Sonochemical Reaction Mechanism of a Polycyclic Aromatic Sulfur Hydrocarbon in Aqueous Phase

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Hydroxybenzothiophenes, dihydroxy-benzothiophenes, and benzothiophenedione were identified as intermediates of benzothiophene (BT) exposed to ultrasonic irradiation. It is proposed that benzothiophene is oxidized by OH radical to sequentially form hydroxybenzothiophenes, dihydroxybenzothiophenes, and benzothiophenedione. Benzothiophene is decomposed rapidly following pseudo-first-order kinetics in a first-order manner by ultrasonic irradiation in aqueous solution. The toxicity of sonochemically treated solutions was checked by *E. coli* and a less inhibition in bacterial respiration was observed from the 120-min treated benzothiophene sample than from the untreated benzothiophene sample. Also evolution of carbon dioxide and sulfite was observed during ultrasonic reaction. A pathway for ultrasonic decomposition of benzothiophene in aqueous solution is proposed.

Keywords : Ultrasonic irradiation. Benzothiophene, Advanced oxidation process, Hydroxy radical.

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. These compounds are also present in the wastewaters from petroleum and coal liquefaction industries.[4] PASHs were found to bioconcentrate more significantly than sulfur-free polycyclic aromatic compounds[5,6] and have been shown to readily accumulate in sediments,[7] plants and animal tissues.[8] The conventional activation sludge process can not effectively degrade these toxic compounds.[9] PASHs are among the most refractory residuals at contaminated sites.[10,11] The low biodegradability of PASHs suggests that physical-chemical methods may be more effective for degrading PASHs in wastewaters.

In recent years, there has been an increasing interest in the use of ultrasound to treat organic contaminants in aqueous solutions.[12-15] 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).[16] Under such extreme conditions the solvent molecules undergo homolytic bond breakage to generate radicals. When water is sonicated, H and OH radicals are produced,[17] the latter being a strong oxidizing agent (E°$_h$ = 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 temperature and pressure.[18]

Much research has been conducted to study the ultrasonic destruction of aromatic compounds in water. Petrier *et al.*[19]

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. 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.*[14] 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.*[20] 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 on aromatic compounds. 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, a pathway and a kinetic model were proposed, and the relative importance of the two ultrasonic degradation mechanisms were evaluated. In addition, toxicity reduction due to ultrasonic treatment was also assessed.

Experimental Section

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 HClO$_4$ was used to keep the pH at a constant value.

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 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 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 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 flow rate 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.[21]

The acute toxicity was evaluated with a short-term toxicity test using *Escherichia coli*.[32] *E. coli* population was exposed for 2 days to samples from treated and untreated BT solutions. The acute toxicity test was based on the degree of inhibition of the metabolic activity of *E. coli*, measured as CO_2 production due to stress induced by aqueous BT and its reaction intermediates. The CO_2 determination is carried out by Warburg respirometer (Fisher, Pittsburgh, PA) with paired, identical samples. One sample with NaOH in the center well measures only the oxygen uptake, while the sample without NaOH measures the pressure change due to oxygen uptake and carbon dioxide release. The culture that received no BT served as a control.

Results and Discussion

Identification of Benzothiophene Intermediates. The chromatogram of BT and intermediates is shown in Figure 1a. The mass spectra of BT and its intermediates are shown in Figure 1b to 1e. 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.[22,23]

The mass spectra of peaks at retention times 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 1b-e). The m/z value of the molecular ion of the peak at 9.94 min (Figure 1c) differs from that of peak at 11.04 min (Figure 1e) 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.[22]

