Sonolysis of 2,4-Dichlorophenoxyacetic Acid in Aqueous Solutions. Evidence for •OH-Radical-Mediated Degradation

Julie Peller,[†,‡] Olaf Wiest,*[,‡] and Prashant V. Kamat*[,†]

Radiation Laboratory and Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556

Received: September 25, 2000; In Final Form: December 7, 2000

2,4-dichlorophenoxyacetic acid (2,4-D) undergoes efficient degradation when an O_2- or Ar-saturated aqueous solution is subjected to high-frequency (640 kHz) sonolysis. 2,4-dichlorophenol, hydroquinone, and catechol are major reaction intermediates common to various experimental conditions. The similarities between the reaction intermediates of sonolytic and radiolytic reactions indicate •OH radical as the primary reactive species responsible for 2,4-D degradation. Very little 2,4-D degradation occurs if the sonolysis is carried out in the presence of the •OH radical scavenger *tert*-butyl alcohol, also indicating that little or no pyrolysis of the compound occurs. Most of the 2,4-D eventually forms oxalic acid, which, unlike other •OH-mediated oxidation methods, is not easily mineralized with high-frequency ultrasound.

Introduction

2,4-Dichlorophenoxyacetic acid (2,4-D) is a common herbicide. The fate of this compound in the environment is of great interest because of its high-quantity usage and its chlorinated aromatic nature. Recent experiments have shown that 2,4-D residues from lawn applications are present in homes and that the quantities and locations of the herbicide are dependent on traffic patterns in the homes.[1] Although herbicide applications are designed to deposit on plants or grass, inadvertent translocation occurs to nearby areas or indoor residential areas.[2] Because herbicides are used in large quantities on farms and lawns, they contaminate water supplies through runoff and other means. Unfortunately, 2,4-D breaks down slowly in water, with half-lives reported from 6 to 170 days, depending on environmental conditions.[3−5] The toxicity data on 2,4-D is limited, but it is considered moderately toxic toward aquatic life[6] and the LD_{50} for mice is 368 mg/kg.

Advanced oxidation processes, namely, photocatalysis, radiolysis, and UV/H_2O_2, have been used to degrade a variety of environmentally hazardous compounds (see, for example, refs 7−17). Several recent studies have used some of these methods to break down 2,4-D into nontoxic substances and to eventually mineralize the herbicide.[18−23] Often these breakdown sequences were found to introduce new chemical intermediates/products that are more toxic than the parent compound. For example, one of the main intermediates in the breakdown of the herbicide 2,4-D is 2,4-dichlorophenol (2,4-DCP). This intermediate exhibits higher toxicity than 2,4-D as determined from the microtox bioassay.[22,24] Along with 2,4-DCP, other chlorinated aromatic compounds have also been reported using photocatalysis,[19,21] the Fenton-type oxidation,[18,25] and UV/hydrogen peroxide oxidation systems.[26,27] Whereas most of these studies employ UV light as an activation source to initiate the oxidation, the advanced oxidation process of sonolysis utilizes sound waves and a sparging gas. To substantiate the role of the •OH radical in the sonolytic degradation of 2,4-D, we also employed γ radiolysis in our investigation, which allows for oxidative conditions in which the •OH radical is the exclusive reactive species.

When ultrasound waves are introduced into an aqueous solution, cavitation occurs, as bubbles rapidly form and subsequently collapse inward from the buildup of pressure through rarefaction/compression cycles. Under these sonolytic conditions, high temperatures and pressures accompany the implosion of the cavitation bubbles. The specific conditions created during implosion depend on a few variables, namely, the frequency and power of the sound waves, the dissolved gas, and the solute(s) present in the medium.[28−31]

Sonolysis can induce the degradation of organic compounds along two different pathways. Upon collapse of the cavitation bubble, volatile compounds are vaporized and destroyed via pyrolytic or combustive reactions.[32] Hydrocarbons and other volatile compounds form intermediates and products that mirror those of pyrolysis or combustion.[33−36] The second reaction pathway is a chemical process at the interface of the bubble, induced by hydrogen atoms and hydroxyl radicals formed from the homolysis of water. Solute molecules that do not diffuse into the bubble are likely to undergo radical attack by •OH or •H.[37] The concentration of hydroxyl radicals at the interface is believed to be as high as 1×10^{-2} M upon bubble collapse. Hydrogen radicals are present in about a 1:4 ratio to hydroxyl radicals.[38]

In oxygen-saturated aqueous solutions, oxidizing radicals are formed according to the following series of reactions:[39]

$$H_2O \rightarrow H^\bullet + {}^\bullet OH \qquad (1)$$

$$H^\bullet + O_2 \rightarrow HO_2^{\bullet} \rightarrow {}^\bullet OH + \frac{1}{2}O_2 \qquad (2)$$

$$2{}^\bullet OH \rightarrow H_2O_2 \qquad (3)$$

$$2HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \qquad (4)$$

---

* Author to whom correspondence should be addressed. Tel.: (219) 631-5411. Fax: (219) 631-8068. E-mail: pkamat1@nd.edu. Web: http://www.nd.edu/~pkamat.

[†] Notre Dame Radiation Laboratory.

[‡] Department of Chemistry and Biochemistry.

