Radiolytic Transformations of Chlorinated Phenols and Chlorinated Phenoxyacetic Acids

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Hydroxyl radical reactions of selected chlorinated aromatic phenols (2,4-dichlorophenol, 2,4,6-trichlorophenol, and pentachlorophenol) and chlorinated phenoxyacetic acids [2,4-dichlorophenoxyacetic acid (2,4-D), 2,4-D methyl ester, 2-(2,4-dichlorophenoxy)propionic acid (2,4-DP)] were studied using the radiolysis techniques of pulse radiolysis and γ radiolysis. Hydroxyl radical addition was the prominent reaction pathway for the chlorinated phenoxyacetic acids and also for the chlorinated phenols at pH values below the pK_a of the compounds. A very prominent change in $^{\bullet}$OH reactivity was observed with the chlorinated phenoxide ions in high pH solutions. Two different reaction pathways were clearly present between the hydroxyl radical and the chlorinated phenoxide ions. One of the reaction pathways was suppressed when the concentration of chlorinated phenoxide ions was increased 10-fold. Amid a greater electron-withdrawing presence on the aromatic ring (higher chlorinated phenoxide ions), the hydroxyl radical reacted preferably by way of addition to the aromatic ring. Steady-state experiments utilizing γ radiolysis also showed a substantial decrease in oxidation with an increase in pH of substrate.

Introduction

Over the past few decades, it has become clear that most organic compounds are readily oxidized by the hydroxyl radical during advanced oxidation remediation processes.[1−7] Oxidations can take place by hydroxyl radical addition to an electron rich system, by abstraction of a hydrogen atom, or by the transfer of an electron. The hydroxyl radical is electrophilic and readily forms $^{\bullet}$OH-adducts in its addition reactions with a variety of aromatic organics.[8−12] Recent experimental and computational studies have shown that the widely utilized herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) is oxidized by the hydroxyl radical, by way of $^{\bullet}$OH-addition to the aromatic ring; the stable compound 2,4-dichlorophenol (2,4-DCP) forms through this oxidative transformation.[13−15]

The importance of gaining knowledge of the $^{\bullet}$OH reactions with 2,4-D is evident considering 2,4-dichlorophenoxyacetic acid (2,4-D) is one of the most widely used herbicides in the United States, and the huge dependence by the agricultural community on herbicides has led to the detection of these compounds and their degradation products in natural bodies of water.[16−18] To ensure safe water supplies, advanced water treatments, which eliminate the dangers of herbicidal contamination, are an anticipated necessity and have been under scrutinous study for many years. Termed advanced oxidation processes (AOPs) or technologies (AOTs), these treatments rely largely on the highly reactive hydroxyl radical to render oxidation products that are harmless.[2] The main stable product of the initial 2,4-D transformation is 2,4-DCP, a compound considered more toxic than the herbicide and slightly less reactive with the hydroxyl radical.

Although 2,4-dichlorophenol possesses similar aromatic structure to 2,4-D, the rates of oxidative degradation by the hydroxyl radical reaction differ.[6] A major goal of the reported study was to investigate the differences in hydroxyl radical reactivity with chlorinated aromatic compounds such as 2,4-D and 2,4-DCP, as a function of the number of chlorines and/or type of oxygen substituents on the ring and also as a function of pH. The difference in oxidation potentials of chlorinated phenols has been reported and shows clear evidence of more than one oxidative mechanism, dependent on the number of chlorine substituents.[19] Pentahalophenol oxidations show variation in reactivity according to the halide substituent.[20] Many other substituent effects have been investigated to better comprehend the reactivity of the hydroxyl radical with a wide variety of aromatic compounds.[21−25] The aromatic compounds selected for this study (in addition to 2,4-D and 2,4-DCP) include 2-(2,4-dichlorophenoxy)propionic acid (2,4-DP), 2,4-D methyl ester, 2,4,6-trichlorophenol (2,4−6-TCP), and pentachlorophenol (PCP), all of which are displayed in Figure 1. These compounds possess varied degrees of electron density in their aromatic rings, due to the effects of the electron-withdrawing chlorine atoms, and small differences in structure and electronics from the oxygen substituents.

To realize the complete value of $^{\bullet}$OH-mediated processes, the chemical pathways must be defined. The most controlled conditions for the study of $^{\bullet}$OH reactions are met through radiolytic systems, even though the hydroxyl radical can be produced through a number of different means: high frequency ultrasound, photocatalysis, and ozonolysis, etc. Pulse radiolysis is a radiolysis technique that utilizes a high-energy source such as an electron accelerator to form transients which are detected on very short time scales. These experiments relay information about the initial steps of the hydroxyl radical reaction pathways. The determination of the early radical reactions in the mechanistic pathways offers insight into the ensuing chemistry involved in the oxidations. γ radiolysis is a useful radiolysis technique for the steady-state investigations of organic compounds in aqueous solutions. High-energy γ rays promote the formation of hydroxyl radicals in aqueous solutions. Product analyses at various times in the hydroxyl radical oxidations offer

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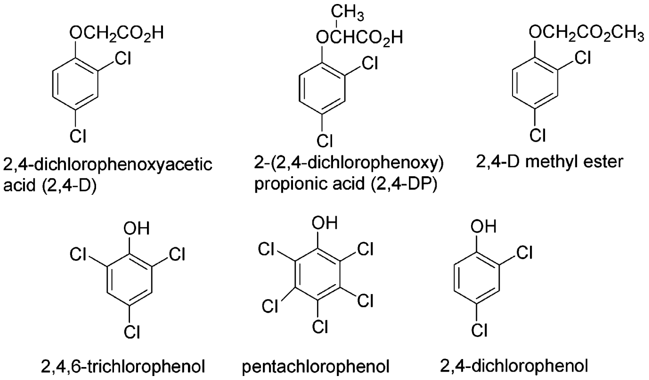


Figure 1. Compounds utilized in this study.

data on the mechanistic pathways, when the intermediates of the processes are identified.

