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ARTICLE *in* ENVIRONMENTAL SCIENCE AND TECHNOLOGY · JULY 2003

Impact Factor: 5.33 · DOI: 10.1021/es026190q · Source: PubMed

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Environ. Sci. Technol. **2003**, *37,* 2421−2430

Oxidative Transformation of Triclosan and Chlorophene by Manganese Oxides

HUICHUN ZHANG AND CHING-HUA HUANG*

School of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332

The antibacterial agents triclosan (5-chloro-2-(2,4-dichlorophenoxy)phenol) and chlorophene (4-chloro-2-(phenylmethyl)phenol) show similar susceptibility to rapid oxidation by manganese oxides (δ-MnO_2 and MnOOH) yielding Mn^{II} ions. Both the initial reaction rate and adsorption of triclosan to oxide surfaces increase as pH decreases. The reactions are first-order with respect to the antibacterial agent and MnO_2. The apparent reaction orders to H^+ were determined to be 0.46 ± 0.03 and 0.50 ± 0.03 for triclosan and chlorophene, respectively. Dissolved metal ions (Mn^{II}, Zn^{II}, and Ca^{II}) and natural organic matter decrease the reaction rate by competitively adsorbing and reacting with MnO_2. Product identification indicates that triclosan and chlorophene oxidation occurs at their phenol moieties and yields primarily coupling and *p*-(hydro)quinone products. A trace amount of 2,4-dichlorophenol is also produced in triclosan oxidation, suggesting bond-breaking of the ether linkage. The experimental results support the mechanism that after formation of a surface precursor complex of the antibacterial agent and the surface-bound Mn^{IV}, triclosan and chlorophene are oxidized to phenoxy radicals followed by radical coupling and further oxidation to form the end products. Compared to several structurally related substituted phenols (i.e., 2-methyl-4-chlorophenol, 2,4-dichlorophenol, 3-chlorophenol, and phenol), triclosan and chlorophene exhibit comparable or higher reactivities toward oxidation by manganese oxides. The higher reactivities are likely affected by factors including electronic and steric effects of substituents and compound hydrophobicity. Once released into the environment, partitioning of triclosan and chlorophene to soils and sediments is expected because of their relatively hydrophobic nature. Results of this study indicate that manganese oxides in soils will facilitate transformation of these antibacterial agents.

Introduction

Triclosan (5-chloro-2-(2,4-dichlorophenoxy)phenol) and chlorophene (4-chloro-2-(phenylmethyl)phenol) are commonly used broad-spectrum antibacterial agents (Figure 1). Triclosan is widely used in many personal care (e.g., toothpaste, soaps, deodorants, shampoos, and cosmetics) and consumer (e.g., plastic kitchenware and footware) products, and chlorophene is commonly used in hospitals and households for general cleaning and disinfecting. In a recent U.S. Geological Survey (USGS) study surveying the occurrence of emerging organic pollutants in surface streams, triclosan was one of the most frequently detected compounds with a median concentration of 0.14 μg/L (*1*). Others also reported detection of triclosan and its methyl derivative (a potential biotransformation product) in urban wastewater (*2*−*4*), surface water (*4, 5*), sediments (*5*), and fish (*5*).

Several concerns have been raised about triclosan. As a biocide, triclosan blocks lipid biosynthesis by specifically inhibiting the enzyme enoyl acyl carrier protein reductase and may induce bacterial resistance development (*6, 7*). Orvos et al. (*8*) recently examined the toxicity of triclosan on various aquatic organisms and determined that certain algae species are the most susceptible organisms. Furthermore, triclosan may form chlorodioxins during heating and incineration (*9, 10*) and under the influence of sunlight (*11*).

To properly assess the risks of triclosan and chlorophene, a better understanding of their environmental fate is imperative. Sorption to activated sludge and aerobic biodegradation have been suggested as the dominant mechanisms for high removal of triclosan in wastewater treatment systems (*3, 12*). Direct photolysis was recently suggested as an elimination pathway for dissolved triclosan in sunlit lake water. Direct photolysis is much more important at pHs where triclosan is present in its phenolic form (reported pK_a at 7.9−8.1) (*4, 13*). Triclosan and chlorophene are both relatively hydrophobic, with estimated octanol−water partition coefficients (log K_{ow}) of 4.86 and 3.99, respectively (*14*). Because of their hydrophobic nature, triclosan and chlorophene are likely to partition to soils and sediments once entering the aquatic environment. Their reactions with metal oxides in soils and sediments may significantly impact their environmental fate, particularly when conditions are not suitable for biological or photochemical transformation.

Oxides of Mn, Fe, and Al commonly found in soils and sediments have been shown in many studies to facilitate abiotic reactions of organic pollutants via hydrolysis, oxidation, or reduction. As part of a study assessing the potential reactions of triclosan and chlorophene with metal oxides, this paper reports the transformation with manganese dioxide (MnO_2, similar to the naturally abundant birnessite) and manganite (MnOOH). Manganese (hydr)oxides in soils and sediments are probably some of the most important natural oxidants and play a critical role in affecting the transformation of phenol, aniline, aliphatic amine, and triazine compounds (*15*−*20*). Earlier work has shown that manganese (hydr)-oxides oxidize and promote polymerization of phenolic compounds (*15, 16, 21*−*23*). As will be shown later, both triclosan and chlorophene are highly susceptible to such transformation reactions.

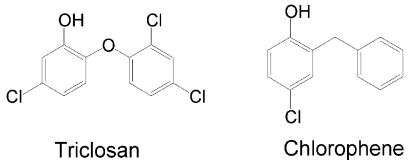
In this study, experiments were conducted to determine reaction kinetics and product formation. The influence of environmental conditions (e.g., pH) and the presence of co-solutes (e.g., metal ions and organic matter) on reaction kinetics were also assessed. On the basis of the kinetic results and product identification, reaction schemes were proposed. Comparison of triclosan and chlorophene with structurally related substituted phenols was also conducted to assess compound reactivities.

Materials and Methods

Chemicals and Oxide Preparation. Reagent grade water (18.3 MΩ-cm resistivity) was prepared using a Barnstead Nanopure water system. Triclosan, chlorophene, phenol, 3-chlorophenol, 2,4-dichlorophenol, 2-methyl-4-chlorophenol, and 2-(3-chlorophenyl)-[1,4]benzoquinone were purchased from Al-

* Corresponding author phone: (404)894-7694; fax: (404)894-8266; e-mail: ching-hua.huang@ce.gatech.edu.

10.1021/es026190q CCC: $25.00
Published on Web 04/26/2003



Triclosan Chlorophene

FIGURE 1. Structures of triclosan and chlorophene.

drich at greater than 98% purity and used without further purification. Other employed chemical reagents were obtained from Fisher Scientific or Aldrich at greater than 98% purity and used without further purification.

Manganese dioxide (δ-MnO_2) was synthesized according to the method by Murray (*24*). Briefly, 160 mL of 0.1 M $NaMnO_4$ and 320 mL of 0.1 M NaOH were added to 3.28 L of N_2-sparged reagent water, followed by a dropwise addition of 240 mL of 0.1 M $MnCl_2$ while keeping the solution constantly stirred. The formed MnO_2 particles were allowed to settle, and the supernatant was decanted and replaced with reagent water several times until the supernatant reached a conductivity of less than 2 $\mu S\text{-}cm^{-1}$. Finally, the oxide suspensions were stored at 4 °C and were diluted to appropriate concentrations in the experiments. A portion of the MnO_2 suspension was freeze-dried and the oxide surface area was determined to be approximately 255 m^2/g by the BET method of N_2 adsorption (Micromeritics). Powder X-ray diffraction analysis indicated that the synthesized MnO_2 is largely amorphous, consistent with the large surface area determined.