The m/z value of the molecular ion of the peak at 11.04 min (Figure 1e) differs from that of peak of benzothiophene (Figure 1b) 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 1d) differ from that of benzothiophene (Figure 1b) by 16. This 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 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
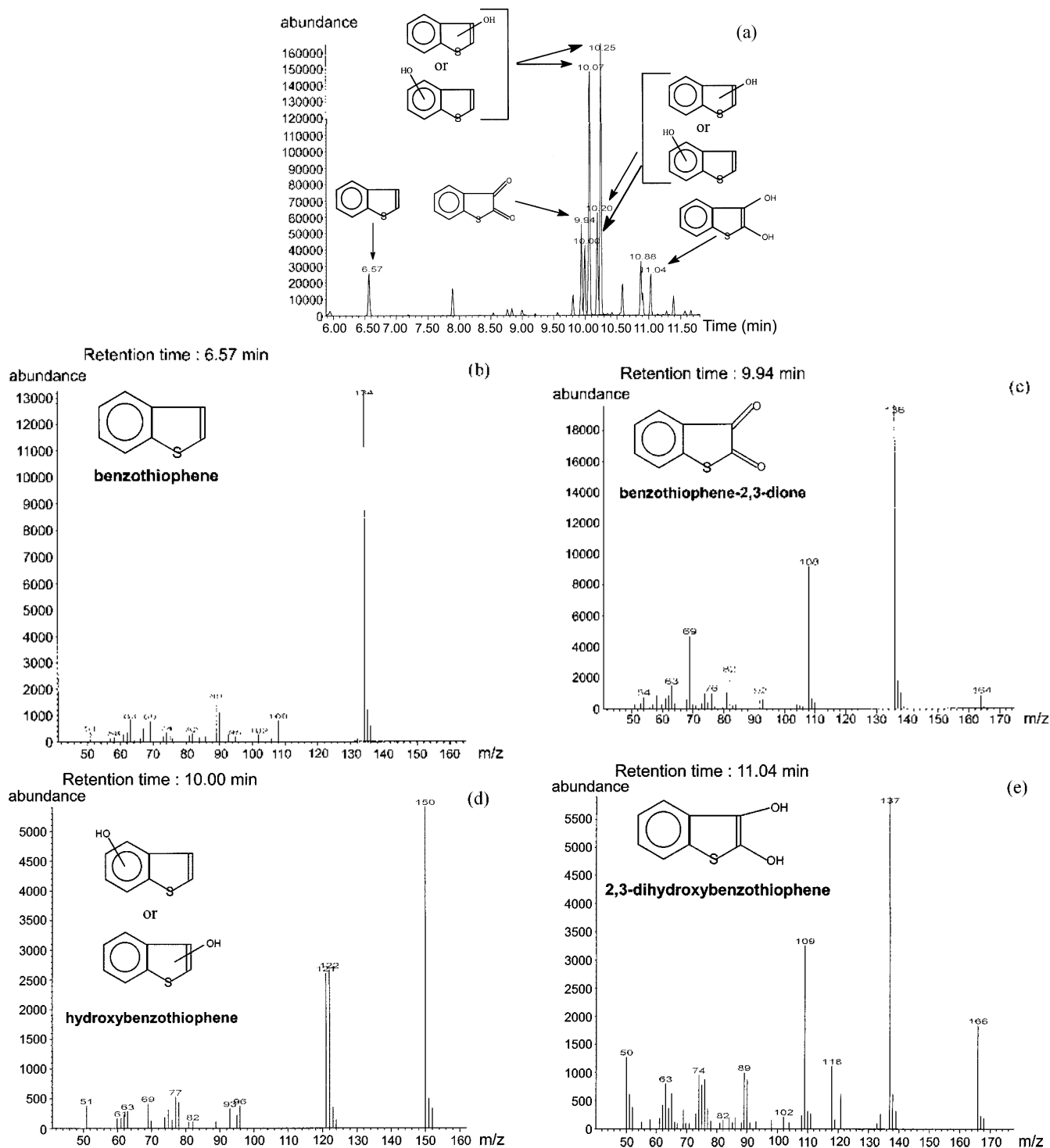
Figure 1. Identification of ultrasonic reaction intermediates. (a) total ion chromatogram of BT (b) mass spectrum of BT (c) mass spectrum of Benzothiophene-2.3-dione (d) mass spectrum of hydroxylbenzothiophene (e) mass spectrum of 2,3-dihydroxylbenzothiophene. Experimental conditions: reaction time = 120 min., energy intensity = 300 watts/cm^2. pH = 5, initial concentration = 0.2 mM. temperature = 25 °C, ionic strength = 0.05 M NaCl$_4$.

