

Reaction Pathways and Kinetic Modeling for Sonochemical Decomposition of Benzothiophene

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Abstract—Benzothiophene (BT) decomposed rapidly following pseudo-first-order kinetics by ultrasonic irradiation in aqueous solution. The rate constant increased with increasing ultrasonic energy intensity. Hydroxybenzothiophenes, dihydroxy-benzothiophenes, and benzothiophene-dione were identified as reaction intermediates. It was proposed that benzothiophene was oxidized by OH radical to sequentially form hydroxybenzothiophenes, dihydroxybenzothiophenes, and benzothiophene-dione. Evolution of carbon dioxide and sulfite was also observed during ultrasonic reaction. Kinetic analysis suggested that approximately 77% of the benzothiophene decomposition occurred via OH radical addition. Pathways and a kinetic model for ultrasonic decomposition of benzothiophene in aqueous solution were proposed.

Key words: Sonochemical Decomposition, Pathway, Benzothiophene, Kinetic Modeling, Hydroxy Radical Reaction

INTRODUCTION

Polycyclic aromatic sulfur hydrocarbons (PASHs) are the group of toxic and/or mutagenic compounds [Eastmond et al., 1974; Karcher et al., 1981; McFall et al., 1984] that are abundant in petroleum and coal tars. These compounds are also present in the wastewater from the petroleum and coal liquefaction industries [Smith et al., 1978]. PASHs were found to bioconcentrate more significantly than sulfur-free polycyclic aromatic compounds [Dillon et al., 1978; Vassilaros et al., 1982] and have been shown to readily accumulate in sediments [Boehm et al., 1981], plants and animal tissues [Ogata and Fujisawa, 1985]. The conventional activated sludge process cannot effectively degrade these toxic compounds [Petrasek et al., 1983]. PASHs are among the most refractory residuals at contaminated sites [Boehm et al., 1981; Berthou et al., 1981; Teal et al., 1978]. The low biodegradability of PASHs suggests that physical-chemical methods may be more effective for degrading PASHs in wastewaters.

Moreover, the combustion of PASHs in fossil fuels produces sulfur oxides, which results in serious environmental problems. Therefore, many researches have been conducted to remove the sulfur from PASHs in fossil fuels [Kim and Choi, 1988; Kim and Kim, 1996; Park et al., 1998; Kim et al., 2002; Luo et al., 2003].

In recent years, there has been an increasing interest in the use of ultrasound to treat organic contaminants in aqueous solutions [Gondrexon et al., 1978; Huang and Hao, 1994; Kotronatou et al., 1991; Petrier et al., 1992; Hoffmann et al., 1996; Hua and Hoffmann, 1996; Hua and Hoffmann, 1997; Kang and Hoffmann, 1998; Kang et al., 1999; Weavers et al., 1998, 2000; Colussi et al., 1999; Destailats et al., 2000; Zhang and Hua, 2000; Beckett and Hua, 2000]. Ultrasonic decomposition of organic pollutants was brought on by the formation and collapse of high-energy cavitation bubbles. Upon collapse, the solvent vapor is subjected to enormous increases

in both temperature (up to 5,000 °K) and pressure (up to several thousand atm) [Mason and Lorimer, 1988]. Under such extreme conditions the solvent molecules undergo homolytic bond breakage to generate radicals. When water is sonicated, H[•] and OH[•] radicals are produced [Riesz et al., 1990], the latter being a strong oxidizing agent ($E_h^0=2.33$ V) which can react with organic pollutants. Alternatively, organic compounds in the vicinity of a collapsing bubble may undergo pyrolytic decomposition due to the high local temperature and pressure [Suslick, 1986].

Much research has been conducted to study the ultrasonic destruction of aromatic compounds in water. Petrier et al. [1998] proposed that the ultrasonic degradation of 4-chlorophenol would be characterized as a stepwise reaction involving a number of intermediates including hydroquinone and 4-chlorocatechol. The 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. [1991] reported that p-nitrophenol was degraded primarily by denitration yielding NO₂⁻, NO₃⁻, 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. [1996] 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 has not been investigated.

The objectives of this study were 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

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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, a pathway and a kinetic model were proposed, and the relative importance of the two ultrasonic degradation mechanisms was evaluated.

EXPERIMENTAL

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 with 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 with circulation (Frigomix 1495 Water Circulation and Temperature Control System, Braun Biotech International, Goettingen, Germany) to maintain a pre-selected 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.

At different elapsed times, 0.5 mL aqueous samples were withdrawn and extracted with 1 mL hexane. Two μL of the extract was analyzed by GC/MS, while the remaining extract was analyzed with a UV-visible spectrophotometer (HP 8452A Diode-array, Hewlett-Packard).