10.1021/jp003478y CCC: $20.00

Argon and molecular oxygen are the gases often used in aqueous sonochemistry because they have high specific heat ratios and are conducive to radical formation. When Ar is used as the sparging gas, OH radicals are produced with greater efficiency.[38] The main source of H_2O_2 in the aqueous system is from the recombination of hydroxyl radicals (reaction 3). Solute present at the interface of the bubble will scavenge the hydroxyl radicals and decrease the formation of hydrogen peroxide.[38] The Ar-sparged sonolytic system is never anoxic because of the thermolysis of water vapor.[32]

As previously mentioned, hydrogen atoms are present in about a 1:4 ratio to hydroxyl radicals. The participation of hydrogen atoms in reaction 5 accounts for some of the difference, and notably, hydroxyl radicals are produced. Equation 6 shows another fate for hydrogen atoms.[40]

$$^{\bullet}H + H_2O \rightarrow H_2 + {}^{\bullet}OH \tag{5}$$

$$^{\bullet}H + {}^{\bullet}H \rightarrow H_2 \tag{6}$$

In the present study, we demonstrate the feasibility of sonolysis as an effective method for the destruction of 2,4-D. By comparing intermediates and products of the sonolytic degradation with those determined in γ-radiolysis experiments, we elucidate the role of $^{\bullet}$OH radical in the breakdown of 2,4-D in aqueous solutions.

Experimental Section

Materials and Reagents. 2,4-Dichlorophenoxyacetic acid (Aldrich, 99%), 2,4-dichlorophenol (Aldrich, 99%), catechol (Aldrich, 99%), chlorohydroquinone (Aldrich, 85%), sodium hydroxide (Fisher, ACS), hydrochloric acid (Fisher, ACS), 4-chlorocatechol (TCI, 99%), *tert*-butyl alcohol (Fisher, ACS), and hydroquinone (Aldrich, 99%) were used as supplied. Chlorohydroquinone (Aldrich) was recrystallized from methanol/water. Unbuffered aqueous solutions were prepared using Milli-Q purified water. The pH of the solutions was adjusted by adding either HCl or NaOH. A small drop in pH (0.5−2.0 pH units) was noted at the end of the sonolysis experiments. High-purity N_2O, O_2, and Ar gases were supplied by Mittler Supply Co., South Bend, IN.

γ-Radiolysis. γ-Radiolysis experiments were conducted in a 109 Shepherd, cobalt-60 (^{60}Co) source. The aqueous solutions were sparged with $N_2O(g)$ for 45 min in glass vials that were capped with a rubber septum before γ irradiation. Samples were taken at the indicated times. Fricke dosimetry was performed to determine the dose rate. A dose rate of 5.3 krad/min was determined using the following dosimetry solution: 0.40 mM H_2SO_4, 10.0 mM $FeNH_4SO_4$.

Sonolysis. Sonolysis experiments were performed using an ultrasound of 640-kHz frequency (Ultrasonics Energy Systems, Panama City, FL). The cell has a volume capacity of approximately 600 mL and consists of a polyethylene base (PE window) that is mounted about 4 cm above the transducer (Figure 1). This configuration allows for the separation of the transducer from the reaction mixture. The power output as determined by the calorimetric method was approximately 50 W. Throughout the experiments, the transducer and the lower portion of the cell remained submerged in an ice water bath. The solutions were initially saturated with either oxygen or argon and were continuously sparged with either gas throughout the experiments. The average temperature of the solution during sonolysis was 303 K.

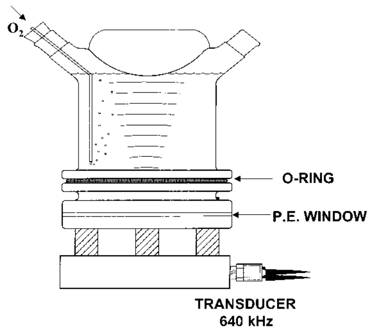


Figure 1. Ultrasound sample cell. The transducer is separated from the sample solution by a polyethylene film. The lower portion of the glass holder and the transducer are submerged in ice water during sonolysis experiments.

Analysis. The samples were taken out at different time intervals during γ irradiation or sonolysis. The progress of the degradation was monitored using a Shimadzu 3101PC UV/vis spectrometer. Intermediates were identified by comparison with authentic samples using a Waters HPLC system (Milennium 2010, Waters 717 plus Autosampler, Waters 600 Controller Solvent Pump) with three separate columns: Alltech Econosil C18, 10 μm (250 × 4.6 mm) and Alltech Econosphere C8, 5 μm (150 and 250 × 4.6 mm). A solvent gradient consisting of methanol, water, and water containing 1% acetic acid was utilized with all three columns. A photodiode array detector monitored the 200−400 nm range. Intermediates were identified by comparison of their retention times and spectra with those of authentic samples. Detection of short-chain carboxylic acids was achieved using a Phenomenex AQUA, 5μ, C18 column. The mobile phase was 20 mM potassium phosphate at a pH of 2.5. Chloride ion concentrations were monitored using a Dionex ion chromatographer fitted with an Ionpac AS12A column preceded by an AG12A guard column. An eluent solution consisting of 2.7 mM $NaCO_3$/0.3 mM $NaHCO_3$ was set at an isocratic flow rate of 1.5 mL/min. Mineralized carbon was measured using a Shimadzu total organic carbon analyzer, model TOC-5050, equipped with an ASI-500A autosampler. All experiments were carried out at least in duplicate. The reported values are within the experimental error of 5%.