This study reports the reactions of the model compounds with the hydroxyl radical using the radiolysis techniques of pulse radiolysis and γ radiolysis. The pH effect was also an important aspect of the investigation. A very prominent change in early reactivity was seen in the cases of the chlorinated phenoxide ions, where one-electron oxidations are prevelant.[21,26,27] An increase in the number of electron-withdrawing chlorine atoms on the aromatic ring corresponded to a significant shift in the preferred pathway of the chlorinated phenoxide ions with the hydroxyl radical.

Experimental Section

γ-Radiolysis and Pulse Radiolysis. The cobalt-60 source used as the source of γ rays is a Shepherd 109, manufactured by the Shepherd Co. Cobalt-60 emits high-energy (1.25 MeV) photons. For oxidative conditions, aqueous solutions were sparged with N_2O(g) to saturate the solutions before γ-irradiation. Samples were irradiated for the indicated times. The dose rate was 3 krad/min, as measured by Fricke dosimetry.

Pulse radiolysis experiments were performed with the 8-MeV Titan Beta model TBS-8/16-1S linear accelerator, using pulses of 2 ns, which generate radical concentrations of 1−3 μM per pulse. All experimental data were taken by averaging 6 replicate shots using the continuous flow mode of the instrument. Solutions of 10 mM KSCN, N_2O-saturated, producing $[(SCN)_2^{\bullet-}]$ were used to determine the dose, based on a radiation chemical yield of 6.13 (0.635 μM J^{-1}) and an extinction coefficient of 7580 M^{-1} cm^{-1} at 472 nm.[28] The actual dose was determined to be 0.7−0.8 krad/pulse.

The effect of the ionizing radiation on the water solvent is illustrated in eq 1. The numbers in parentheses represent the G values, the number of species formed per 100 eV of energy. As long as the concentration of the solute in water is moderate (<0.1 M), the yields of aqueous electrons and hydroxyl radicals are equal. Nitrous oxide gas is used to scavenge the electrons and ultimately doubles the amount of hydroxyl radicals available for oxidation reactions (eq 2). The reactions of the hydroxyl radical were studied by using nitrous oxide-saturated solutions.

$$H_2O \rightsquigarrow e^-_{aq}\,(2.6) + H^\bullet\,(0.6) + {}^\bullet OH\,(2.7) + H_2\,(0.45) + H_2O_2\,(0.7) + H_3O^+ \quad (1)$$

$$H_2O + N_2O + e^-_{aq} \rightarrow N_2 + OH^- + {}^\bullet OH \quad (2)$$

When electron transfer conditions were desired, the azide radical was formed according to reaction 3. For the production of azide radicals, nitrous oxide conditions were utilized along with a relatively large amount of sodium azide solute, 10 mM.

$$N_3^- + {}^\bullet OH \rightarrow {}^\bullet N_3 + OH^- \; (k = 1.2 \times 10^{10}\ M^{-1}\,s^{-1}) \quad (3)$$

Reagents. The compounds, their sources, and purity are as follows: 2,4-dichlorophenoxyacetic acid (Aldrich, 99%), 2,4-dichlorophenol (Aldrich, 99%), 2,4-D methyl ester (Chem Service, 99.5%), 2-(2,4-dichlorophenoxy)propionic acid (Aldrich, 95%), 2,4,6-trichlorophenol (98%), pentachlorophenol (Aldrich, 98%), sodium azide (Fisher, granular), and sodium hydroxide (Fisher, pellets, Certified ACS).

HPLC Analyses. A Waters HPLC system (Milennium 2010 and Empower software, Waters 717 plus Autosampler, Waters 600 Controller Solvent Pump) with the Supelco Discovery HSF5 column (5 μm; 250 × 4.6 mm) was used. A solvent gradient consisting of acetonitrile and water (and water with 1% acetic acid) was utilized, beginning and ending with 100% acetonitrile. The gradient changed to 65% water approximately halfway through the analysis.

Results and Discussion

Pulse Radiolysis of 2,4-Dichlorophenol and Pentachlorophenol. 2,4-Dichlorophenol (2,4-DCP) is a toxic compound and the main intermediate in the 2,4-D degradation pathway.[15] The O−H bond present on the 2,4-DCP molecule is slightly acidic with a pK_a value of 7.89. The oxidation potential of the compound differs from that of the herbicide 2,4-D and from other chlorinated compounds.[19,29] Such differences in the oxidation potentials and substituents makes it important to compare the reactivity of chlorinated phenolic compounds toward hydroxyl radicals.

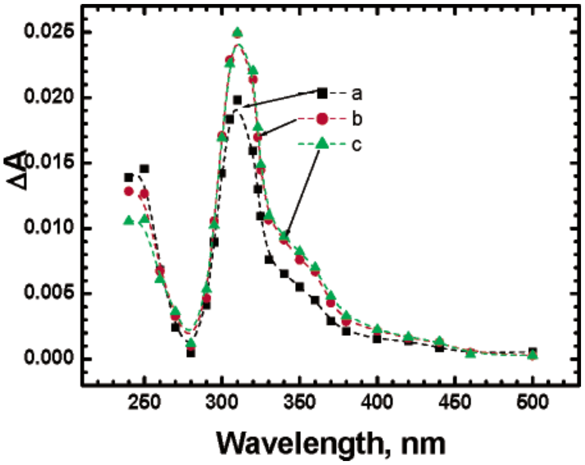


Figure 2. Difference absorption spectrum of the transient formed from the reaction between 2,4-DCP (0.23 mM and pH 5) and the hydroxyl radical at 750 nm recorded after electron pulse excitation: (a) 0.75, (b) 2.0, and (c) 3.0 μs.

Pulse radiolysis experiments were conducted with use of a 0.23 mM solution of 2,4-DCP at pH 5, which was saturated with nitrous oxide gas. As the reaction between ${}^\bullet$OH and 2,4-DCP proceeded, we observed an increase in the absorbance of the transient. The maximum absorbance of the transient, formed on the nanosecond time scale, was seen around 310 nm and is shown in Figure 2. The lifetime of the transient species was several microseconds and the transient absorption at 310 nm was assigned to the hydroxycyclohexadienyl radical of 2,4-dichlorophenol.