For GC/MS identification of intermediates, 40 mL aqueous sample was transferred to a glass tube and gently evaporated to dryness by using a gentle 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 maintained 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). The concentrations of the hydroxylated intermediates such as hydroxybenzothiophene, dihydroxybenzothiophene and benzothiophene-dione were determined based on external calibration curves constructed by using standard solutions of 4-oxo-4,5,6,7-tetrahydrobenzothiophene and benzothiophene-sulfur dioxide, respectively. This quantification is based on the assumption that the intermediates and their commercially available structural analogues have similar mass spectrometric response factors.

Concentration of sulfite and sulfate ions was measured by 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 analyzing 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 [Jardim et al., 1990].

RESULTS AND DISCUSSION

1. Decomposition of Benzothiophene

The concentration of benzothiophene decreases exponentially with reaction time, where little decomposition was observed in the controls (Fig. 1). 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.

It has been shown that increasing energy intensity increases the decomposition rate of organic compounds [Huang and Hao, 1994]. We also observed that the apparent rate constant of benzothiophene decomposition increased with increasing energy intensity. The pseudo-first-order rate constant, k , was proportional to the energy intensity within the range studied (Fig. 2). Therefore, the apparent BT degradation rate can be expressed as:

$$\frac{-d[BT]}{dt} = -k[BT] = k'I[BT] \quad (2)$$

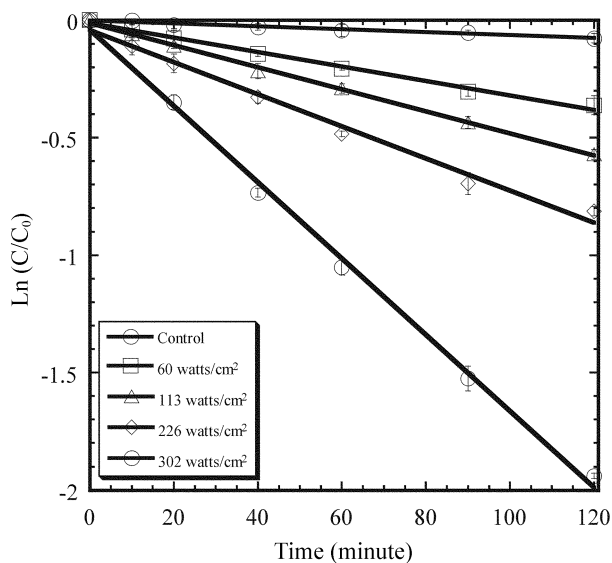


Fig. 1. Effect of ultrasonic energy intensity on ultrasonic decomposition of benzothiophene. Experimental conditions: total volume=40 mL, C_0 =0.12 mM, pH=5, temperature=25 °C, ionic strength=0.05 M NaClO₄.

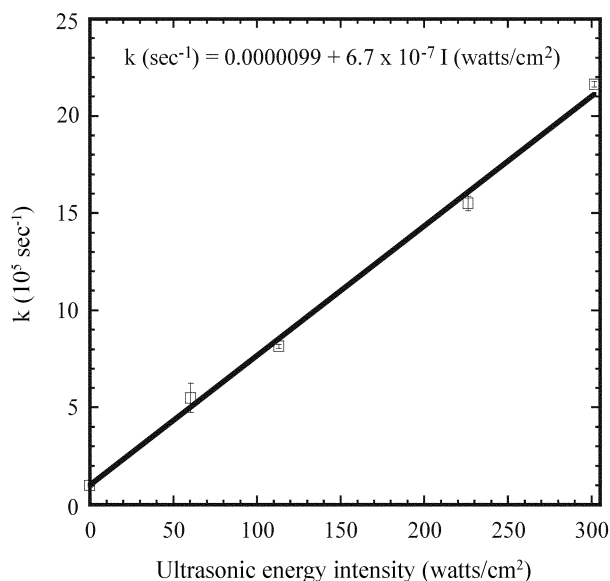


Fig. 2. Relationship between energy intensity and the rate of BT decomposition. Experimental conditions: total volume=40 mL, ionic strength=0.05 M NaClO₄, temperature=25 °C, pH=5, initial concentration=0.12 mM.

where I is the ultrasonic energy intensity and k' has a value of 6.7×10^{-7} (watts/cm²-sec).

2. Reaction Intermediates

The chromatogram of BT and intermediates is shown in Fig. 3a. The mass spectra of BT and its intermediates are shown in Fig. 3b to 3e. 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 [Fedorak and Grbic-Galic, 1991; Eaton and Nitterauer, 1994].