Results and Discussion

Sonochemistry of 2,4-D in Aqueous Solutions. High-frequency sonolytic systems have proven to be effective in the degradation of organic compounds.[29,30,36,41,42] In the present study, we were able to degrade 2,4-D in both Ar- and O_2-saturated solutions using high-frequency (660 kHz) sonolysis. Figure 2A shows the absorption spectra recorded during the sonolysis of 0.20 mM 2,4-D in an Ar-sparged aqueous solution. Figure 2B shows the decay of 2,4-D as monitored from the absorption band at 285 nm under different sparging gas conditions.

In the case of Ar(g) as the sparging gas, nearly 90% degradation was achieved in less than 100 min. When oxygen was used as the sparging gas, the degradation occurred at a similar rate (lifetime of 29 min). The use of Ar(g) as the sparging gas is expected to allow for the creation of higher temperatures upon collapse of the cavitation bubbles as the temperature attained inside the bubble depends on the average specific heat ratio and the thermal conductivity of the dissolved gas.[28,29] These higher temperatures, in turn, create a more efficient system for the production of hydroxyl radicals as measured by the terephthalate dosimetry.[38] In our experiments, the sparging gas

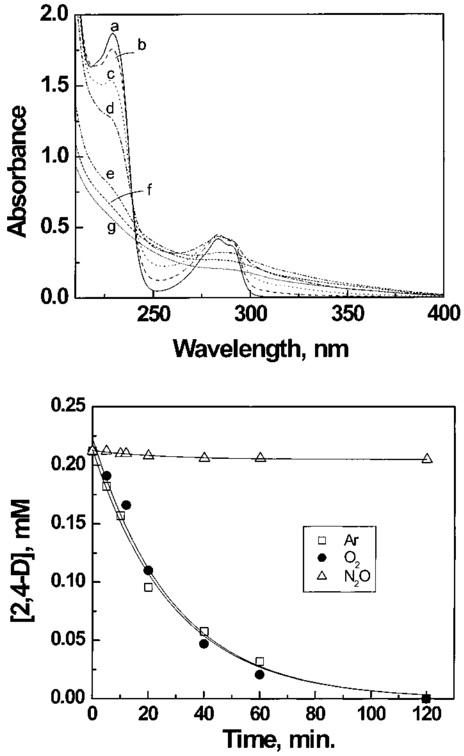


Figure 2. (A) UV absorbance spectra of 0.20 mM 2,4-D recorded at different times during 2-h sonolysis of the Ar(g)-sparged aqueous solution: a = 0, b = 5, c = 10, d = 20, e = 40, f = 60, g = 120 min. (B) Sonolytic degradation of 0.20 mM 2,4-D in aqueous solution using different sparging gases, Ar (□), O_2 (●), and N_2O (△).

(viz., Ar and O_2) did not have a significant effect on the rate of degradation or on the intermediates that were formed.

The sonolytic degradation was quite effective at lower pH. When an aqueous 2,4-D solution at pH 2.2 was subjected to high-frequency ultrasound waves, the degradation occurred with a lifetime of 21 min. Under alkaline conditions (pH = 11.8), 2,4-D remained in the solution for much longer, with a degradation lifetime of 38 min. The difference in reactivity at these two pH values arises from the difference in absorptivity of the protonated and unprotonated forms of 2,4-D to the ultrasonic bubbles.

Because 2,4-D is a polar, nonvolatile compound, the sonochemical reaction with the hydroxyl radical is expected to take place at the cavitation bubble interface where the hydroxyl radical concentration is a maximum.[32] Recently, Greiser and coworkers[43] proposed that $^{\bullet}$OH radicals are scavenged by solute molecules at the bubble surface when the volatility of the solute is low. They performed extensive studies on phenol in various pH solutions. When phenol is in its ionized form, the rate of degradation is lowest. This observation is in agreement with earlier work reported by Currell et al.[44] We found the same type of reactivity with 2,4-D. The hydrophobic character of 2,4-D is highest at very low pH conditions where the compound is in its protonated form ($pK_a = 2.9$), and the degradation rate of 2,4-D is highest at the low pH. In its protonated form, 2,4-D exists in higher concentrations at the bubble surface and thus, is more readily subjected to the OH radical attack. High-pH solutions undergo sonolytic degradation at a much slower rate. In higher-pH solutions, 2,4-D is present in its ionized form and does not readily accumulate at the bubble interface. The ionized form of the 2,4-D molecules does not adsorb as well to the air/water interface as the protonated form. The observed lifetime of 2,4-D at the high-pH conditions, which is considerably longer than that of the lower-pH solutions (Table 1 and Figure 3), supports such an argument.

TABLE 1: Sonolysis of 2,4-D and 2,4-DCP under Various Conditions of pH and Sparging Gas

compound	sparging gas	pH	lifetime[a] (min)
2,4-D	O_2	3.8	29
2,4-D	Ar	3.8	29
2,4-D	Ar	2.2	21
2,4-D	Ar	11.8	38
2,4-DCP	O_2	5.7	15
2,4-DCP	Ar	5.7	13
2,4-DCP	Ar	3.1	12

[a] Values obtained from the first-order kinetic analysis of the decay of the parent compound. The standard deviation in these measurements is ±2 min.

