in the formation of quinone, sulfonic acid, and organic acids. Carbon dioxide and sulfite were detected as reaction products.

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