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 (Fig. 3b-e).

The m/z value of the molecular ion of the peak at 9.94 min (Fig. 3c) differs from that of peak at 11.04 min (Fig. 3e) 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 [Fedorak and Grbic-Galic, 1991].

The m/z value of the molecular ion of the peak at 11.04 min (Fig. 3e) differs from that of peak of benzothiophene (Fig. 3b) 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 (Fig. 3d) differ from that of benzothiophene

(Fig. 3b) by 16. This difference indicates 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 have 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 Fig. 3d [Eisenhauer, 1968]. 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-hydroxy-benzothiophene. 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 methylbenzothiophenes [Andersson and Bobinger, 1992; Bobinger and Andersson, 1998]. The thiophene ring with smaller resonance energy (29 kcal/mole) appears to be more reactive than the benzene ring with resonance energy (36 kcal/mole) [Solomons, 1988; Fringuel et al., 1974].

3. Reaction Pathways

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 (Fig. 4). Eventually, these intermediates will be mineralized to end products such as carbon dioxide and inorganic sulfur species. Fig. 4 shows one of the possible reaction pathways involving OH radical attack. The compounds in the boxes are those that have been identified.

The first step of the reaction is the OH radical addition, which yields the 3-hydroxy-2,3-dihydrobenzothiophene (step 1). The thiophene ring moiety is more susceptible to the hydroxyl radicals than the benzene moiety [Andersson and Bobinger, 1992; Bobinger and Andersson, 1998] because the thiophene ring with a resonance energy of 29 kcal/mole appears to be more reactive than the benzene ring with a resonance energy of 36 kcal/mole [Solomons, 1988; Fringuel et al., 1974]. After the addition of the first OH radical, 3-hydroxy-2,3-dihydrobenzothiophene can be changed to 3-hydroxybenzothiophene by the elimination of a proton to recover the aromatic resonance stability at the thiophene ring moiety (step 2). The electron-releasing effect of OH through resonance increases the susceptibility of thiophene ring moiety to the electrophilic attack of OH radical [Solomons, 1988]. Then further reaction with OH radical generates 2,3-dihydroxybenzothiophene as a main intermediate product (step 3). The 2,3-dihydroxybenzothiophene undergoes further radical reaction, then generates the benzothiophene-2,3-dione (step 4). It was observed that further decomposition generated sulfobenzoic acid and quinone during photochemical degradation of benzothiophene [Andersson and Bobinger, 1992; Bobinger and Andersson, 1998]. Subsequent cleavage of the quinone would result in the formation of organic acids, as has also been observed in Fenton's reaction [Eisenhauer, 1968]. Carbon dioxide and sulfite were detected as reaction products.