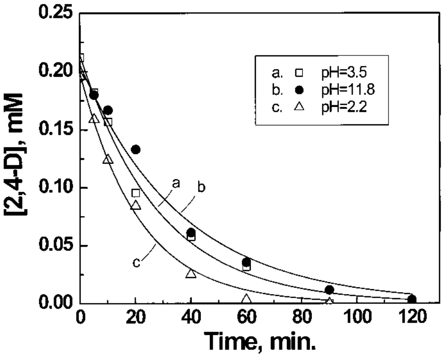


Figure 3. Sonolytic degradation of 0.20 mM 2,4-D in various pH solutions using Ar as the sparging gas. The degradation was monitored over a 2-h period: a = pH 3.5, b = pH 11.8, c = pH 2.2.

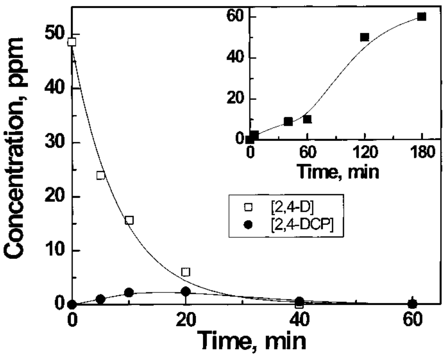


Figure 4. Sonolytic breakdown of 0.20 mM 2,4-D (□) and the growth and decay of the reaction intermediate 2,4-DCP (●) in aqueous solution using Ar as the sparging gas. Inset shows the growth of the end product, oxalic acid, during the sonolysis.

One of the prominent intermediates in the sonolysis of 2,4-D was 2,4-dichlorophenol (2,4-DCP). This primary intermediate was detected as soon as we initiated the sonolysis of 2,4-D in aqueous solution. The chlorinated phenol as the major reaction intermediate has also been detected in the degradation of 2,4-D using other advanced oxidation processes.[19−23,27] An important observation concerning the chlorinated phenol intermediate in these experiments was its short existence under ultrasonic conditions. The concentration of 2,4-DCP never rose above 7% of the 2,4-D concentration (Figure 4). The half-lives of 2,4-D and 2,4-DCP under the various experimental conditions are summarized in Table 1.

In addition to 2,4-DCP, we were also able to identify several other aromatic intermediates using HPLC with comparison to standards. The aromatic intermediates identified in the sonolytic degradations of 2,4-D include 4-chlorocatechol, 2-chlorohydroquinone, 4-chlorophenol, catechol, hydroquinone and

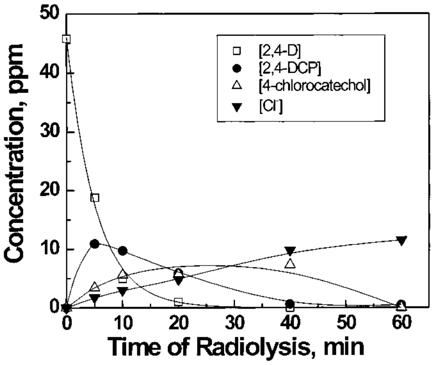


Figure 5. Radiolytic breakdown of 2,4-D (□) and intermediate formation of 2,4-DCP (●), 4-chlorocatechol (△), and chloride ion (▼) using a ^{60}Co source. The initial concentration of 2,4-D was 47 ppm, and the solution was saturated with N_2O gas.

1,2,4-benzenetriol. The nature of the chemical intermediates formed during the ultrasonic destruction of the 2,4-D solutions indicates a hydroxyl-radical-induced oxidation process.

γ-Radiolysis of 2,4-D Solutions. To independently assess the role of hydroxyl radical in the oxidation process, we carried out γ radiolysis of 2,4-D solutions in aqueous solution (pH = 3.5). In the radiolysis experiments, aqueous electrons were scavenged using dissolved N_2O to achieve an exclusive $^{\bullet}$OH-radical reactive environment to study the oxidative degradation processes.

$$H_2O + N_2O + e_{aq} \rightarrow N_2 + OH^- + {}^{\bullet}OH \quad (7)$$

The *G* value for the disappearance of 2,4-D was calculated for the initial 5 min of radiolysis and was determined to be 4.4. This value is comparable to the *G* values of other aromatic compounds under similar radiolytic conditions and suggests direct interaction with $^{\bullet}$OH, which has a *G* value of 6.0.[45]

Once again, 2,4-DCP was the prominent intermediate in the hydroxyl-radical attack on 2,4-D using γ radiolysis. The concentration of 2,4-DCP reached a maximum of 9.7 ppm at 10 min into the radiolysis and was almost completely degraded in 60 min. At 40 min into the radiolysis, the parent compound, 2,4-D, was no longer detected. 4-Chlorocatechol was also a readily detected intermediate.