Experiments were then performed with 2,4-DCP solutions at high pH, in the range of 9.0−11.0, using NaOH to adjust the solution pH. In this pH range, the 2,4-dichlorophenoxide ion is

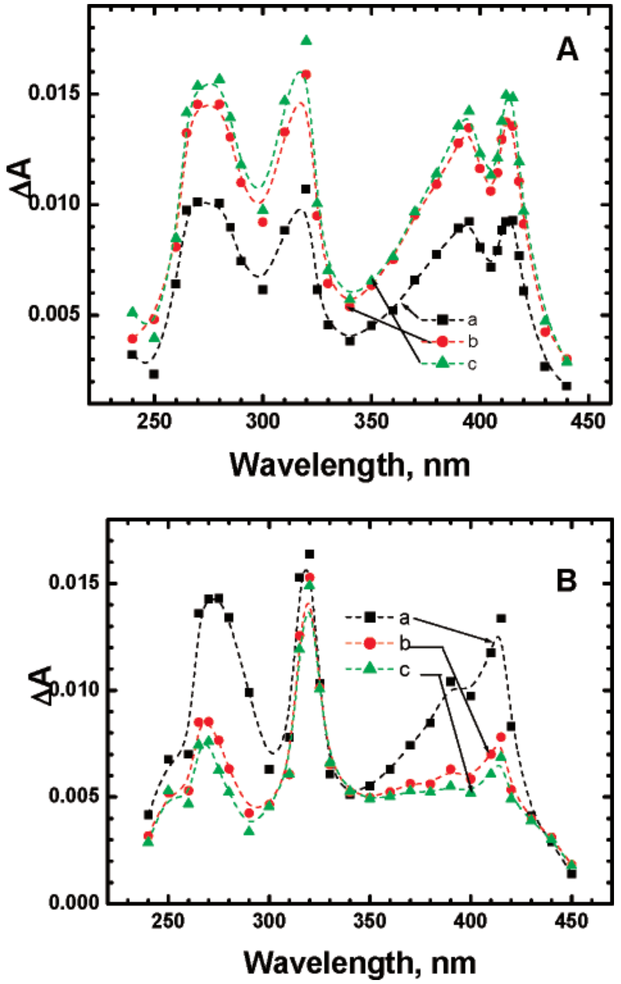


Figure 3. Time-resolved difference absorption spectrum of the transient formed from the reaction between 2,4-DCP (0.50 mM and pH 11) and the hydroxyl radical recorded after electron pulse excitation: (A) (a) 1.0, (b) 2.5, and (c) 5.0 μs and (B) (a) 20, (b) 120, and (c) 200 μs.

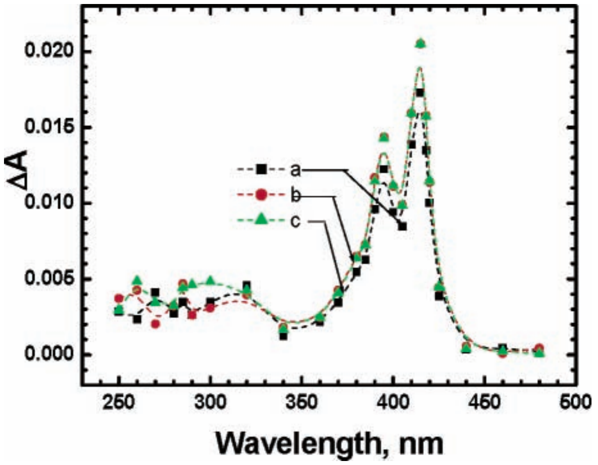


Figure 4. Difference transient absorption spectrum generated from the reaction between the azide radical and 1.0 mM 2,4-DCP (pH 9) at (a) 500 ns (■), (b) 1.5 μs (●), and (c) 3.0 μs (▲).

the major species in solution. With conditions established for the production of hydroxyl radicals, pulse radiolysis experiments were carried out. A transient profile was generated that differed significantly from the one at pH 5. Four prominent absorption peaks were noted on the difference transient absorption spectrum, illustrated in Figure 3. Although the transient absorbance at 273 nm formed and decayed on a time scale similar to the peaks at 390 and 415 nm, the absorption peak at 320 nm decayed much slower. The peak around 320 nm corresponds to the •OH-adduct of the 2,4-DCP anion or a species that forms from this radical anion. The double absorbance peaks centered around 400 nm represent the 2,4-dichlorophenoxyl radical.

The transient species responsible for the peaks centered around 400 nm in Figure 3 was verified by reacting the 2,4-dichlorophenoxide ion with the azide radical, an electron-transfer oxidant. Different from the •OH radical, the azide radical reacts selectively with aromatic compounds by direct electron transfer.[30] A solution of 1.0 mM 2,4-DCP and 10.0 mM sodium azide was adjusted to a pH of 9. The solution was saturated with nitrous oxide gas to ensure the scavenging of aqueous electrons. The transient spectrum generated under these conditions (displayed in Figure 4) shows two peaks centered around 400 nm, at approximately 393 and 415 nm. Various phenoxyl radicals show characteristic double absorbance peaks around 400 nm.[31−33] These results support our assignment of the peaks in the 400 nm region to the 2,4-dichlorophenoxyl radical. Furthermore, the rate of formation of the 2,4-DCP phenoxyl radical was determined to be (3.1 ±.2) × 10^9 M^{-1} s^{-1} at 415 nm, which corresponds well with the rates of the azide radical reactions with similar aromatic compounds,[30] and with the rate of formation of these peaks using the hydroxyl radical (5.5 ± 0.3) × 10^9 M^{-1} s^{-1}.

The formation and decay rates associated with the 2,4-dichlorophenoxyl radical from the •OH reaction (Figure 3 peaks at 390 and 415 nm) match those generated in the reaction between the 2,4-dichlorophenoxide ion and the azide radical (Figure 4). Furthermore, the peaks at 390 and 415 nm in Figure 3 are not linked with the growth and decay of the peak at 320 nm, which is assigned to a species from the hydroxyl radical addition to the 2,4-dichlorophenoxide ion. The transient at 320 nm decays at a slower rate than the 2,4-dichlorophenoxyl radical, indicating that two separate species exist in the •OH-mediated oxidation of the 2,4-dichlorophenoxide ion. This is evident from the transient spectrum in Figure 3B, recorded on the longer time scale, and is further clarified in the absorption decay graphs in Figure 5. The first graph represents the decay of the 2,4-dichlorophenoxyl radical (415 nm), while the second one is the •OH-addition transient (320 nm) decay.