Manganite (MnOOH) synthesized according to the method by McArdell et al. (*19*) was provided by Dr. A. T. Stone at the Johns Hopkins University. The synthesized MnOOH revealed an average manganese oxidation state of +3.0, morphology of fine needles, and *d*-spacings that are consistent with the mineral manganite (*19*).

Reaction Setup. All glassware was soaked in 5 N HNO_3 and thoroughly rinsed with reagent water prior to use. Experiments were conducted in 25-mL screw-cap amber glass bottles with Teflon septa. The reaction bottles were continuously stirred on a magnetic stir plate in a 22 °C water basin. Reaction solutions were maintained at constant pH with 10 mM buffer: acetic acid/sodium acetate for pH 4−5, 4-morpholinepropanesulfonic acid (MOPS) and its sodium salt for pH 6−8, and 2-(cyclohexylamino)ethanesulfonic acid (CHES) and its sodium salt for pH 9−10. NaCl (0.01 M) was also added to the solutions. Stocks of triclosan, chlorophene, and related phenols were prepared in methanol at 1−2 mM, stored at 4 °C and used within a month of preparation. Reactions were initiated by adding a small amount of the organic reactant stock to suspensions containing manganese oxide, buffer, and constant ionic medium. Aliquots were periodically collected for analysis.

To monitor the reaction time course, three approaches were used to quench the reaction: (i) reaction aliquots were centrifuged (at 12 000 rev/min for 20 min) and the supernatants were transferred to separate vials for later analysis; (ii) immediately after sampling, the reaction aliquots were added with excess amounts of L-ascorbic acid to convert the remaining Mn oxide to Mn^{II} ions; and (iii) immediately after sampling, the reaction aliquots were added with NaOH to increase the pH to above 10 (preliminary studies indicated negligible degradation of triclosan by Mn oxides at pHs above 9). The pH >10 aliquots were then centrifuged and the supernatants were transferred to separate vials for later analysis.

Preliminary studies were conducted to assess whether the presence of O_2 affected the degradation of triclosan with manganese oxides. Two sets of experiments under N_2-purging anoxic condition and non-N_2-purging air condition were compared. Results showed that within the reaction time period (hours to several days), N_2 purging did not affect reaction rates and thus subsequent experiments were conducted without extra efforts to exclude O_2.

Analysis of Organic Reactants and Mn^{II} Ions. Decreases in the concentrations of triclosan, chlorophene, and related compounds were monitored using a reverse-phase HPLC with a Zorbax XDB-C18 column (4.6 × 250 mm, 5 μm) and a diode-array UV detector at wavelength 220 nm (1100, Agilent Technology). The mobile phase consisted of 65% acetonitrile and 35% 2 mM acetic acid solution at a flow rate of 1 mL/min.

Generation of Mn^{II} ions from reductive dissolution of manganese oxides was monitored using an inductively coupled plasma (ICP) spectrometer (Thermo Jarrell ash trace analyzer). At predetermined time intervals, samples of 5 mL were taken and passed through Millipore Durapore membrane filters (0.22 μm × 13 mm GVPP). The filtrate was then acidified to contain 1% HNO_3 and the emission of Mn^{2+} was measured at 257.61 nm using yttrium as the internal standard. Controls with only manganese oxide and pH buffers but without triclosan revealed that dissolution of manganese oxides did not occur in the absence of triclosan.

Analysis of Organic Products. For product identification, 80−120 mL of reaction suspensions containing the test organic reactant and MnO_2 were prepared at pH 5. Reactions were stopped after 1−4 days by adding ascorbic acid or centrifuging the sample. Analyses indicated that the water-soluble products accounted for only a small fraction of the total products. Products adsorbed on the manganese oxide were difficult to extract and were most adequately detected after dissolving the manganese oxide by ascorbic acid. Despite that, similar products were observed by both quenching methods.

For GC/MS analysis, organics from the acid-quenched reaction solutions, the centrifugation supernatants, and manganese oxides were extracted by vigorous shaking with 20 mL of methylene chloride for 10 min. The $MeCl_2$ extract was then concentrated to 1 mL under a gentle stream of N_2 gas. Controls with only organic reactants and pH buffers but without manganese oxides were extracted in a similar fashion and yielded >90% extraction efficiency for triclosan, chlorophene, 2,4-dichlorophenol, and 2-(3-chlorophenyl)-[1,4]-benzoquinone. Compounds were analyzed by a Hewlett-Packard GC/MS (6890/5973) with a HP-5MS 5% phenyl methyl siloxane capillary column (30 m × 250 μm × 0.25 μm). The GC conditions were as follows: splitless injection at 250 °C and the oven temperature from 70 to 280 °C at 10 °C/min followed by a 6-min hold at 280 °C, with helium as the carrier gas at 1.2 mL/min. Electron ionization at 70 eV with mass scan range 35−550 m/z was conducted. The temperatures of the ion source and the transfer line were 250 °C.

For LC/MS analysis, ENVI-18 SPE tubes (3 mL, Supelco) were used to extract organics from the acid-quenched reaction solutions and the filtrates of reaction solutions after passing through 0.5-μm glass-fiber filters. Acetonitrile (5 mL) was applied to elute organics from the cartridge and was subsequently blown down to 1 mL under N_2 gas. For manganese oxides left on the filter, 10 mL of acetonitrile was used to rinse the oxides and filter, followed by blowing down to 1 mL. Extraction of the control samples yielded extraction efficiencies at 26, 31, and 79% for triclosan, chlorophene, and 2-(3-chlorophenyl)benzo[1,4]quinone, respectively. Compounds were analyzed by a Hewlett-Packard LC/MS (1100/1100MSD) with a Zorbax SB-C18 column (2.1 × 150 mm, 5 μm). The eluent consisted of two mobile phases at 0.20 mL/min: (A) 0.02% acetic acid in 90:10 water/acetonitrile (v/v) and (B) acetonitrile. The gradient was as follows: B started at 10% for the first min, increased to 60% by 10 min, increased

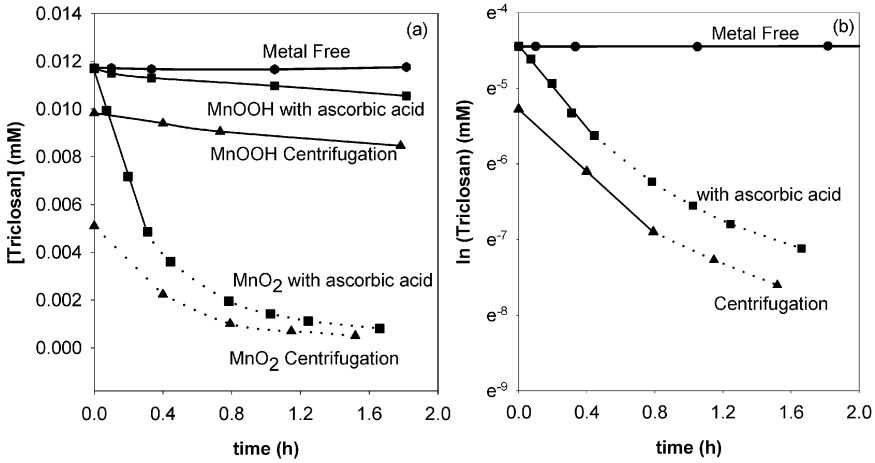


FIGURE 2. Time course of triclosan oxidation by MnO_2 and MnOOH: (a) triclosan concentration vs time; (b) logarithm of triclosan concentration vs time for the reaction with MnO_2. Reactions contained 100 μM MnO_2 or 1 mM MnOOH and 10 μM triclosan initially with pH 5 acetate buffer at 22 °C.

to 80% by 25 min, and increased to 100% by 25.01 min. Then the column was flushed by 100% B for 10 min followed by a 15-min post time which allowed reequilibration of the column. Electrospray negative ionization at fragmentor voltage of 80−120 V with mass scan range 50−1000 m/z was conducted. The drying gas was operated at 10 mL/min at 325 °C. The nebulizer pressure was 30 psig and the capillary was set at 4000 V.