The chloride ion concentration was followed during the radiolysis of 2,4-D. After 60 min of radiolysis, close to 90% of the chloride ion was detected via ion chromatography, corresponding to the absence of 2,4-D, 2,4-DCP, and 4-chlorocatechol. Only trace amounts of smaller chlorinated components were possibly still present. These results are summarized in Figure 5. The similarity between the reaction intermediates identified in the γ radiolysis and sonolysis experiments further supports our argument that $^{\bullet}$OH-mediated reactions dominate the destruction of 2,4-D and 2,4DCP.

Effect of *tert*-Butyl Alcohol on the Sonolytic Degradation of 2,4-D. If indeed the hydroxyl radical is a major participant in the sonolytic degradation of 2,4-D, we should be able to suppress this reaction by using a known $^{\bullet}$OH radical scavenger in the solution. Sonolysis experiments were performed using *tert*-butyl alcohol, which is a common $^{\bullet}$OH radical scavenger in the radiolysis of water (reaction 8).

$$(CH_3)_3COH + {}^{\bullet}OH \rightarrow (CH_3)_2{}^{\bullet}CH_2COH + H_2O \quad (8)$$

Extensive work on the sonochemistry of *tert*-butyl alcohol has recently been reported by von Sonntag and co-workers.[32] They determined that the alcohol is pyrolized in the bubble via a free-radical-induced pyrolysis reaction mechanism. The *tert*-butyl alcohol is able to scavenge $^{\bullet}$OH radicals in the bubble and prevent the accumulation of $^{\bullet}$OH radicals at the interface of the bubble. In our experiments, varying concentrations of *tert*-butyl alcohol were added to 0.20 mM 2,4-D solutions. The results are summarized in Figure 6. In the presence of adequate $^{\bullet}$OH radical scavenger (0.05%), very little degradation of 2,4-D took place. The small decrease in the concentration of 2,4-D with adequate scavenger was accompanied by the presence of 2,4-DCP and catechol, both products of $^{\bullet}$OH-mediated reactions. At lower concentrations of the *tert*-butyl alcohol scavenger (<0.05%), 9−24% of the 2,4-D was degraded during 60 min of sonolysis. At these low *tert*-butyl alcohol concentrations, 2,4-D was able to compete for the $^{\bullet}$OH radicals at the bubble surface. As the *tert*-butyl alcohol continued to degrade, more hydroxyl radicals were available at the bubble interface for the 2,4-D to react. Another factor that also affects the rate of 2,4-D degradation is the formation of volatile products from the *tert*-butyl alcohol degradation that accumulate inside the bubble. Such volatile products decrease the temperature inside the bubble, which, in turn, slow the sonolytic reactions.[32] From these studies, we can infer that 2,4-D does not undergo direct pyrolysis in the sonolytic bubbles but rather becomes oxidized at the interface by reacting with $^{\bullet}$OH radicals.

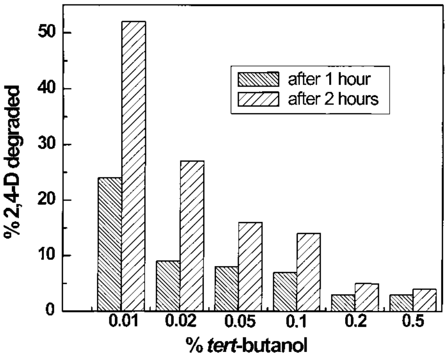


Figure 6. Degradation of 0.20 mM 2,4-D in the presence of *tert*-butyl alcohol (0.01−0.5%). The data show the percent degradation following 1 and 2 h of sonolysis using Ar as the sparging gas.

Analysis of 2,4-Dichlorophenol. A closer study of the intermediates and products formed in the sonolytic degradation of 2,4-D provided some additional insights into the $^{\bullet}$OH-mediated reactions. As mentioned earlier, the first stable intermediate formed in the $^{\bullet}$OH attack on 2,4-D is the corresponding phenolic form, 2,4-DCP. 2,4-Dichlorophenol has been reported to be a more toxic and problematic intermediate in $^{\bullet}$OH-mediated processes than the parent compound, 2,4-D.[22] In the present sonolysis work, the concentration of 2,4-DCP never increased above the level of 0.015 mM when 2,4-D (0.20 mM) was subjected to high-frequency ultrasound waves, indicating that it is readily degraded.

The low-level accumulation of 2,4-DCP is indicative of the fact that it also competes well for the OH radicals at the bubble surface. Separate sonolysis experiments were performed using 0.18 mM 2,4-dichlorophenol solution (pH 5.7). Under Ar-saturated conditions, the lifetime of 2,4-DCP in the solutions at pH 5.7 was 13 min. When oxygen was used as the sparging gas, the lifetime was slightly increased to 15 min. A 2,4-DCP solution adjusted to pH 3 was tested under the same experimental conditions. The rate of reaction was slightly greater at the lower pH, with a calculated lifetime of 12 min (See Table 1). The rate of degradation of the chlorinated phenol was faster than that of the organic acid 2,4-D under all conditions tested. The greater hydrophobicity of 2,4-DCP is likely to be the reason

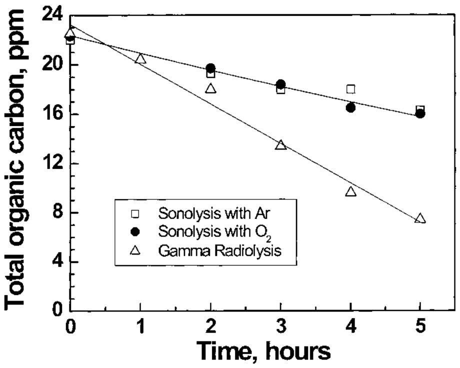


Figure 7. Change in total organic carbon (TOC) of 2,4-D in aqueous solution during 5 h of sonolysis and γ radiolysis. Sparging gases: Ar (□), O_2 (●), and N_2O(g) with γ radiolysis (△).

for the increased reactivity as it will accumulate preferentially at the air/water interface over the 2,4-D.