Experiments that involved variation in substrate concentration further suggested the presence of more than one oxidative pathway with the hydroxyl radical. The solution concentrations prepared for the enhanced concentration experiments were 0.5 and 5.0 mM 2,4-DCP at natural pH values and at adjusted values of pH 10−11. While the concentration did not affect the chemistry of the reaction of 2,4-DCP and the hydroxyl radical at the natural pH (protonated form), a significant difference was detected in high pH solutions.

Pulse radiolysis of a 0.5 mM 2,4-DCP solution at pH 11 was a repeated experiment that, once again, generated the strong absorbance peaks displayed in Figure 3 at 275, 318, 393, and 415 nm. At pH 11 and 5.0 mM 2,4-DCP, the absorbance peaks that developed in the pulse radiolysis experiments at 393 and 415 nm were readily detected as early as 100 ns, while very little absorbance was noted at 318 nm (Figure 6). The high concentration of the 2,4-dichlorophenoxide ion in reaction with hydroxyl radicals resulted in a spectrum void of the lower wavelength absorbance peaks (275 and 318 nm). Clearly, one of the reaction pathways utilized by 2,4-dichlorophenoxide and •OH was affected by the higher ground-state concentration of 2,4-dichlorophenoxide ions. The elevated concentration of ground-state 2,4-DCP$^-$ interfered with the •OH-addition reaction pathway. The reaction pathway involving the formation of the

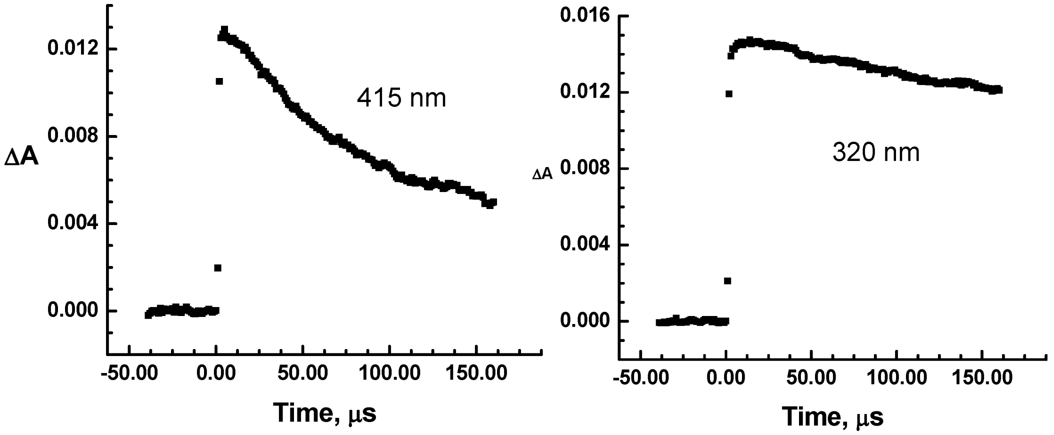


Figure 5. Decay of the 2,4-dichlorophenoxyl radical at 415 nm and decay of the •OH-adduct at 320 nm on the 200 *μ*s time scale.

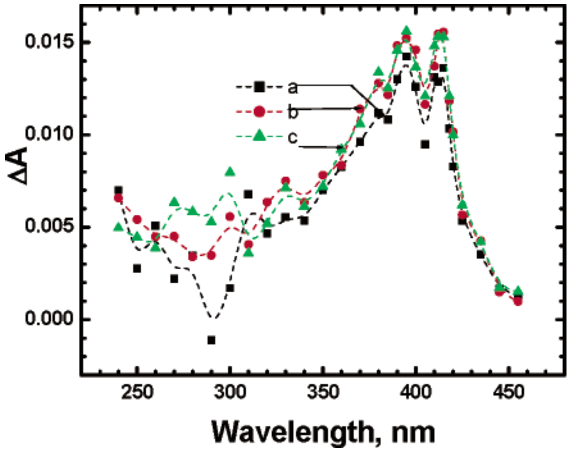


Figure 6. Difference absorption spectra of the transient generated from reaction of the 2,4-DCP anion with •OH using 5.0 mM 2,4-DCP at (a) 100, (b) 500, and (c) 900 ns.

2,4-dichlorophenoxyl radical was not affected by the high concentration of ground-state 2,4-dichlorophenoxide ions, an indication that it evolves separately from the 320 nm species.

In one mechanistic pathway, the electrophilic hydroxyl radical adds to the aromatic ring of the chlorinated phenoxide ion, and a relatively long-lived transient appears at 320 nm. Other halogenated phenoxide ions have generated very similar difference transient absorption spectra when reacted with the hydroxyl radical.[20] A separate reaction pathway between the hydroxyl radical and the deprotonated form of 2,4-DCP involves the formation of the 2,4-dichlorophenoxyl radical; its presence was verified by comparison to the spectrum generated from the reaction of the 2,4-dichlorophenoxide ion with the azide radical. The 2,4-dichlorophenoxyl radical likely forms through a direct electron-transfer reaction.

While many papers in the literature support a phenoxyl radical formation mechanism that begins with an •OH attack on the aromatic ring,[34−38] no evidence exists in these studies to support such a pathway to the phenoxide ion. To accept this mechanism, the argument would have to be made that at least two different types of •OH addition reactions take place, one of which would lead to the phenoxyl radical, and one which would lead to the transient at 320 nm. An ipso addition would be one type of •OH addition, and the second type of addition would take place at an unsubstituted carbon of the aromatic ring. Moreover, one of these addition reactions would account for the presence of the transient at 320 nm (i.e., an ipso attack), and the other addition would lead to formation of the radical species which gives rise to the transient absorption at 390 and 415 nm.