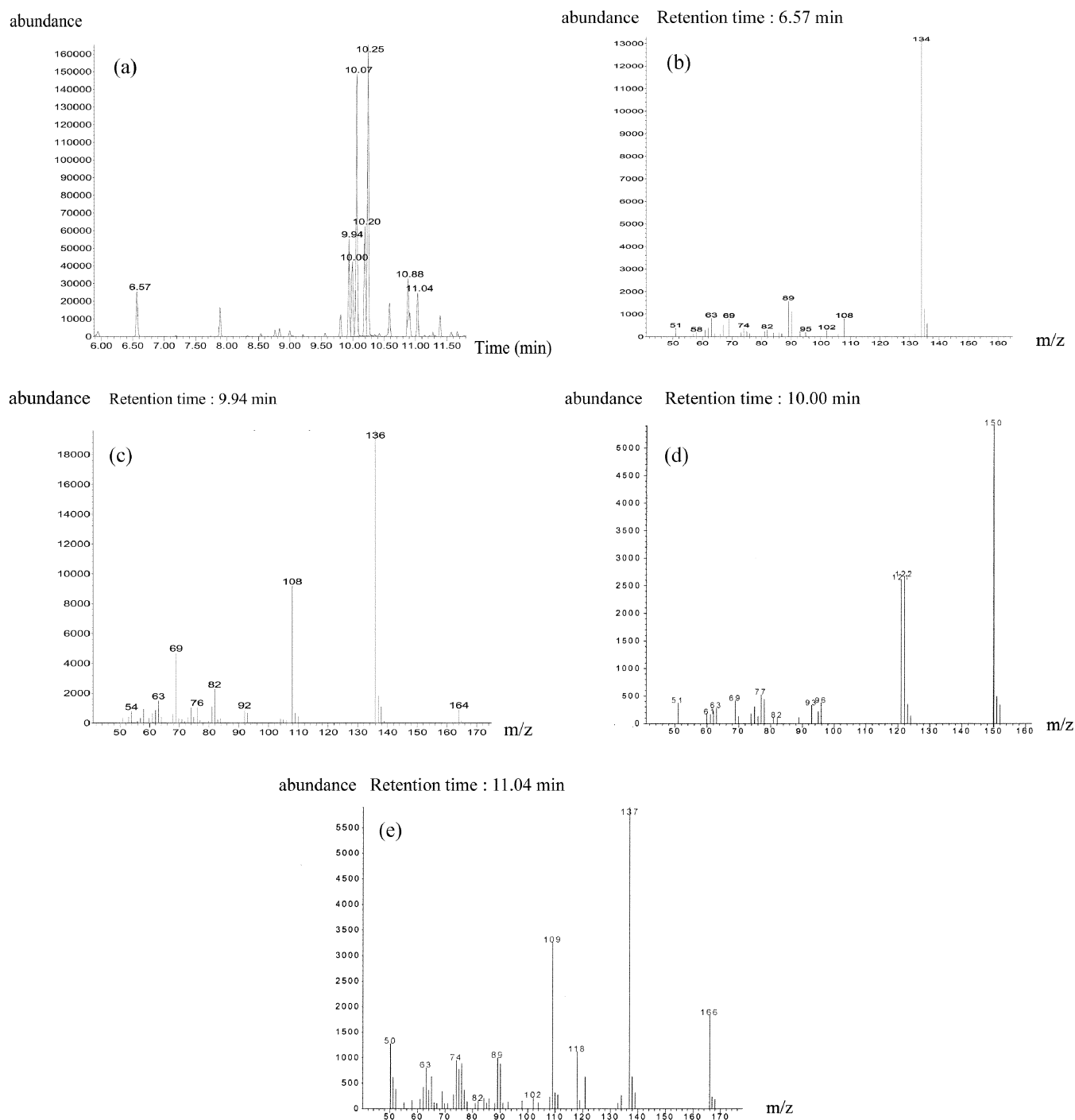


Fig. 3. Identification of ultrasonic reaction intermediates. (a) total ion chromatogram of BT (b) mass spectrum of BT (c) mass spectrum of Benzothiophene-2,3-dione (d) mass spectrum of hydroxybenzothiophene (e) mass spectrum of 2,3-dihydroxybenzothiophene. Experimental conditions: reaction time=120 min, energy intensity=300 watts/cm², pH=5, initial concentration=0.2 mM, temperature=25 °C, ionic strength=0.05 M NaCl.

Another decomposition pathway of benzothiophene is proposed in Fig. 5. The benzothiophene would generate monohydroxybenzothiophenes and subsequently dihydroxybenzothiophenes through the addition of hydroxyl radicals to benzene ring moiety. Then further decomposition of intermediates to end products, carbon dioxide and sulfite is proposed.

4. Kinetic Modeling

Based on the intermediates identified, kinetic analysis can be performed by assuming that benzothiophene is degraded through one of the two main mechanisms, pyrolysis and OH radical reaction. A reaction scheme for kinetic model is shown in Fig. 5. According to Fig. 5, it is seen that OH radical reaction of benzothiophene can be achieved through OH radical addition and ring-cleavage.

All reactions are assumed to be pseudo-first order. For benzothio-

phene degradation, the rate is described as:

$$\frac{dC_{BT}}{dt} = -k_1 C_{BT} - k_2 C_{BT} - k_3 C_{BT} \quad (3)$$

where k_1 and k_2 are pseudo-first-order degradation constants of benzothiophene through OH radical addition and k_3 is pseudo-first-order degradation constant through pyrolysis. Note that the sum of k_1 , k_2 and k_3 is equal to the observed overall benzothiophene decomposition rate constant, k_A .

For 4-, 5-, 6-, and 7-hydroxybenzothiophenes, the rate expression is as follows:

$$\frac{dC_{4567\text{ HXBT}}}{dt} = k_1 C_{BT} - k_4 C_{4567\text{ HXBT}} \quad (4)$$

By the same way, the rate expression for 2-, and 3-hydroxybenzothiophenes is as follows:

$$\frac{dC_{23\text{ HXBT}}}{dt} = k_2 C_{BT} - k_5 C_{23\text{ HXBT}} \quad (5)$$

For 2,3-dihydroxybenzothiophene, the rate expression is:

$$\frac{dC_{23\text{ OH}}}{dt} = k_5 C_{23\text{ HXBT}} - k_6 C_{23\text{ OH}} \quad (6)$$

For benzothiophene-2,3-dione; the rate expression is:

$$\frac{dC_{BT\ 23\ DN}}{dt} = k_6 C_{23\text{ OH}} - k_7 C_{BT\ 23\ DN} \quad (7)$$

Each differential equation can be solved analytically. The following integrated expressions are obtained.

$$C_{BT} = C_{BT,0} \exp(-k_A t) \quad (8)$$

where $k_A = k_1 + k_2 + k_3$ and $C_{BT,0}$ is the initial benzothiophene concentration.