Results and Discussion

Kinetics of Triclosan and Chlorophene Oxidation by MnO_2. In the absence of manganese oxide, loss of triclosan or chlorophene was not detected after a week. In the presence of manganese oxide, oxidative degradation occurred readily. A typical time course of triclosan oxidation by MnO_2 is shown in Figure 2, where the initial concentrations of triclosan and MnO_2 were 10 and 100 μM, respectively. Although the experiments were performed with a 10-fold excess of MnO_2, the loss of triclosan slowed as the reaction progressed and deviated from the pseudo-first-order kinetics (Figure 2b). Such complex reaction kinetics were also observed in previous studies (*16*−*18*, *21*, *25*) and were attributed to changing properties of manganese oxide as the redox reaction occurred. Thus, the initial reaction rates in $mM \cdot h^{-1}$ (i.e., the slopes over the first few time increments in Figure 2a) and the initial rate constants k_{init} in h^{-1} (i.e., the slopes within the time period where pseudo-first-order kinetics can be approximated in Figure 2b) were determined to evaluate the reaction kinetics. The 95% confidence limits for the reaction rates and rate constants were also determined from the replicate results.

The three approaches (centrifugation, ascorbic acid addition, and base addition) used to quench the reactions yielded similar k_{init} values for triclosan (1.76−1.90 h^{-1} at pH 5, Figure 3), validating that all three methods were appropriate for determining reaction kinetics. Compared to centrifugation, addition of ascorbic acid or sodium hydroxide quenched the reaction and also released the adsorbed triclosan from the oxide as shown by the higher triclosan concentrations detected by these two approaches (Figure 3). Comparison between centrifugation and ascorbic acid addition indicated that approximately 55% of triclosan was adsorbed to MnO_2 at pH 5. These results show that appreciable amounts of triclosan adsorb onto manganese oxide followed by the transformation reaction.

Parallel to monitoring the triclosan loss, the production of Mn^{2+} ions from manganese oxide was also analyzed. Similar to previous studies (*18*, *26*), tests performed in this

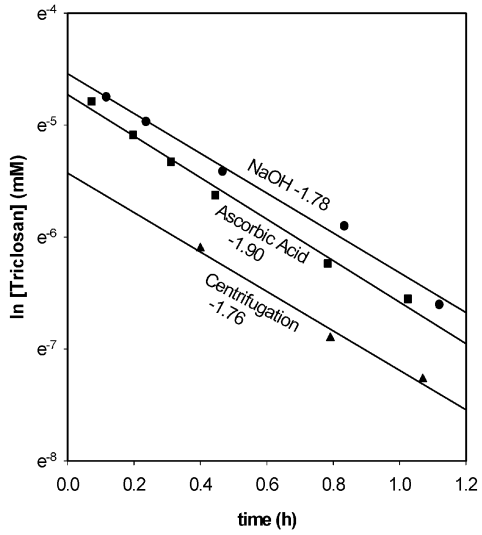


FIGURE 3. Logarithm of triclosan concentration vs time determined by three different quenching methods: centrifugation, ascorbic acid addition, and NaOH addition. The slope of linear regression is shown for each method. Reactions contained 100 μM MnO_2 and 10 μM triclosan initially with pH 5 acetate buffer at 22 °C.

study also found strong adsorption of Mn^{2+} to manganese dioxide, i.e., greater than 90% of the added Mn^{2+} adsorbed to 100 μM MnO_2 at pH 5 to 7. As a result, the measured Mn^{2+} concentration was lower than the triclosan loss throughout the reaction. Despite that, the k_{init} values for Mn^{2+} production (1.45 h^{-1}, after adsorption correction) and triclosan loss (1.74 ± 0.08 h^{-1}) were quite comparable. These results indicate that MnO_2 oxidizes triclosan leading to its reductive dissolution and that MnO_2 and triclosan are consumed at similar rates in the initial stage of the reaction.

The reaction kinetics were further investigated for the reaction orders with respect to the triclosan and manganese oxide concentrations and the influence of pH. Experiments were conducted by varying the initial triclosan concentration from 5 to 20 μM at each of three different MnO_2 loadings (20, 48, and 100 μM) (pH 5). The log of the initial reaction rate plotted versus the log of triclosan concentration yielded lines with slopes close to 1 (Figure S1 in the Supporting Information). Experiments were conducted with the initial MnO_2 concentration from 48 to 100 μM and the triclosan concentration at 10 μM at pH 5. Plotting the log of the initial reaction rate versus the log of oxide concentration also yielded a line

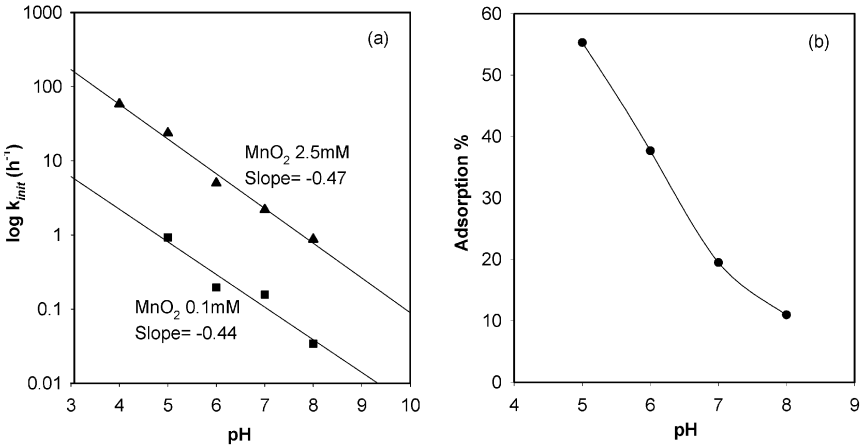


FIGURE 4. (a) Effect of pH on triclosan oxidation at two different initial MnO_2 loadings. (b) Effect of pH on the adsorption of triclosan to 100 μM MnO_2. Reactions contained 10 μM triclosan initially at 22 °C.

with a slope close to 1 (data not shown). These results indicate that the reaction is first-order with respect to triclosan and manganese oxide within the investigated conditions.

As shown in Figure 4a, pH markedly affected the reaction rate of triclosan oxidation by MnO_2. At both MnO_2 loadings, the log k_{init} decreased linearly as the pH was increased by the slope of −0.44 to −0.47, indicating that the reaction order was around 0.46 ± 0.03 with respect to H^+. Adsorption of triclosan to MnO_2 at different pHs was approximated by comparing the results from centrifugation and ascorbic acid addition as described earlier. Adsorption of triclosan to MnO_2 also decreased with increasing pH (Figure 4b). Over 55% of triclosan was adsorbed at pH 5, but only about 10% was adsorbed at pH 8.