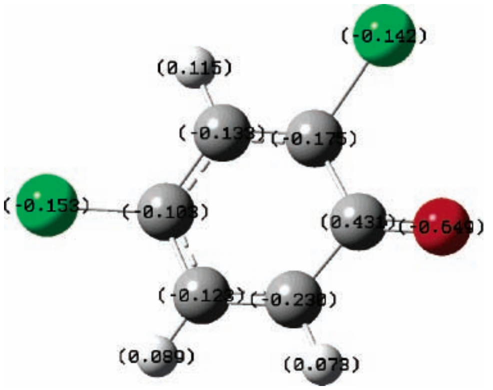


Figure 7. Mulliken charges calculated for the 2,4-dichlorophenoxide ion.

If the first of the two possible •OH additions considered is an ipso attack, the •OH reacts at a substituted position of the 2,4-DCP anion. Carbon atoms 2 and 4 on the ring are each bonded to a chlorine atom, and carbon 1 is bonded to the oxygen. Attack of the electrophilic hydroxyl radicals at carbon 1 (C−O) is the least likely, due to the electropositive nature of the site. Other studies have also concluded this ipso site is less subject to hydroxyl radical attack.[22] An analysis of the Mulliken charges on the 2,4-dichlorophenoxide ion (Figure 7) clearly indicates that carbon 1 is least likely to be attacked by an electrophilic species. Assuming that carbon 1 is not a site of reactivity, carbons 2 and 4 are equivalent ipso attacks, while the unsubstituted carbon atoms offer the other reactive sites.

To reduce the prospect of two different types of •OH addition reactions, a fully substituted compound, the pentachlorophenoxide ion, was tested. If only the addition−elimination mechanism is in place with the hydroxyl radical, the pentachlorophenoxide ion should show exclusive formation of either the corresponding phenoxyl radical or the product of the •OH-addition transient. To test this hypothesis and verify the findings of Terzian et al.,[20] experiments were performed with the pentachlorophenoxide ion.

A 0.50 mM solution of pentachlorophenol, PCP, was prepared and the solution pH was adjusted to 11. The transient absorption spectrum generated from the pulse radiolysis experiments (Figure 8) clearly indicates the presence of both the pentachlorophenoxyl radical (430 nm, 452 nm) and the species formed from hydroxyl radical addition (330 nm). Once again, the absorption peaks for the different radical species formed on a similar time scale. The spectral features of Figure 8 lead to the conclusion that both •OH-addition and electron transfer mechanistic pathways are utilized by the hydroxyl radical in the

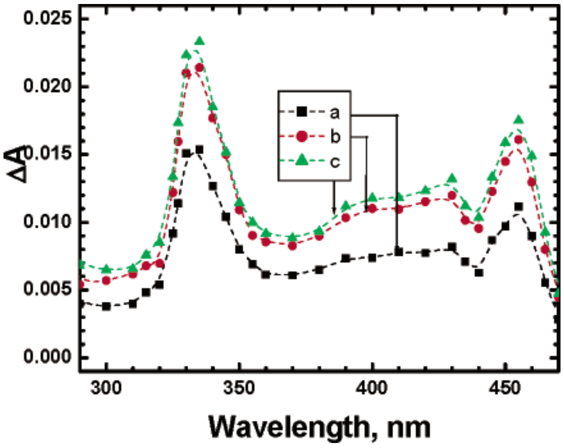


Figure 8. Difference transient absorption spectrum from the reaction between 0.50 mM pentachlorophenol, saturated with N_2O, at pH 11 and the hydroxyl radical at (a) 300 ns, (b) 1.0 μs, and (c) 3.0 μs.

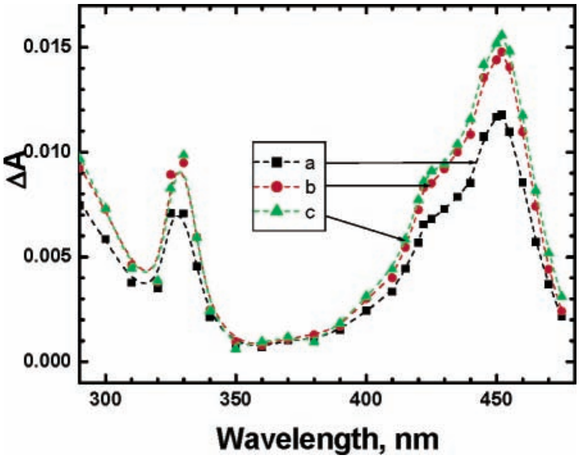


Figure 9. Difference absorption spectra of the transient generated from the reaction of 0.50 mM pentachlorophenol, saturated with N_2O, at pH 10 and 10.0 mM NaN_3 at (a) 500 ns, (b) 1.0 μs, and (c) 3.0 μs.

presence of the pentachlorophenoxide ion. Since all the ring carbons are substituted, only ipso additions by the hydroxyl radical can take place in the reaction with the pentachlorophenoxide ion. The absorption peak at 330 nm is assigned to the transient species formed from the hydroxyl radical addition to the aromatic ring. While an argument for the $^{\bullet}$OH attack at carbon 1 may exist in the formation of the pentachlorophenoxyl radical, the initial step would be accompanied by the loss of OH^- to form the pentachlorophenoxyl radical. The logistics of this pathway requires the appearance of one transient species followed by its decay and the formation of another transient. None of the transient data collected in this study support this type of mechanism, but the possibility does exist that a transient forms, which is too short-lived to be detected under the experimental conditions. The transient absorption peaks present at 430 and 452 nm, which form at a similar rate to the aforementioned absorption peak (330 nm), represent the pentachlorophenoxyl radical, likely formed through an electron-transfer reaction.