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$$C_{4567\text{ HXBT}} = \frac{k_1 C_{BT,0}}{(k_A - k_4)} [\exp(-k_A t) - \exp(-k_4 t)] \quad (9)$$

$$C_{23\text{ HXBT}} = \frac{k_2 C_{BT,0}}{(k_A - k_5)} [\exp(-k_A t) - \exp(-k_5 t)] \quad (10)$$

$$C_{23\text{ OH}} = C_{BT,0} \left[\frac{k_2 k_5 \exp(-k_A t)}{(k_6 - k_A)(k_5 - k_A)} - \frac{k_2 k_5 \exp(-k_5 t)}{(k_6 - k_5)(k_5 - k_A)} - \frac{k_2 k_5 \exp(-k_6 t)}{(k_6 - k_5)(k_6 - k_A)} \right] \quad (11)$$

$$\begin{aligned} \frac{C_{BT\ 23\ DN}}{C_{BT,0}} = & \frac{k_6 k_5 \exp(-k_2 t)}{(k_5 - k_2)(k_6 - k_2)(k_7 - k_2)} - \frac{k_6 k_5 \exp(-k_5 t)}{(k_5 - k_2)(k_6 - k_5)(k_7 - k_5)} \\ & + \frac{k_5 (k_5 - k_2) \exp(-k_6 t)}{(k_5 - k_2)(k_6 - k_2)(k_6 - k_5)(k_7 - k_6)} \\ & - \frac{k_6 k_5 \exp(-k_7 t)}{(k_5 - k_2)(k_6 - k_2)(k_6 - k_5)(k_7 - k_2)} \\ & + \frac{k_6 k_5 \exp(-k_7 t)}{(k_5 - k_2)(k_6 - k_2)(k_6 - k_5)(k_7 - k_5)} \\ & - \frac{k_5 (k_5 - k_2) \exp(-k_7 t)}{(k_5 - k_2)(k_6 - k_2)(k_6 - k_5)(k_7 - k_6)} \end{aligned} \quad (12)$$

Fig. 7 shows both the measured concentrations of benzothiophene and intermediates and the model calculations for a typical experiment. The measured pseudo-first-order rate constant ($k_A = k_1 + k_2 + k_3$) of benzothiophene was $3.5 \times 10^{-4} \text{ s}^{-1}$. The other rate constants were obtained by using a non-linear curve fitting program in *Matlab*TM (The MathWorks, Inc., Natick, MA), which gave least squares fits using the measured concentrations of the hydroxylated intermediates. The rate constant values were $(0.80 \pm 0.017) \times 10^{-4} \text{ s}^{-1}$, $(1.9 \pm 0.026) \times 10^{-4} \text{ s}^{-1}$, $(0.82 \pm 0.012) \times 10^{-4} \text{ s}^{-1}$, $(1.7 \pm 0.032) \times 10^{-4} \text{ s}^{-1}$, $(2.0 \pm 0.047) \times 10^{-4} \text{ s}^{-1}$, $(1.8 \pm 0.034) \times 10^{-4} \text{ s}^{-1}$ and $(1.6 \pm 0.043) \times 10^{-4} \text{ s}^{-1}$ for k_1 , k_2 , k_3 , k_4 , k_5 , k_6 , and k_7 , respectively.