Oxidation of chlorophene by MnO_2 showed kinetics very similar to those of triclosan. Under the conditions of 10 μM chlorophene and 100 μM MnO_2 at pH 5, the k_{init} for chlorophene was 2.67 ± 0.37 h^{-1}, comparable to that of triclosan. The log k_{init} of chlorophene also decreased linearly as the pH was increased (Figure S2 in the Supporting Information), yielding a reaction order of 0.50 ± 0.03 with respect to H^+. Because of their similar kinetic trends and product formation as discussed later, triclosan and chlorophene are likely oxidized by MnO_2 via similar mechanisms. Although not determined experimentally, it is reasonable to assume that chlorophene oxidation is also first-order with respect to both chlorophene and MnO_2.

On the basis of the kinetic results, the initial rate of triclosan or chlorophene oxidation by MnO_2 can be described by the following kinetic expression:

$$\text{initial rate} = \frac{\mathrm{d}[\text{antibacterial}]}{\mathrm{d}t} = k_{\text{init}}[\text{antibacterial}] = k_{\text{exp}}[\text{antibacterial}][MnO_2][H^+]^{0.46-0.50} \quad (1)$$

From the values of k_{init} at various initial MnO_2 loadings and pHs, the third-order rate constant k_{exp} (applicable within the employed experimental conditions) was computed to be 1.82-(± 0.37) × 10^6 $M_{MnO_2}{}^{-1}\cdot M_{H^+}{}^{-0.46}\cdot h^{-1}$ (n = 20) for triclosan and 3.50(± 0.78) × 10^6 $M_{MnO_2}{}^{-1}\cdot M_{H^+}{}^{-0.50}\cdot h^{-1}$ (n = 9) for chlorophene.

Surface Reactions. Overall, the kinetic trends of triclosan and chlorophene oxidation by MnO_2 are in good agreement with previous studies on the oxidation of hydroquinone, substituted phenols, and substituted anilines by manganese oxides (*16*−*18*, *21*). A surface reaction kinetic model proposed by Stone (*16*) for the oxidation of organics at manganese oxide surfaces is likely suitable to describe the reactions of triclosan and chlorophene. For the redox reaction to occur, formation of a precursor complex between the organic reductant and the oxide bound Mn^{IV} is necessary. Electron transfer occurs at the closely associated precursor complex followed by release of the organic oxidation products and Mn^{2+} from the oxide. The precursor complex formation and electron transfer are believed to be rate-limiting.

Properties of organic reductants and manganese oxide affect the precursor complex formation and electron transfer reactions. The precursor complex formation is also affected by the concentrations of organic reductant and manganese oxide. At a fixed amount of triclosan, the initial reaction rate increased linearly as expected with increasing amount of MnO_2 due to increased number of active surface sites and consequently increased precursor complex formation. Similarly, the results also showed that at a fixed amount of MnO_2, the initial reaction rate increased linearly with increasing triclosan concentration, indicating that the triclosan concentrations employed in this study were below the point of saturating the oxide surface. Once the surface sites are saturated with organics, additional organic reductant will not increase the formation of precursor complex. The actual number of active surface sites on the MnO_2 is not known. The slowing reaction rate even with an excess amount of MnO_2 suggests that the number of active sites which determine the initial reaction rate of triclosan is relatively small. Furthermore, the transformation products of triclosan and MnO_2 may block or react with the oxide surface, and thus as more products are formed, the greater the reaction inhibition effect (see more discussion in the following section).

A constant reaction order with respect to H^+ was observed in the oxidation of triclosan and chlorophene. This is in contrast to the results found in the oxidation of substituted phenols where the order with respect to H^+ decreases from 1.3 to 0.45 between pH 7 and pH 4.4 (*16*). Compared to the study by Stone (*16*), this study employed a considerably lower organic reductant to manganese oxide ratio (0.1 vs 1.6−2.8) and utilized a slightly different manganese oxide preparation procedure. These factors may contribute to the different pH dependence observed.

The strong pH dependence of the reaction rate can be attributed to the effect of pH on the adsorption of triclosan to oxide surface (i.e., precursor complex formation) and on the electron-transfer reaction. Deprotonation of triclosan (pK_a = 7.9 to 8.1 (*4*, *13*)) becomes significant when solution pH is near or higher than 8. The result that adsorption of triclosan decreased as pH was increased from 5 to 8 (Figure 4b) indicates that protonated triclosan adsorbs more strongly to MnO_2 than the deprotonated form. Using the reported pH_{zpc} (zero point of charge) of 2.4 for δ-MnO_2 (*24*), most oxide surface is negatively charged under the experimental condi-

TABLE 1. Initial Rate Constant k_{init} (h^{-1}) of Triclosan Oxidation by MnO_2 in Various Aqueous Compositions[a]

matrix	k_{init}	matrix	k_{init}
reagent water	1.74 ± 0.08	river water	0.30

M^{2+}(%)[b]	$k_{init}(Mn^{2+})$	$k_{init}(Ca^{2+})$	$k_{init}(Zn^{2+})$	NOM (mg/L)	k_{init}(NOM)
0.1	1.66		1.60	5	1.50
0.5	1.65		1.59	10	1.12
1	1.60	1.66	1.55	15	0.68
5	1.03	1.50	1.36		
10	0.50	1.51	1.12		
20		1.39			

[a] Reactions contained 10 μM triclosan and 100 μM MnO_2 initially with pH 5 acetate buffer at 22 °C. $MnCl_2$, $CaCl_2$, $ZnCl_2$, or the Suwanee River organic matter was added to the reactions. [b] % of the initial MnO_2 concentration.

tions and the negative charge decreases as pH decreases. The observed adsorption trend suggests that lowering the solution pH creates a greater number of surface species that favor interaction with triclosan. For electron transfer, protons are required for reduction of MnO_2 to release Mn^{2+} ions (i.e., $^1/_2\ MnO_2(s) + 2\ H^+ + e^- \rightarrow {}^1/_2\ Mn^{2+}(aq) + H_2O$). When pH is decreased from 8 to 4, the reduction potential of MnO_2 (E°(pH)) increases from 0.76 to 0.99 V (*27*). In addition to the increased reduction potential for the oxidant at lower pH, protonation of the precursor complex may also facilitate the electron-transfer reaction. The constant reaction order with respect to H^+ observed in this study suggests that the reaction mechanism does not change as a function of pH within the investigated conditions (*18*).

Effect of Oxide Properties and Co-Solutes on the Reaction Rate. Selected experiments were conducted on the reaction of triclosan with MnOOH (manganite). In general, triclosan oxidation was slower by MnOOH than by MnO_2 even when a higher loading of MnOOH was employed (Figure 2a). When equal amounts of oxides were employed (250 μM oxide and 10 μM triclosan at pH 5), the k_{init} values of triclosan oxidation were 23.60 h^{-1} and 7.16 × 10^{-2} h^{-1} for MnO_2 and MnOOH, respectively. The synthesized MnO_2 is predominately amorphous whereas MnOOH is more crystalline. The faster reaction rate by MnO_2 is likely due to its large surface area (~255 m^2/g) and highly amorphous nature, rendering the active surface sites more accessible to the incoming organics. The abundance and reactivities of the surface sites may also differ between the two oxides.