The pentachlorophenoxide ion forms the pentachlorophenoxyl radical upon reaction with the azide radical. This reaction was used to verify the electron-transfer reaction that takes place between the hydroxyl radical and pentachlorophenoxide ion. In the experiments, a solution containing 10 mM NaN_3 and 0.5 mM pentachlorophenol was prepared and adjusted to pH 10. (It is worthwhile to note that the azide radical shows strong absorption at 274 nm on the transient absorption spectrum in the absence of a suitable reductant.) The bimolecular rate constant for the reaction between the hydroxyl radical and the azide ion, where the rate is pH dependent, was calculated as 3 ($\pm$ 0.6) $\times$ 10^9 M^{-1} s^{-1} at a solution pH of 8.1, slightly lower than that reported by Alfassi and Schuler[30] and Hayon and Simic[39] (1 $\times$ 10^{10} M^{-1} s^{-1}). In competition with the azide ion for the hydroxyl radical is the pentachlorophenoxide ion. The rate constant for the reaction between the hydroxyl radical and PCP^- was calculated as 5.0 ($\pm$ 0.3) $\times$ 10^9 M^{-1} s^{-1}. While the concentration of azide ions was much higher in the experiment, the competition by the pentachlorophenoxide ion for the hydroxyl radical existed. The difference transient absorption spectrum displays very clear peaks for the pentachlorophenoxyl radical formed by the reaction between the pentachlorophenoxide ion and the azide radical and a smaller peak for the $^{\bullet}$OH-addition product at 338 nm, from the competition reaction (Figure 9).

The rate of the electron-transfer reaction between the azide radical and PCP^-, 4.1 ($\pm$ 0.1) $\times$ 10^9 M^{-1} s^{-1}, is the same as the rate calculated for the reaction between the hydroxyl radical and PCP^- for the species at 430/452 nm, 4.2 ($\pm$ 0.3) $\times$ 10^9 M^{-1} s^{-1}. This further substantiates the existence of a competetive pathway (electron transfer) in the formation of the chlorinated phenoxyl radical. Furthermore, neither the chlorinated phenoxyl radicals nor their formation is affected by high solute concentrations.

While all of the chlorinated phenoxide ions in this study lead to the formation of more than one transient species, a notable distinction exists in the preferred reaction with the $^{\bullet}$OH according to the degree of chlorine substituents. The transient absorbance peaks representing the pentachlorophenoxyl radical (430 nm, 452 nm) are weak relative to the absorbance peak for the $^{\bullet}$OH-addition transient (335 nm). Chlorine atoms attached to the aromatic ring withdraw electron density, leaving the oxygen of pentachlorophenoxide slightly less negative than a lesser or nonchlorinated ring. Therefore, the electron transfer pathway between the pentachlorophenoxide ion and the hydroxyl radical is predicted to take place to a lesser extent; the hydroxyl radicals are more likely to add to the ring. To verify the differences in the negative character of the oxygens of the various phenoxide ions, calculations of the Mulliken charges of the pentachlorophenoxide ion and the other chlorinated phenoxide ions were performed. The calculations indicate lower electron density on the oxygen of pentachlorophenoxide in comparison to the lesser chlorinated phenoxide ions.

Reaction Pathways of Chlorinated Phenols. While the chlorinated phenols in the protonated state react with the hydroxyl radical almost exclusively via hydroxyl radical addition, the chlorinated phenoxide ions are able to react through either an electron transfer mechanism or an addition reaction, which is likely followed by elimination. Both reaction mechanisms take place according to the data gathered in this study when the hydroxyl radical reacts with 2,4-dichlorophenoxide, 2,4,6-trichlorophenoxide, and pentachlorophenoxide ions. The formation of chlorinated phenoxyl radicals, known to be quite stable,[40−42] varies according to the number of chlorine atoms on the aromatic ring. The behavior of 4-chlorophenoxide ion has also been reported to follow this pattern of reactivity.[43] The phenoxide ion (nonchlorinated), which harbors the largest electron density on the oxygen since the aromatic ring carbons are not bonded to any electron withdrawing chlorine atoms, was reported to react with the hydroxyl radical exclusively forming the phenoxyl radical, with no $^{\bullet}$OH-addition transient detected.[34,44] Selective reactions are displayed in Scheme 1.

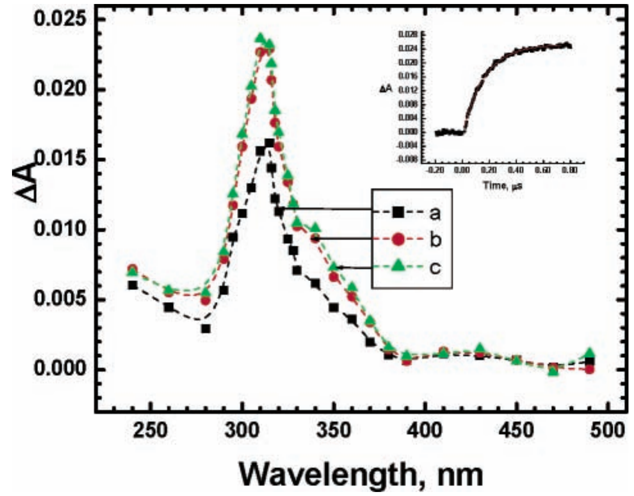
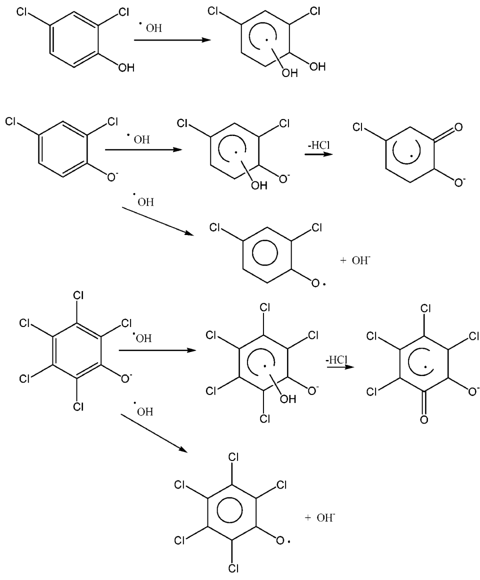


Figure 10. Difference absorption spectrum of the transient formed from the reaction between 2,4-D and the hydroxyl radical at (a) 200 ns, (b) 600 ns, and (c) 1.0 μs. The insert shows the growth of the transient at 310 nm.