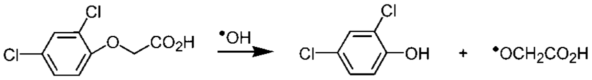
Extent of Mineralization. In the sonolytic degradation of 2,4-D, the final product before mineralization to carbon dioxide is oxalic acid. When solutions of oxalic acid were subjected to high-frequency ultrasound waves under O_2-saturated and Ar-saturated conditions for 2 h, no change in concentration was detected under either atmosphere. Furthermore, the ultrasonic degradation of 2,4-D showed very little change in overall carbon content after 3 h, where oxalic acid accounted for 95% of the remaining carbon. This suggests that oxalic acid constitutes an endpoint in the mechanistic pathways for the sonolytic degradation of 2,4-D. Solutions of glyoxylic acid and glycolic acid were also subjected to high-frequency ultrasonic waves. Both compounds underwent chemical transformations to yield oxalic acid, at which point little or no further change took place. Other papers have reported similar findings of low mineralization in sonolytic degradation of organic compounds.[46,47]

The accumulation of oxalic acid might arise from either the lack of reactivity of oxalic acid toward •OH radicals or its inability to accumulate at the bubble (air/water) interface. To examine the reactivity of •OH radicals, we analyzed the oxalic acid concentration and total organic carbon (TOC) in the γ radiolysis of N_2O-saturated aqueous solutions of 2,4-D. The mineralization of 2,4-D proceeds at a much higher rate under radiolytic conditions than in sonolysis (Figure 7). After 4 h of radiolysis, 60% of the 2,4-D was mineralized, whereas less than 25% of the 2,4-D was mineralized after 4 h using high-frequency ultrasound. Thus, it is evident that lack of reactivity toward •OH radicals is not the major cause for oxalic acid accumulation in the sonolysis of 2,4-D solutions.

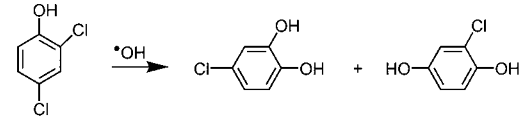
Moreover, oxalic acid is known to degrade via hydroxyl radicals.[48,49] Therefore, the origin of the slow mineralization of oxalic acid is not an inherently slow reaction with hydroxyl radicals. γ-Radiolysis experiments conducted using a N_2O-saturated oxalic acid solution revealed a lifetime of approximately 35 min. However, the concentration of oxalic acid was not affected during 2 h of sonolysis. The extremely high polarity of oxalic acid makes its adsorption at the bubble interface less probable. Because most of the hydroxyl radical attack occurs at the bubble interface, we see little chemical transformation of oxalic acid. These studies, as well as those showing the difference in reactivity of protonated and deprotonated forms of other compounds, lead us to believe that the extent of hydroxyl radical attack in the bulk solution is extremely small compared to that of the reaction pathways at the bubble interface.

Mechanism of 2,4-D Degradation. Another important aspect that can shed light into the •OH-radical-mediated transformations of 2,4-D is the release of chloride ion. The chloride ion concentration in the sonolysis and radiolysis of 2,4-D was monitored using ion chromatography. Figure 5 shows the buildup of the chloride ion concentration following the radiolysis of a 2,4-D solution. The release of chloride ion in the first few minutes is rather slow, and its growth rate is independent of 2,4-D decay. A similar pattern of chloride ion accumulation was also noted in the sonolysis experiments. The slow chloride ion buildup in these experiments correlated with the formation of chlorinated aromatic intermediates, viz., 2,4-DCP. The delayed appearance of chloride ions along with the clear presence of 2,4-DCP suggests that the initial step in the mechanism is the •OH attack ipso to the ether substituent (Scheme 1). The next steps in the mechanism involve hydroxyl radical attacks on 2,4-DCP at the carbons containing the chlorines (ipso attacks), which corresponds to the steady increase in chloride ions. The hydroxyl attack is followed by loss of HCl, which restores the aromatic ring and affords the monochlorinated intermediates 4-chlorocatechol and 2-chlorohydroquinone (Scheme 2). Further radical reactions with hydroxyl or hydrogen atoms (sonolysis) leads to the dechlorinated aromatics (hydroquinone, catechol, and 1,2,4-benzenetriol), which were detected readily via HPLC throughout the degradation process (Scheme 3). The oxidative degradation of these primary intermediates proceeds with a ring-opening reaction via hydroxyl radical attack. In sonolysis, the degradation of 2,4-D yields oxalic acid as the end product. However, with a proper strategy of •OH radical attack, it can be further mineralized (e.g., via radiolysis) to carbon dioxide and water. Studies indicate that the intermediate steps from oxidized aromatics to highly oxidized short-chain acids involve many competing pathways,[50,51] thus adding further complexity to the simple degradation mechanism presented here. Further modeling work is being done in our laboratory to better understand the mechanism of the hydroxyl-radical-mediated degradation.