As shown in Table 1, addition of metal ions and the Suwannee River organic matter considerably decreased the reaction rate of triclosan oxidation by MnO_2. The inhibitory effect increased as the co-solute concentration was increased, although not in a linear fashion. The presence of low concentrations (at 5% MnO_2 concentration) of Mn^{2+}, Zn^{2+}, and Ca^{2+} ions decreased the reaction rate by 41, 22, and 14%, respectively. Addition of 5 mg/L of the organic matter decreased the reaction rate by 14%. In a river water matrix that was filtered (0.5-μm glass fiber filters) and buffered at pH 5, the reaction rate was slower by 83% than that in reagent water.

As mentioned earlier the number of active surface sites is likely limited, thus small amounts of co-solutes compared to the total added MnO_2 can still cause a significant inhibitory effect by blocking some of the active surface sites. The inhibitory effect of Mn^{2+} is considerably greater than those of $Zn^{2+}$and Ca^{2+}. Compared to Zn^{2+} and Ca^{2+}, Mn^{2+} adsorbs more strongly to MnO_2 (*28*). Furthermore, the adsorbed Mn^{2+} may oxidize or precipitate at the manganese oxide surfaces, thus blocking the surface sites (*29*−*31*). Considering Mn^{2+} is a reaction product, it likely contributes to the slowing rate observed as the reaction progresses (i.e., an auto-inhibiting effect). The Suwannee River organic matter probably inhibits the reaction by adsorbing and reacting with MnO_2 because humic material is known to adsorb and reductively dissolve manganese oxides (*32*, *33*). The slower rate of triclosan oxidation in the river water is likely caused by a combination of inhibitory effects from dissolved metal ions, natural organic matter, and other inorganic anions such as phosphate (*21*).

Oxidation Products of Triclosan. Using solvent extraction and GC/MS analysis, one major and two minor products were detected (Figure 5a). The minor product at 5.67 min was 2,4-dichlorophenol. The products at 16.89 and 17.67 min showed highly similar spectra and a difference of 2 in the m/z ratios of their molecular and the second largest fragment ions (Figure 5c and d), indicating that these two compounds were quinone and hydroquinone of a base structure (*34*). The spectra indicate that the products are *p*-quinone and *p*-hydroquinone of triclosan, i.e., 2-chloro-5-(2,4-dichlorophenoxy)-[1,4]benzoquinone (A) and 2-chloro-5-(2,4-dichlorophenoxy)benzene-1,4-diol (B). The assignment of the fragment ions from A is shown in Figure 5c. Formation of the m/z 185 fragment supports para- rather than ortho-

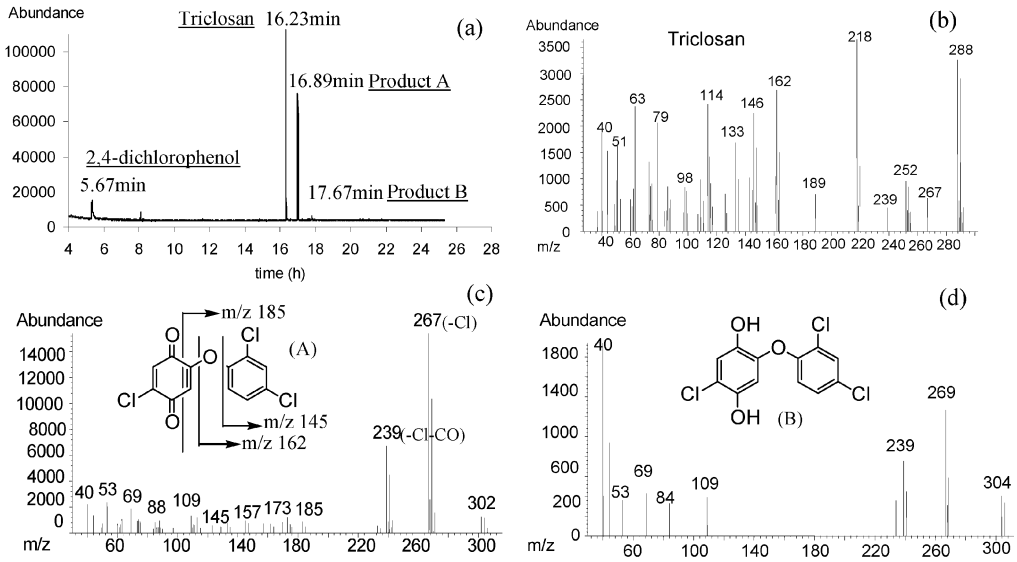


FIGURE 5. Oxidation of triclosan analyzed by GC/MS: (a) chromatogram of triclosan reaction extract; (b)−(d) mass spectra of triclosan, product A, and product B.

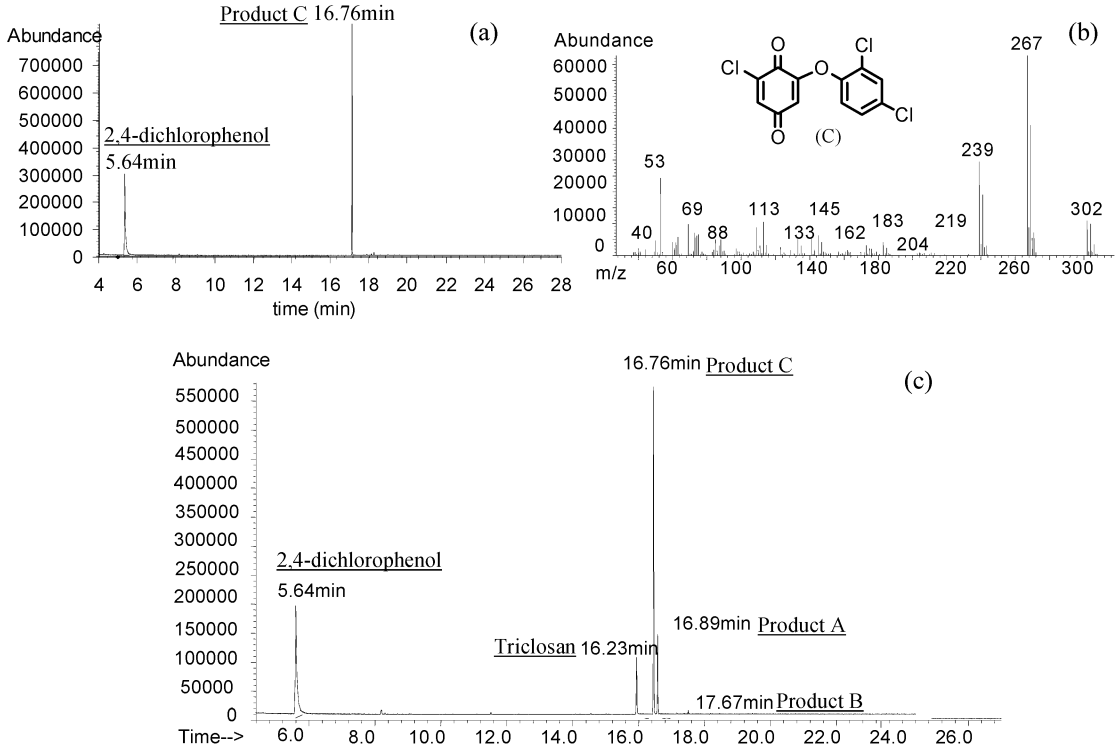


FIGURE 6. Oxidation products of 2,4-dichlorophenol analyzed by GC/MS: (a) chromatogram of 2,4-dichlorophenol reaction extract; (b) mass spectrum of product C; (c) chromatogram of the mixture of triclosan and 2,4-dichlorophenol reaction extracts.