SCHEME 1: Reactions of 2,4-DCP and PCP with the Hydroxyl Radical



Pulse Radiolysis of 2,4-D and Its Derivatives. After establishing the reactivity of chlorinated phenols, we extended this study to probe the effect of other substituents while maintaining the aromatic core. Pulse radiolysis experiments were carried out to determine the initial reactions that take place between •OH or $^{\bullet}N_3$ and the herbicide 2,4-D and its derivative compounds 2,4-DP and 2,4-D methyl ester (shown in Figure 1). Structural differences between 2,4-D and the derivative compounds are located specifically on the side chain of the ring. Any variation in pulse radiolysis-generated spectra would then point to radical reactions taking place on the side chain of the compounds. Steady state radiolysis experiments have conclusively shown that the main intermediate in the oxidative breakdown of 2,4-D and the derivative compounds is 2,4-dichlorophenol (2,4-DCP).[13]

The first of several pulse radiolysis experiments was conducted with use of an N_2O-saturated, 1.0 mM 2,4-D solution (pH 2.5). A strong transient absorption peak at 310 nm, shown in Figure 10, represents the product of •OH addition to the ring of 2,4-D, typical of aromatic compounds.[5,20] The •OH-addition transient of 2,4-D formed on the nanosecond time scale and survived on the microsecond time scale. The growth of the transient at 310 nm is shown in the insert of Figure 10. The bimolecular rate constant was determined by following the formation kinetics at 310 nm at different concentrations and was calculated to be 5.2 (± 0.4) × 10^9 M^{-1} s^{-1}. This value is similar to the one reported by Zona and co-workers 6.6 (± 0.5) × 10^9 M^{-1} s^{-1}.[45]

In addition to the •OH addition adduct, a peak is observed from the H atom reaction with 2,4-D in Figure 10, due to the fact that 10% of the reactive species present under the nitrous oxide conditions are hydrogen atoms. The shoulder present on the difference absorption spectrum of the •OH-2,4-D adduct at approximately 345 nm is assigned to the addition reaction between the hydrogen atom and 2,4-D. This absorbance is more prominent on the longer time scale. A separate experiment was performed to verify the identity of this •H-adduct. A 0.55 mM 2,4-D solution was adjusted to pH 1.5 using $HClO_4$ with 2% *tert*-butyl alcohol to scavenge the hydroxyl radicals. At acidic pH, the reaction $e^-(aq) + H^+(aq) \rightarrow {}^{\bullet}H$ takes place, where $k = 2.3 \times 10^{10}$ M^{-1} s^{-1}.[12] The pulse radiolysis experiment conducted at the acidic pH exhibited a difference absorbance spectrum peak at 345 nm. The maximum absorbance was attained at approximately 20 μs, indicating a much slower reaction than the hydroxyl radical reaction. Hydrogen atoms are known to react at a slower rate than hydroxyl radicals.[12]

The reactivity of the hydroxyl radical with the deprotonated form of the 2,4-D compound was also examined. A 2,4-D solution was adjusted to pH 9.0, to ensure the compound was present only in its carboxylate form. The aqueous solution was saturated with nitrous oxide and subjected to pulse radiolysis conditions. No discernible change in the difference transient absorption at 310 nm from the natural pH solution (2.5) was noted, signifying that the reaction of the •OH is not sensitive to changes in the terminal end of the side chain of 2,4-D. These data offer support to a mechanism where the initial step of the •OH reaction is on the aromatic ring of 2,4-D.

The methyl ester of 2,4-D was reacted with the hydroxyl radical to further confirm the lack of reactivity of the side chain of the herbicide with the hydroxyl radical. The absorption peak of the transient appeared at 310 nm and was almost identical with that seen for the 2,4-D-•OH adduct. Similar results were realized with 2,4-DP, a derivative herbicide of 2,4-D. The structure of 2,4-DP is shown in Figure 1 and only varies from 2,4-D by the methyl group attached to the methylene carbon. The bimolecular rate constant was calculated as 5.5 (± 0.5) × 10^9 M^{-1} s^{-1}, the same as the rate determined for the reaction between 2,4-D and •OH. It was concluded that the •OH reacts by addition to the aromatic ring of 2,4-D, 2,4-D methyl ester, and 2,4-DP based on the typical absorptions of the •OH-addition products.[20,46]

The azide radical was utilized in this pulse radiolysis study to expand on the understanding of the oxidation of 2,4-D and its derivatives. In aqueous solutions of 0.5 mM 2,4-D and 10 mM of NaN_3 saturated with N_2O gas, the azide radicals are the oxidative species available to react with the 2,4-D molecules. Under these pulse radiolysis experimental conditions, no transient species were detected, signifying the inability of the azide radical (oxidation potential = 1.3 V vs NHE) to oxidize 2,4-D. The azide ion is simply not a strong enough oxidant to cause an oxidative transformation of the herbicide 2,4-D, unlike the situation with the chlorinated phenols.

Reaction Pathway Overview of 2,4-D with •OH. The reaction of the hydroxyl radical with 2,4-D is not pH dependent. In both protonated and deprotonated forms, addition of the

SCHEME 2: Reaction of 2,4-D with the Hydroxyl Radical

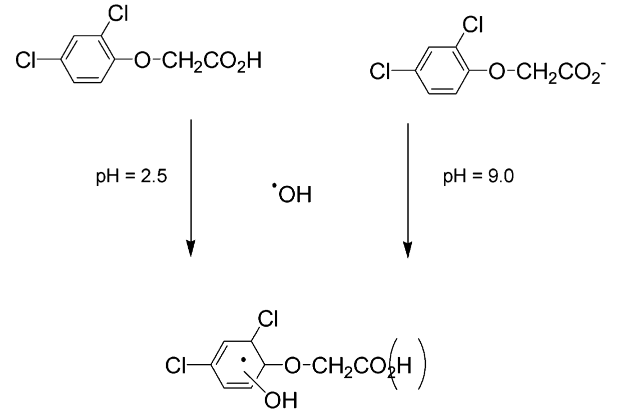


TABLE 1: Reaction Rates for the Model Compounds with the Oxidants

	$k(^{\bullet}OH)$, $\times 10^9$ M^{-1} s^{-1}	$k(^{\bullet}N_3)$, $\times 10^9$ M^{-1} s^{-1}
2,4-D	5.2(±0.4)[a]	not detected
2,4-DP	5.5(±0.5)[a]	not detected
2,4-DCP	7.4(±0.5)[a]	
2,4-DCP$^-$	5.7(±0.4)[a]	
	5.3(±0.3)[b]	3.1(±0.4)[b]
PCP$^-$	5.3(±0.4)[a]	
	4.2(±0.3)[c]	4.1(±0.1)[c]

[a] At 320 nm. [b] At 420 nm. [c] At 452 nm.