Figure 1d.[23] 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.[24,25] 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).[26,27]

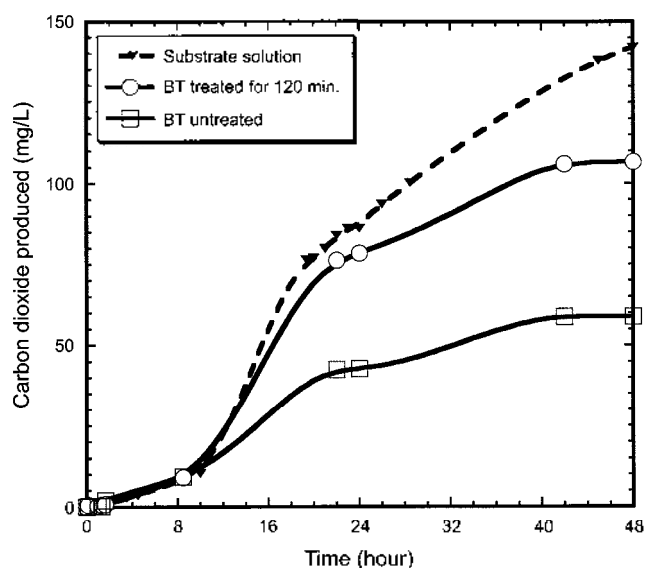Figure 2 presents the concentration change of benzothio-
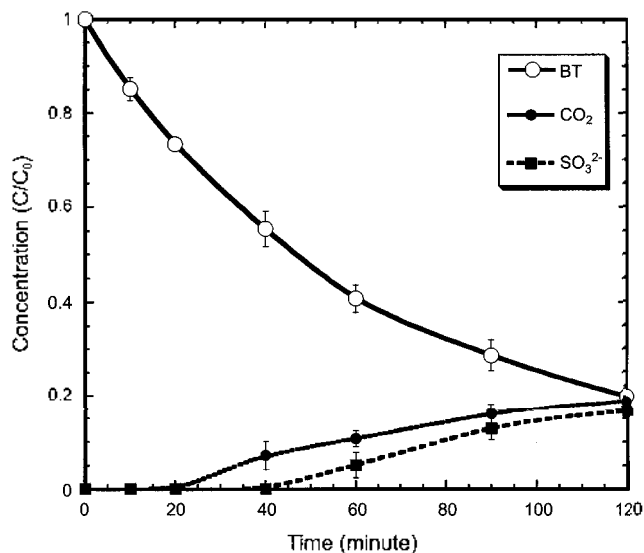
Figure 2. Evolution of carbon dioxide and sulfite from ultrasonic decomposition of benzothiophene (BT). Experimental conditions: ultrasonic energy intensity = 300 watts/cm², total volume = 40 mL, pH = 5, C_0 = 0.21 mM, temperature = 25 °C. ionic strength = 0.05 M $NaClO_4$.

Figure 3. The acute toxicity test for the treated and the untreated benzothiophene (BT) samples. Experimental conditions: total volume = 100 mL, pH = 7.2, temperature = 25 °C (A) substrate solution: glucose 10 g/L, K_2HPO_4 3.5 g/L, KH_2PO_4 1.5 g/L, $(NH_4)_2SO_4$ 0.5 g/L, citric acid 0.25 g/L, $MgSO_4$ 0.0025 g/L (B) untreated BT solution: C_0 = 12 mg-BT/L in substrate solution, (C) Treated BT solution: C_0 = 1 mg-BT/L in substrate solution.

phene and the generation of carbon dioxide and inorganic sulfur species. The concentration of other sulfur species remains at the low value (1 mg/L) during the reaction.