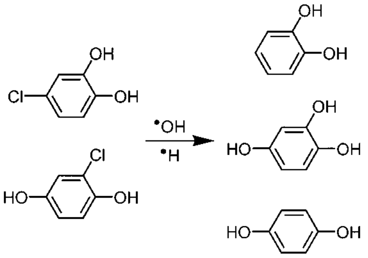
SCHEME 1



SCHEME 2



SCHEME 3



Conclusion

In this investigation, high-frequency sonolysis has been shown to be effective in the degradation of the herbicide 2,4-D. The technique is extremely useful for minimizing the accumulation of the toxic intermediate 2,4-dichlorophenol. The major end product of the degradation of 2,4-D is oxalic acid, which is resistant to sonochemical degradation. Comparisons with the γ-radiolysis experiments confirm that the hydroxyl radical is the main reactive species in the ultrasonic destruction of 2,4-dichlorophenoxyacetic acid and 2,4-dichlorophenol. The hydroxyl radical attack is limited mainly to the organics accumulated near the cavitation bubble interface. Efforts are underway to couple this technique with another advanced oxidation process (e.g., photocatalysis) and complete the mineralization process.

Acknowledgment. We thank I. Duncanson for the design of the sonolysis cell; Dr. K. Vinodgopal for many useful discussions; and the Department of Chemistry, Indiana University Northwest, for providing the facilities to perform HPLC and TOC analysis. The work described herein was supported by the Office of the Basic Energy Sciences of the U.S. Department of Energy. This is Contribution No. 4151 from the Notre Dame Radiation Laboratory.

References and Notes

(1) Nishioka, M. G.; Burlholder, H. M.; Brinkman, M. C.; Battelle, C.H. *Trasnport of Lawn-Applied 2,4-D from Turf to Home: Assessing the Relative Importance of Transport Mechanisms and Exposure Pathways*; National Exposure Research Laboratory; U.S. Environmental Protection Agency: Washington, D.C., 1999.

(2) Nishioka, M. G.; Burkholder, H. M.; Brinkman, M. C.; Gordon, S. M. *Environ. Sci. Technol.* **1996**, *30*, 3313−3320.

(3) Aly, O. M.; Faust, S. D. *J. Agric. Food Chem.* **1964**, *12*, 541.

(4) Erne, K. *Acta Chem. Scand.* **1963**, *17*, 1663−1676.

(5) Robson, T. O. Some studies of the persistence of 2,4-D in natural surface waters in Britain. *Proc. 8th Brit. Weed Control Conf.*, British Crop Protection Council Farnham, Surrey, U.K., 1966.

(6) *The Agrochemicals Handbook*, 2nd ed.; The Royal Society of Chemistry: Cambridge, U.K., 1990.

(7) Serpone, N.; Pelizzetti, E. *Photocatalysis. Fundamentals and Applications*; John Wiley and Sons: New York, 1989.

(8) Legrini, O.; Oliveros, E.; Braun, A. M. *Chem. Rev.* **1993**, *93*, 671−698.

(9) Ollis, D. F.; Pelizzetti, E.; Serpone, N. *Environ. Sci. Technol.* **1991**, *25*, 1523−1529.

(10) Zeltner, W. A.; Hill, C. G., Jr.; Anderson, M. A. *CHEMTECH* **1994**, 21−27.

(11) Hoffmann, M. R.; Martin, S. T.; Choi, W.; Bahnemann, D. W. *Chem. Rev.* **1995**, *95*, 69−96.

(12) Stafford, U.; Gray, K. A.; Kamat, P. V. *Heterogeneous Chem. Rev.* **1996**, *3*, 77−104.

(13) Gray, K. A.; Cleland, M. R. *J. Adv. Oxid. Technol.* **1998**, *3*, 22−36.

(14) Kamat, P. V.; Vinodgopal, K. Environmental Photochemistry with Semiconductor Nanoparticles. In *Organic and Inorganic Photochemistry*; Ramamurthy, V., Schanze, K., Eds.; Marcel Dekker: New York, 1998; Vol. 2; pp 307−350.

(15) Ibanez, G. J.; Swain, M. G. *J. Appl. Electrochem.* **1994**, *24*, 1077−1091.

(16) Naffrechoux, E.; Chanoux, S.; Petrier, C.; Suptil, J. *Ultrason. Sonochem.* **2000**, *7*, 255−259.

(17) Destaillats, H.; Colussi, A. J.; Joseph, J. M.; Hoffmann, M. R. *J. Phys. Chem. A* **2000**, *104*, 8930−8935.

(18) Sun, Y. F.; Pignatello, J. J. *J. Agric. Food Chem.* **1993**, *41*, 1139−1142.

(19) Sun, Y.; Pignatello, J. J. *Environ. Sci. Technol.* **1995**, *29*, 2065−2072.

(20) Pignatello, J. J. *Environ. Sci. Technol.* **1992**, *26*, 944−951.