TABLE 2. Oxidation Products of Triclosan Analyzed by LC/MS[a]

	RT (min)	$M - H^-$	compound	*m/z*
1	12.5	328		**328** (330, 332), 171 (35%)
2	14.77	468		**468** (470, 472, 474), 454 (60%, 456, 458), 297 (40%)
3	15.66	161	2,4-di	357 (10%, 359, 361), **161** (163, 165), 143 (50%)
4	15.75	377		**377** (379, 381, 383)
5	16.65	303	product B	**303** (305, 307), 267 (100%, 269, 271)
6	19.92	332		**332** (334, 336, 338), 293 (66%)
7	21.43	287	triclosan	571 (5%), **287** (289, 291, 293), 253 (15%, 255, 257)
8	26.93	571	dimer	**571** (573, 575, 577), 339 (72%), 321 (15%), 636 (6%)
9	27.75	573	dimer	**573** (575, 577, 579, 581), 339 (25%), 541 (10%), 161 (5%, 163)
10	30.47	573	dimer	573 (10%, 575, 577, 579, 581), **227**, 161 (5%, 163)
11	31.32	573	dimer	**573** (60%, 575, 577, 579), 539 (20%), 411 (25%, 413), 279 (20%)

[a] Each compound's chromatographic retention time, $[M - H]^-$ molecular ion, and mass spectrum are listed. Each bolded data corresponds to the base peak in each mass spectrum. 2,4-di represents 2,4-dichlorophenol.

position for the quinone. In addition, a trace amount of 2,7-dichloro-dibenzo[1,4]dioxin impurity was found in the triclosan control samples (without MnO_2). This amount did not increase after reaction with MnO_2 and other dioxin compounds were not detected.

Because 2,4-dichlorphenol was detected as a product and could also be oxidized by MnO_2, it was necessary to determine whether the observed products resulted directly from triclosan or from 2,4-dichlorphenol. Experiments were thus conducted to investigate the oxidation of 2,4-dichlorophenol by MnO_2, and analysis showed a major dimeric product of 2-chloro-6-(2,4-dichlorophenoxy)-[1,4]benzoquinone (C) (Figure 6a and b). The product C was identified previously by Ukrainczyk and McBride and was likely formed by oxidation and coupling of two 2,4-dichlorophenol molecules (*15*). Products A and C showed nearly identical spectra (Figures 5c and 6b). When mixed together, A and C yielded two distinct peaks on the GC/MS (Figure 6c). These results strongly suggest that A and C are isomers, resembling each other except for the position of chlorine substituent on the quinone ring. These observations confirm that the (hydro)quinone products of triclosan are produced from oxidation of the phenol moiety of triclosan by MnO_2, rather than from oxidation of 2,4-dichlorophenol intermediate. Detection of 2,4-dichlorophenol as a product suggests bond breaking of triclosan during the redox reaction. Such bond breaking, however, accounted for only a small percentage of the overall reaction as 2,4-dichlorophenol was detected at a small amount (<1% of triclosan loss) and its oxidation products were not detected in triclosan oxidation (Figure 5a).

Authentic standards of products A and B are not available. Instead, a structurally related quinone, 2-(3-chlorophenyl)-[1,4]benzoquinone, was used as a surrogate standard to quantify A. The quantity of A was estimated to be less than 5% of the triclosan loss. The quantity of product B, although not estimated, is likely to be even smaller based upon the considerably smaller MS response (Figure 5a). These results indicate that (hydro)quinone production is not the primary pathway of triclosan oxidation by MnO_2. Products from other reaction pathways are likely present but are unable to be detected by the GC/MS method.

Further investigation of the oxidation products was conducted by LC/MS after solid-phase extraction. As shown in Table 2, several more products were detected in addition

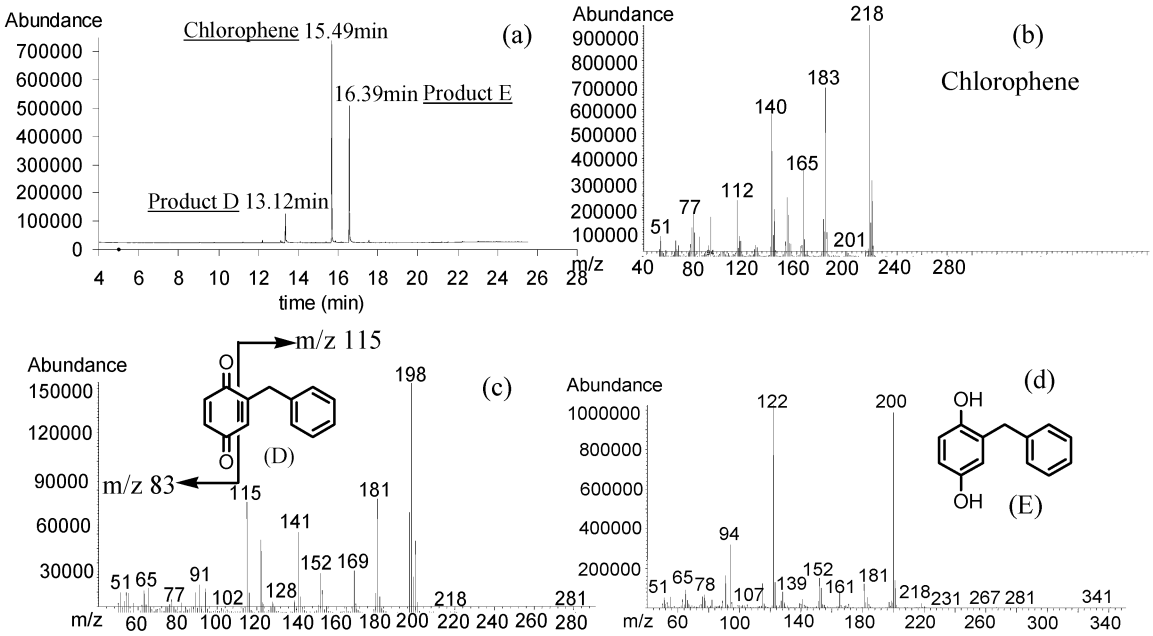


FIGURE 7. Oxidation products of chlorophene analyzed by GC/MS: (a) chromatogram of chlorophene reaction extract; (b)−(d) mass spectra of chlorophene, product D, and product E.

TABLE 3. Oxidation Products of Chlorophene Analyzed by LC/MS[a]

	RT (min)	M − H⁻	compound	*m/z*
1	14.54	199	product E	**199** (198, 200), 108 (12%)
2	17.93	397	dimer	397 (60%, 398), 297 (15%), **233** (235), 197 (8%), 141 (10%)
3	18.99	395	dimer	**395** (397, 399), 304 (65%), 217 (15%, 219), 295 (10%)
4	19.61	217	chlorophene	**217** (219)
5	22.47	415	dimer	**415** (417), 325 (35%), 233 (8%)
6	22.91	415	dimer	415 (15%, 417), **379** (380)
7	24.03	415	dimer	**415** (417), 262 (70%, 264)
8	26.52	413	dimer	413 (415), 325 (45%)
9	27.35	415	dimer	415 (417), 451 (8%), 325 (8%)
10	27.73	415	dimer	415 (60%, 417), **399** (401), 321 (10%), 325 (10%)
11	28.87	413	dimer	449 (30%, 451, 453),**413** (415), 339 (45%)
12	30.20	597		**597** (599, 601), 339 (10%)
13	32.95	433	dimer	631 (30%, 633),**433** (435, 437), 232 (15%, 234)

[a] Each bolded data corresponds to the base peak in each mass spectrum.

to 2,4-dichloropenol and product B. The molecular weights of several products indicate that they are dimers of triclosan. The molecular weight of 574 corresponds to the adduct of two triclosan molecules after losing two hydrogen atoms, and the molecular weight of 572 corresponds to the quinone of a triclosan dimer. Detection of dimers of triclosan indicates that, besides oxidizing triclosan to hydroquinone and quinone counterparts, manganese oxide also promotes dimerization and potentially polymerization of triclosan likely via radical reactions.