The toxicity of sonochemically treated solutions was checked by *F. coli*. Figure 3 shows the bacterial responses to different samples. A less inhibition in bacterial respiration was observed from the BT sample treated for 120 min than from the untreated BT sample. Consequently, the ultrasonic reaction reduced the toxicity of the treated organic compounds to *F. coli*.

Reaction Mechanism. Based on the hydroxylated intermediates tentatively 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 (Scheme 1).
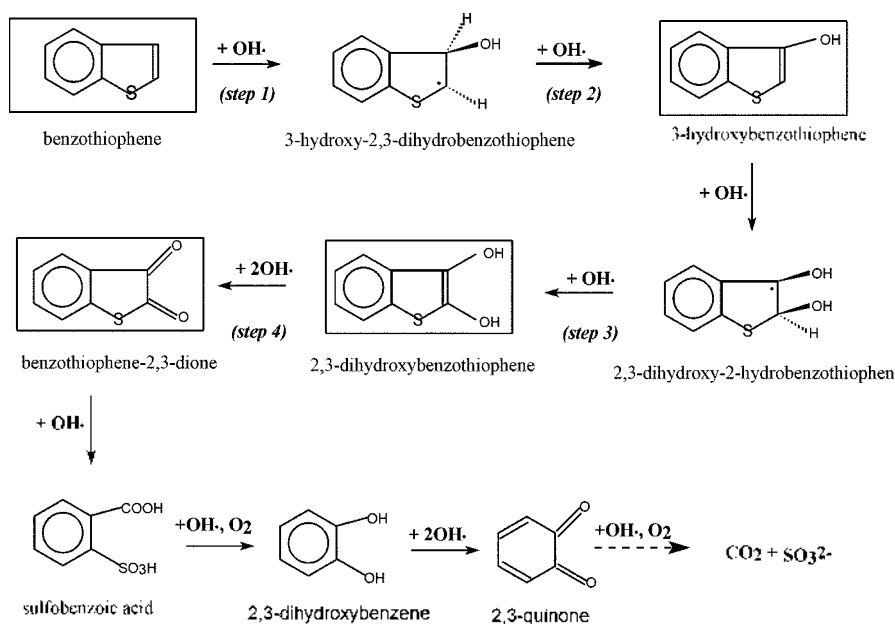
Scheme 1. A proposed reaction pathway of BT decomposition involving OH radicals.

Eventually, these intermediates will be mineralized to end products such as carbon dioxide and inorganic sulfur species. Scheme 1 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[24,25] 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.[26,27] 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.[26] Then further reaction with OH radical generates 2,3-dihydroxy-benzothiophene 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.[24,25] Subsequent cleavage of the quinone would result in the formation of organic acids, as has also been observed in Fentons reaction.[28] Carbon dioxide and sulfite were detected as reaction products.

Conclusion

It is proposed that benzothiophene is oxidized by OH radical to sequentially form hydroxybenzothiophenes, dihydroxybenzothiophenes, and benzothiophene-dione. The thiophene ring moiety is more susceptible to the hydroxyl radicals than the benzene moiety because thiophene ring with larger resonance energy appears to be more reactive than benzene ring. Benzothiophene is decomposed rapidly following pseudo-first-order kinetics in a first-order manner by ultrasonic irradiation in aqueous solution. The toxicity of ultrasonically treated solutions was checked by *E. coli* and a less inhibition in bacterial respiration was observed from the 120-min treated benzothiophene sample than from the untreated benzothiophene sample. Also evolution of carbon dioxide and sulfite was observed during ultrasonic reaction.

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