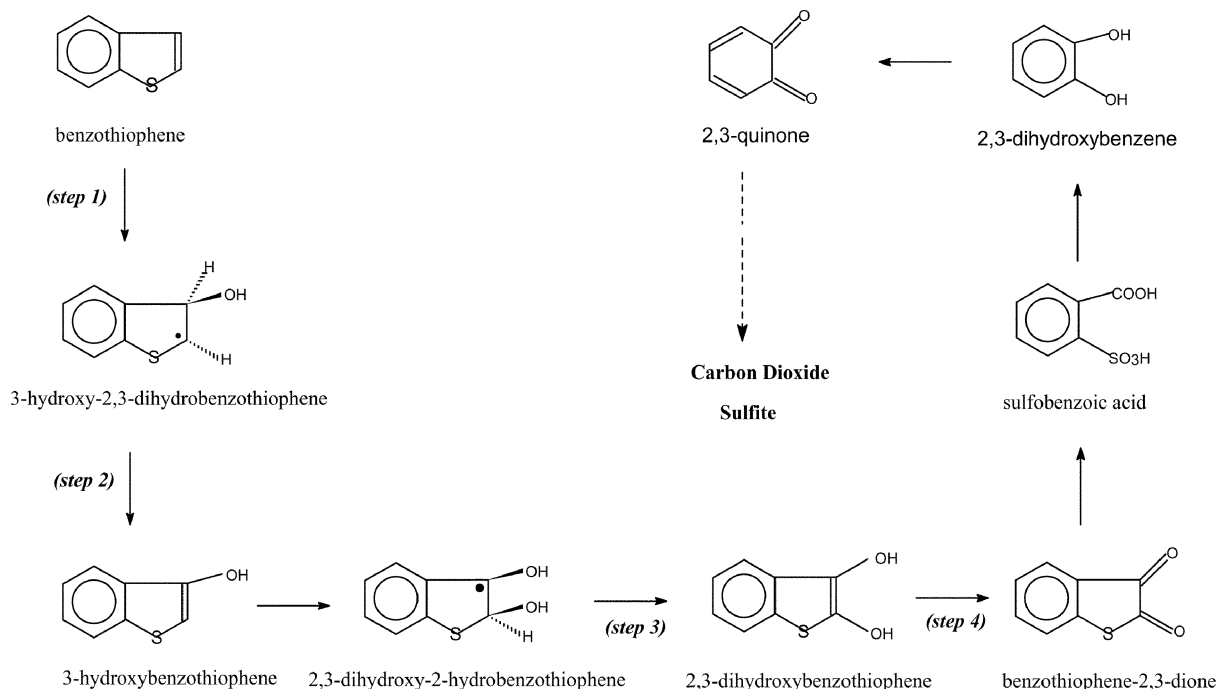


Fig. 4. A proposed reaction pathway of BT decomposition involving OH radicals.