Oxidation Products of Chlorophene. Oxidation products of chlorophene were also studied by both GC/MS and LC/MS. Similar to the results of triclosan, the GC/MS analysis indicated that the products are *p*-quinone and *p*-hydroquinone of chlorophene (i.e., 2-benzyl-[1,4]benzoquinone (D) and 2-benzyl-benzene-1,4-diol (E), Figure 7). Similarly, formation of the *m*/*z* 115 fragment supports para-position for the quinone (Figure 7c). Using the surrogate quinone standard, the quantity of product D was estimated to be 3−4% of the chlorophene loss, similar to the percentage of product A to triclosan loss. The LC/MS analysis showed the presence of a variety of products in addition to product E (Table 3). The molecular weights of most of the products correspond to dimers of chlorophene, indicating that MnO_2 promotes chlorophene dimerization and potentially polymerization. Unlike the detection of 2,4-dichlorophenol in triclosan oxidation, no breakdown products of chlorophene were observed. Compared to the ether linkage of triclosan, the alkyl linkage between the two benzene rings of chlorophene is resistant to substitution and thus is difficult to break under the experimental conditions.

Reaction Schemes. On the basis of the observed surface reaction kinetics, product identification, and literature on the oxidation of phenolic compounds by oxygen and metal complexes (*35*−*38*), the reaction scheme for triclosan oxidation by manganese oxide is proposed in Figure 8. Initially triclosan is bound to the surface Mn^{IV} to form a precursor complex. The phenol moiety of triclosan is then oxidized by Mn^{IV} to lose an electron, forming a phenoxy radical. Accordingly, the Mn^{IV} is reduced to Mn^{III} and further to Mn^{II} likely through reaction with another triclosan or radical. The phenoxy radical is stabilized by electron resonance within the phenol ring. Further reactions of the phenoxy radicals may occur via three different pathways.

Pathway I is coupling of two phenoxy radicals to yield dimeric products. The coupling reactions most likely occur

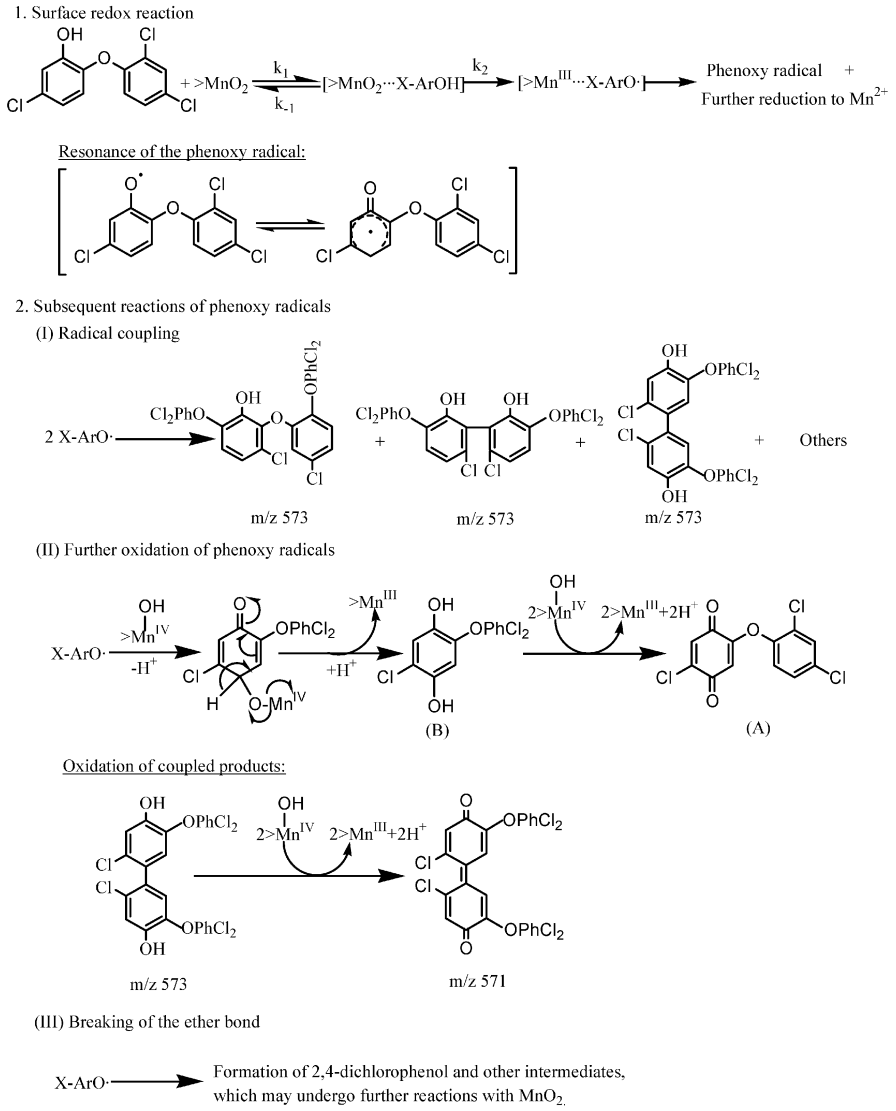


FIGURE 8. Proposed reaction scheme for oxidation of triclosan by MnO_2.

via C−C or C−O coupling at the ortho or para positions (*36*, *37*). At least three coupling products (*m*/*z* 573) were detected in the product identification and their probable structures are shown in Figure 8. Further polymerization is possible, however polymeric products were not detected likely because of low concentrations. Pathway II involves one-electron oxidation of the phenoxy radical by manganese oxide to form hydroquinone B. Further two-electron oxidation of hydroquinone B yields the quinone A. Formation of hydroquinone and quinone accounts for less than 5% of triclosan oxidation. This is consistent with the additional electron transfer reactions required to yield these products. The coupling products may also be subjected to further oxidation to form hydroquinone and quinone products. For instance, oxidation of a dibenzohydroquinone product (*m*/*z* 573) to dibenzoquinone (*m*/*z* 571) is shown in Figure 8. Pathway III involves cleavage of the ether bond of the phenoxy radical, possibly via *o*-dealkylation (*39*, *40*), to yield 2,4-dichlorophenol and other products. Overall, the experimental results suggest that triclosan oxidation by manganese oxide occurs predominantly via pathway I and to a lesser degree via pathway II. The pathway III is the least important in the overall reaction.

The reaction scheme of chlorophene oxidation by MnO_2 is believed to be similar to that shown in Figure 8 because the kinetics and product formation are very similar to those of triclosan. Pathway III, however, can be excluded because breaking of the benzyl linkage of chlorophene does not occur. Reaction pathway II leads to products D and E. Reaction pathway I leads to coupling products of chlorophene. Compared to triclosan, chlorophene exhibits higher complexity in coupling product formation. This is likely due to the fact that the *p*-Cl substituent of chlorophene is susceptible to substitution by hydroxide and consequently increases the variety of product formation. Some plausible structures for the dimeric products of chlorophene are shown in Figure 9. The detection of an *m*/*z* 597 product for chlorophene suggested that polymerization likely occurred.