•OH to the aromatic ring is the only reaction that takes place, forming the hydroxycyclohexadienyl radical of 2,4-D. The radical species at 310 nm decays at the same rate regardless of the pH of the solution. Furthermore, the alterations on the side chain of the 2,4-D structure have no apparent effect on the hydroxyl radical reactivity. Both 2,4-DP and 2,4-D methyl ester exhibited the same reactivity with the hydroxyl radical as that noted with 2,4-D. The electron density of the aromatic ring is the sight for reactivity of the electrophilic hydroxyl radical. Scheme 2 illustrates the addition reaction of the •OH on 2,4-D.

Data from the pulse radiolysis of 2,4-D coincide with the information obtained from steady-state radiolysis experiments. In the γ radiolysis of 2,4-D, the major product of the hydroxyl radical reaction with 2,4-D is 2,4-dichlorophenol, 2,4-DCP. A labeling experiment (using O-18 water) has confirmed that the phenolic oxygen of 2,4-DCP originates from the hydroxyl radicals, indicating that the •OH addition is followed by the loss of the alkoxyl moiety of 2,4-D.[14]

Comparison of Rate Constants of •OH Reactions. A compilation of the rate constants of the model compounds is displayed in Table 1. Bimolecular rate constant values noted for species monitored at 320 nm correspond to the formation of •OH addition products and at 420 or 452 nm represent the formation of the chlorinated phenoxyl radicals. As expected, the aromatic organic compounds react with the hydroxyl radical mainly by •OH addition to the ring and the observed rate constants are similar to those observed for diffusion controlled reactions.

Steady-State Radiolysis of 2,4-DCP. To assess the later steps involved in the •OH-mediated degradation of 2,4-dichlorophenol, γ radiolysis experiments were conducted with use of a ^{60}Co source. The dose rate was calculated at 3 krad/min, yielding a concentration of hydroxyl radicals of about 15 μM. Oxidative transformations were followed over a 3−5 h time period, where solutions were analyzed every 30 min. To maintain consistency with the pulse radiolysis experiments, solutions of 2,4-DCP at concentrations of 0.50 mM were utilized, with pH values of 6.4 and 11 to reveal the pH effect. The disappearance of the 2,4-DCP was followed with HPLC.

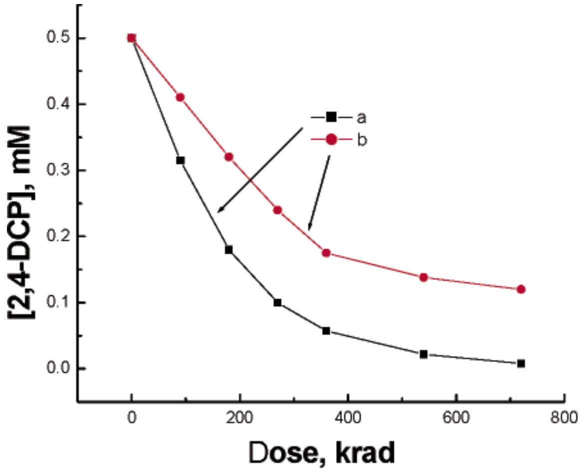


Figure 11. γ radiolysis of 0.5 mM 2,4-DCP (saturated with N_2O) at pH (a) 6.4 (■) and (b) 11 (●).

The •OH-mediated oxidation of 0.50 mM 2,4-DCP was followed over the course of 4 h. Addition of the hydroxyl radical to the aromatic ring of the chlorinated phenol leads to an efficient oxidation pathway at pH 6.4. Less than 3% of the 2,4-DCP was present after 3 h of irradiation, and the oxidation of 2,4-DCP was essentially complete after 4 h (Figure 11). The *G* value, which represents the number of molecules created or destroyed per 100 eV of energy, was estimated from the first 30 min of the 2,4-DCP radiolysis. A value of 3.3 was determined, which compares to the *G* value of 5.4 for the hydroxyl radical in nitrous oxide-saturated conditions.

A switch to a higher pH solution changed the reaction pathway and the oxidative degradation was resolutely affected, clear in both the transient and the steady state data. A 0.50 mM 2,4-DCP solution at pH 11 was followed over a 4-h period of γ radiolysis. A much slower oxidative degradation of 2,4-DCP (2,4-dichlorophenoxide ion) was visible. After 3 h of irradiation, more than 20% of the original compound still remained in solution. The change in concentration with dose at both pH 6.4 and 11 is shown in Figure 11. Intermediate identification is underway to fully elucidate the reaction pathways.

Both hydroxyl radical addition and electron transfer pathways take place for the 2,4-dichlorophenoxide ion reaction with the hydroxyl radical. Pulse radiolysis studies confirmed that the deprotonated form of the chlorinated phenol reacts to a large extent via electron transfer with the hydroxyl radical. Since the steady state studies showed a much slower degradation rate for the 2,4-dichlorophenoxide ion (high pH solution) in comparison to the 2,4-dichlorophenol (lower pH solution), the electron transfer pathway appears to be a less efficient oxidative degradation pathway. This understanding may be extremely valuable in formulating large-scale water remediation processes.

Conclusions

Radiation chemistry is useful for an ostensible understanding of the role of the hydroxyl radical in •OH-mediated oxidation processes. To effectively address the problems associated with contaminated water supplies using advanced oxidation methods, knowledge of the chemical pathways is imperative. The radiation chemical study presented here shows the substantial change in chemistry of the •OH-mediated oxidations by alteration of solution pH and/or concentration of chlorinated aromatic substrate. Clearly, all the oxidative pathways of the hydroxyl radical must be understood to enact effective large-scale cleanup. Other advanced oxidation technologies, such as TiO_2/UV light, may involve oxidative electron transfer reactions at the catalyst surface in addition to hydroxyl radical addition reactions, and the understanding of their mechanistic pathways is enhanced by the radiation studies. The process of intermediate identification in the solutions of high pH or high solute concentration is currently underway to provide more information on the chemical pathways involved in the altered solutions.

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