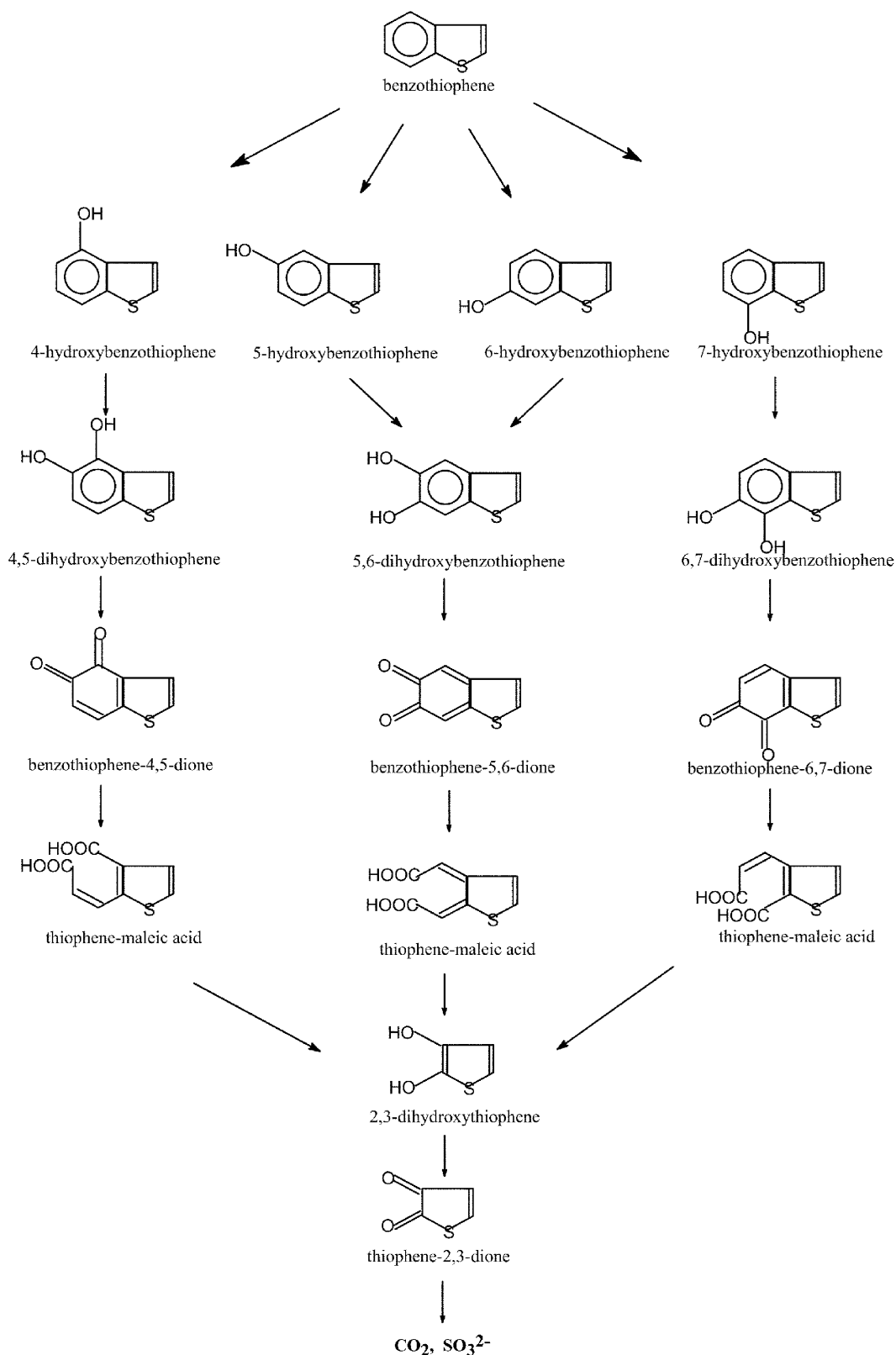


Fig. 5. Proposed reaction pathways of BT decomposition involving OH radicals.

The calculated rate constants, k_A , k_1 , and k_2 , allow us to predict the percent of benzothiophene that reacts to form the sum of 4-, 5-, 6-, and 7-hydroxybenzothiophenes, the sum of 2-, and 3-hydroxybenzothiophenes and pyrolysis products. The percentage is pro-

vided by the ratio $(k_1 + k_2)/k_A$. From this ratio, it is found that approximately 77% of the benzothiophene was transformed via OH radical attack to form monohydroxy-benzothiophenes, whereas the remaining 23% benzothiophene was converted to other unknown