(21) Djebbar, K.; Sehili, T. *Pestic. Sci.* **1998**, *54*, 269−276.

(22) Lu, M.-C.; Chen, J.-N. *Water Sci. Technol.* **1997**, *36*, 117−122.

(23) Herrmann, J. M.; Disdier, J.; Pichat, P.; Malato, S.; Blanco, J. *Appl. Catal. B: Environ.* **1998**, *17*, 15−23.

(24) Beaton, Y.; Shaw, L. J.; Glover, L. A.; Meharg, A. A.; Killham, K. *Environ. Sci. Technol.* **1999**, *33*, 4086−4091.

(25) Sun, Y.; Pignatello, J. J. *J. Agric. Food Chem.* **1993**, *41*, 308−312.

(26) Pichat, P.; D'Oliveira, J.-C.; Maffre, J.-F.; Mas, D. Destruction of 2,4-dichlorophenoxyethanoic acid (2,4-D) in water by TiO2−UV, H2O2−UV or direct photolysis. In *Photocatalytic Purification and Treatment of Water and Air*; Ollis, D. F., Al-Ekabi, H., Ed.; Elsevier: Amsterdam, 1993.

(27) Muller, T. S.; Sun, Z. L.; Kumar, G.; Itoh, K.; Murabayashi, M. *Chemosphere* **1998**, *36*, 2043−2055.

(28) Hart, E. J.; Henglein, A. *J. Phys. Chem.* **1985**, *89*, 4342−4347.

(29) Hua, I.; Hoffman, M. R. *Environ. Sci. Technol.* **1997**, *31*, 2237−2243.

(30) Petrier, C.; Lamy, M.-F.; Francony, A.; Benahcene, A.; David, B.; Renaudin, V.; Gondrexon, N. *J. Phys. Chem.* **1994**, *98*, 10514−10520.

(31) Thompson, L. H.; Doraiswamy, L. K. *Ind. Eng. Chem.* **1999**, *38*, 1215−1249.

(32) Tauber, A.; Mark, G.; Schuchmann, H.-P.; von Sonntag, C. *J. Chem. Soc., Perkin Trans.* **1999**, *2*, 1129−1135.

(33) De Visscher, A.; Van Eenoo, P.; Drijvers, D.; Van Langenhove, H. *J. Phys. Chem.* **1996**, *100*, 11636−11642.

(34) Hart, E. J.; Fischer, C.-H.; Henglein, A. *Radiat. Phys. Chem.* **1990**, *36*, 511−516.

(35) Hart, E. J.; Fischer, C.-H.; Henglein, A. *J. Phys. Chem.* **1990**, *94*, 284−290.

(36) Drijvers, D.; DeBaets, R.; DeVisscher, A.; VanLangenhove, H. *Ultrason. Sonochem.* **1996**, *3*, S83−S90.

(37) Makino, K.; Mossoba, P.; Riesz, P. *Radiat. Res.* **1983**, *96*, 416−421.

(38) Mark, G.; Tauber, A.; Laupert, R.; Schuchmann, H.-P.; Schulz, D.; Mues, A.; von Sonntag, C. *Ultrason. Sonochem.* **1998**, *5*, 41−52.

(39) Fisher, C. H.; Hart, E. J.; Henglein, A. *J. Phys. Chem.* **1986**, *90*, 1954−1956.

(40) Tauber, A.; Schuchmann, H.-P.; von Sonntag, C. *Ultrason. Sonochem.* **2000**, *7*, 45−52.

(41) Petrier, C.; Jeunet, A.; Luche, J.-L.; Reverdy, G. *J. Am. Chem. Soc.* **1992**, *114*, 3148−3150.

(42) Petrier, C.; Jiang, Y.; Lamy, M.-F. *Environ. Sci. Technol.* **1998**, *32*, 1316−1318.

(43) Ashokkumar, M.; Vinodgopal, K.; Grieser, F. *J. Phys. Chem. B* **2000**, *104*, 6447−6451.

(44) Currell, D. L.; Wilheim, G.; Nagy, S. *J. Am. Chem. Soc.* **1963**, *85*, 127−130.

(45) Quint, R. M.; Park, H. R.; Krajnik, Solar, S.; Getoff, N.; Sehested, K. *Radiat. Phys. Chem.* **1996**, *47*, 835−845.

(46) Stock, N. L.; Peller, J.; Vinodgopal, K.; Kamat, P. V. *Environ. Sci. Technol.* **2000**, *34*, 1747−1750.

(47) Colarusso, P.; Serpone, N. *Res. Chem. Intermed.* **1996**, *22*, 61−89.

(48) Draganic, Z. D.; Draganic, I. G.; Kosanic, M. M. *J. Phys. Chem.* **1964**, *68*, 2085−2092.

(49) Draganic, Z. D.; Draganic, I. G.; Kosanic, M. M. *J. Phys. Chem.* **1966**, *70*, 1418−1425.

(50) Li, X. J.; Cubbage, J. W.; Tetzlaff, T. A.; Jenks, W. S. *J. Org. Chem.* **1999**, *64*, 8509−8524.

(51) Li, X. J.; Cubbage, J. W.; Jenks, W. S. *J. Org. Chem.* **1999**, *64*, 8525−8536.