Overall, the results show that triclosan and chlorophene oxidation by manganese oxide occurs at their phenol moieties via mechanisms similar to those of substituted phenol oxidation. Dimerization, and potentially polymerization, occur readily despite the presence of somewhat large substituents (i.e., dichlorophenoxy and benzyl substituents) on the phenol rings of triclosan and chlorophene.

Comparison of Triclosan, Chlorophene, and Simple Substituted Phenols. To evaluate the reactivities of triclosan and chlorophene, oxidation of 2-methyl-4-chlorophenol, 2,4-dichlorophenol, 3-chlorophenol, and phenol by MnO_2 was investigated for comparison (Table 4). These simple substituted phenols are structurally related to the phenol moieties of triclosan and chlorophene. The results show that triclosan and chlorophene have comparable or higher reactivities than

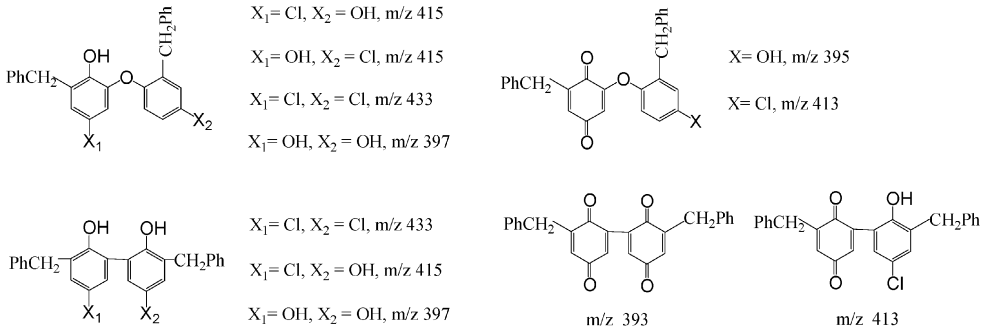


FIGURE 9. Plausible structures for the dimeric products of chlorophene oxidation by MnO_2.

TABLE 4. Initial Oxidation Rate Constant k_{init} (h^{-1}), pK_a, and log K_{ow} for Triclosan, Chlorophene, and Related Phenols[a]

compound	k_{init} (h^{-1})	k'/k^b	pK_a[c]	log K_{ow}
triclosan	1.74 ± 0.08	2.37	7.99	4.86[d]
chlorophene	2.67 ± 0.37	3.63	9.96	3.99[d]
2-methyl-4-chlorophenol	1.75 ± 0.58	2.38	9.76	2.63[e]
2,4-dichlorophenol	1.09 ± 0.30	1.49	7.69	3.06[e]
phenol	0.73 ± 0.22	1.00	10	1.46[e]
3-chlorophenol	0.20 ± 0.09	0.27	9.18	2.50[e]

[a] Reactions contained 10 μM organic reactant and 100 μM MnO_2 initially with pH 5 acetate buffer at 22 °C. [b] k'/k represents the initial rate constant ratio relative to phenol. [c] Estimated by the SPARC program (*41*). [d] Estimated by the ChemProp program (*14*). [e] Hansch et al. (*42*).

the related substituted phenols (i.e., triclosan ≈ chlorophene ≈ 2-methyl-4-chlorophenol > 2,4-dichlorophenol > phenol > 3-chlorophenol).

Substituents on the aromatic ring affect phenol reactivity by electronic (resonance and inductive) and steric effects (*43*). Generally, electron-donating substituents increase the basicity of phenol and thus the susceptibility toward oxidation, whereas electron-withdrawing substituents exert the opposite effect. The position (ortho, meta, or para) of substituents is also critical in affecting the magnitude of electronic and steric effects. Earlier work by Stone (*16*) has shown that the initial oxidation rates of substituted phenols by manganese oxide correlate well with the compounds' pK_a values and half-wave potentials ($E_{1/2}$), particularly when the substituent effect is primarily electronic (the reaction rate increases with increasing pK_a or decreasing $E_{1/2}$). The $E_{1/2}$ is not available for several compounds considered in Table 4 including triclosan and chlorophene. A simple trend cannot be established between the k_{init} and pK_a values, suggesting that the initial oxidation rates of triclosan and chlorophene are probably influenced by a combination of factors. The likely influencing factors include the electronic and steric effects of substituents and compound hydrophobicity.

In terms of electronic influence, triclosan's *o*-dichlorophenoxy group provides strong resonance and weak electron-withdrawing effects, thus overall an activating effect. Triclosan's *m*-Cl substituent exerts an electron-withdrawing effect. The *o*-benzyl group of chlorophene is electron-donating, and the *p*-Cl substituent is weakly electron-withdrawing (the *p*-Cl's electron-withdrawing effect is offset somewhat by its weak resonance effect). Comparable electronic effects from chlorine substituents are also present in the related substituted phenols. For instance, compared to chlorophene, 2-methyl-4-chlorophenol is expected to experience similar electronic effect because of the similar electronic influence from the *o*-methyl and *p*-Cl substituents.

Besides electronic effect, steric hindrance likely occurs for triclosan, chlorophene, 2-methyl-4-chlorophenol, and 2,4-dichorophenol because of *o*-substitution of the phenol ring, and the steric hindrance is probably greater for triclosan and chlorophene due to their larger *o*-substituents. Furthermore, the higher hydrophobicity of triclosan and chlorophene may contribute to higher adsorption to manganese oxide than the related substituted phenols since previous work has shown that adsorption of chlorophenols to manganese oxide increases as the compound's K_{ow} increases (*44*). The higher adsorption to manganese oxide may lead to more surface precursor complex formation and thus the faster reaction rate. Taking chlorophene and 2-methyl-4-chlorophenol for comparison, chlorophene likely experiences greater steric hindrance but also greater adsorption to manganese oxide than 2-methyl-4-chlorophenol. Therefore, a combination of the aforementioned factors likely results in the high reactivities of triclosan and chlorophene to oxidation by manganese oxide; however, more studies are needed to better understand the influencing factors.

This investigation demonstrates high susceptibility of triclosan and chlorophene toward oxidation by manganese oxides and significantly fast reaction rates at pHs below 7. Mild acidic conditions are common in many soils (e.g., *45*, *46*). Assuming a condition of pH 6 and 10 μM manganese dioxide (*45*, *47*), the half-lives of triclosan and chlorophene are calculated to be less than 21 h. However, other constituents such as natural organic matter and dissolved metal ions in natural water and soils likely will slow the reaction rate by competitively interacting with oxide surfaces. Nevertheless, oxidative transformation by manganese oxides is likely an important attenuation process for triclosan and chlorophene in the soil−water environment. Formation of heavier and more hydrophobic products via dimerization and polymerization will decrease the mobility of these antibacterial agents and potentially decrease the biological effects when the larger products become less available for aquatic organisms.

Supporting Information Available

Oxidation of triclosan by MnO_2: the reaction order with respect to triclosan (Figure S1) and effect of pH on chlorophene oxidation by MnO_2 (Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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Received for review September 26, 2002. Revised manuscript received March 24, 2003. Accepted March 28, 2003.

ES026190Q