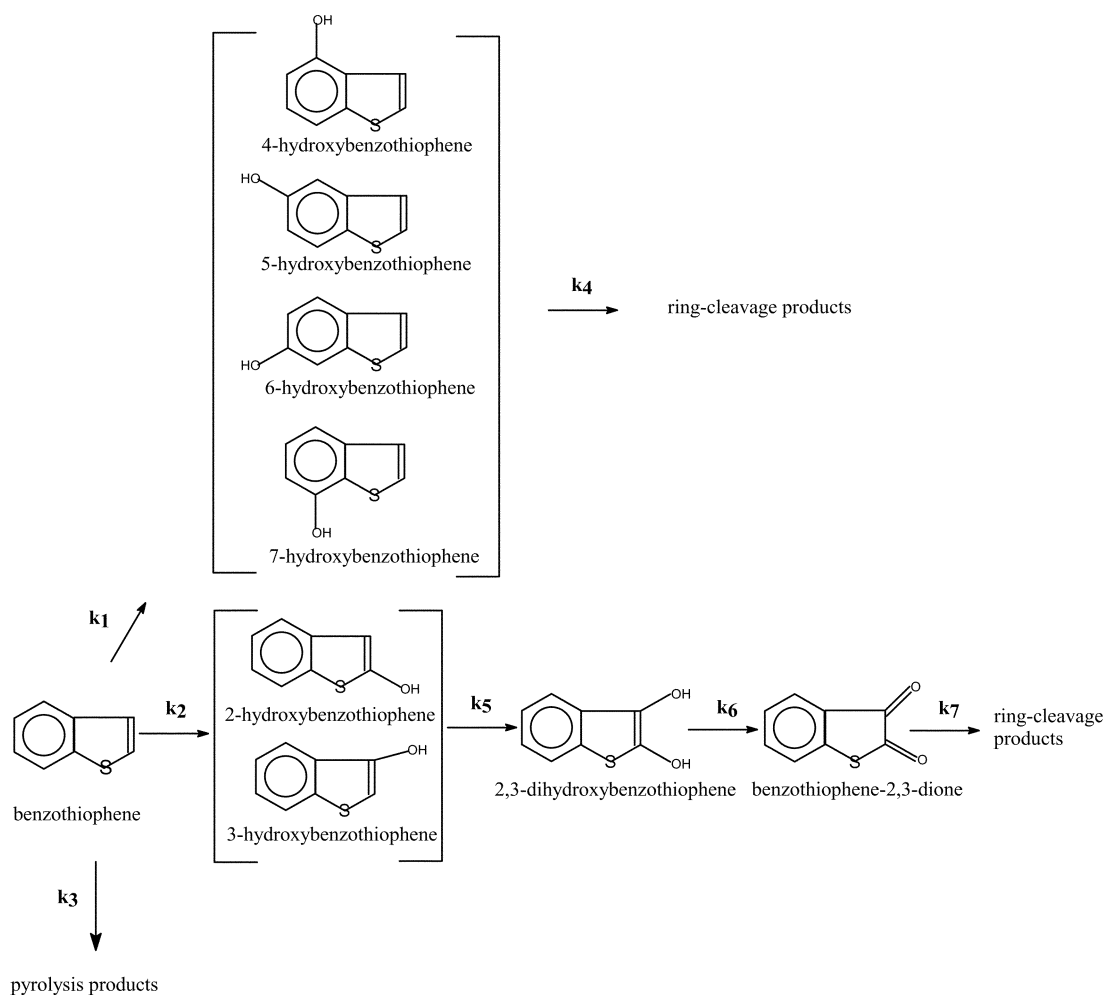


Fig. 6. Simplified reaction pathway of BT decomposition in sonochemical reaction for kinetic modeling.

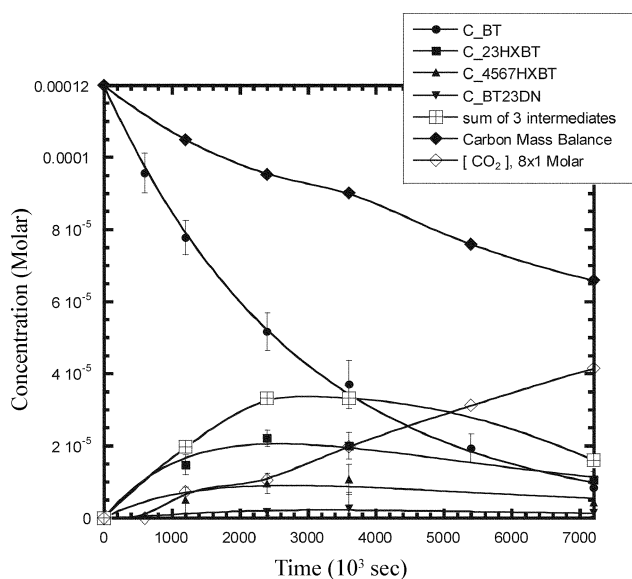


Fig. 7. Concentration changes of benzothiophene and its intermediates. Experimental conditions: ultrasonic energy intensity=300 watts/cm², total volume=40 mL, pH=7, initial concentration=0.12 mM, temperature=25 °C, ionic strength=0.05 M NaClO₄. (The lines are calculated).

reaction products via pyrolysis.

CONCLUSIONS

1. Benzothiophene (BT) is decomposed rapidly following pseudo-first-order kinetics in a first-order manner by ultrasonic irradiation in aqueous solution. The rate constant increased with increasing ultrasonic energy intensity.

2. Hydroxybenzothiophenes, dihydroxy-benzothiophenes, and benzothiophene-dione were identified as reaction intermediates. It is proposed that benzothiophene is oxidized by OH radical to sequentially form hydroxybenzothiophenes, dihydroxybenzothiophenes, and benzothiophene-dione. Also evolution of carbon dioxide and sulfite was observed during sonochemical reaction.

3. Kinetic analysis suggests that approximately 77% of the benzothiophene decomposition occurs via OH radical addition. Pathways and a kinetic model for ultrasonic decomposition of benzothiophene in aqueous solution are proposed.

NOMENCLATURE

E_h° : standard electric potential [V]
 C : concentration [mole/L]

- I : the ultrasonic energy intensity [watts/cm²]
 k : rate constant [watts/cm²-sec]
 C_{BT} : concentration of benzothiophene [mole/L]
 C_{23 HXBT} : total concentration of 2-, and 3-hydroxybenzothiophenes [mole/L]
 C_{23 OH} : concentration of 2,3-dihydroxybenzothiophenes [mole/L]
 C_{BT 23 DN} : concentration of benzothiophene-2,3-dione [mole/L]
 C_{4567 HXBT} : total concentration of 4-, 5-, 6-, and 7-hydroxybenzothiophenes [mole/L]
 k₁-k₇ : pseudo-first-order rate constants [sec⁻¹]
 k_A : the observed overall rate constant [sec⁻¹]

Abbreviation

BT : benzothiophene

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