

FEATURE ARTICLE

Hydroxyl Radical's Role in the Remediation of a Common Herbicide, 2,4-Dichlorophenoxyacetic Acid (2,4-D)

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The massive use of herbicides in the agricultural industry has led to measurable levels in natural bodies of water, many of which supply the human population with fresh drinking water. Advanced oxidation processes such as photocatalysis, sonolysis, and radiolysis show promise in eliminating the dangers of exposure to herbicides and the products of their natural breakdown. A basic understanding of the mechanistic details involved in the oxidative transformations remains the key for improving the effectiveness of the advanced oxidation processes. The role of the hydroxyl radical in the breakdown of the common herbicide 2,4-D (2,4-dichlorophenoxyacetic acid), its breakdown product 2,4-DCP (2,4-dichlorophenol), and related compounds is elucidated through the determination of degradation rates, analyses of the transformation intermediates, and studies using computational chemistry methods.

Agricultural Use of Herbicides and the Impact on the Environment

One of the more heavily used herbicides in the United States and in the world is 2,4-dichlorophenoxyacetic acid (2,4-D). This herbicide belongs to a larger class of herbicides known as the phenoxy herbicides, which have provided control of broadleaf weeds in both agricultural fields and non-cropland grasses for the past 50 years. The structure of 2,4-D is shown in Figure 1, along with the structures of two common derivatives (2,4-DP and 2,4-DME), its major degradation product, 2,4-dichlorophenol (2,4-DCP), and a more highly chlorinated phenol, 2,4,6-trichlorophenol (2,4,6-TCP). 2,4-D is registered for use on 65 different crops in the United States, where it is distributed in either its free form, in its esterified form, as an amine salt, or as a carboxylate salt.¹ The derivative forms often undergo hydrolysis to the parent compound in natural field conditions. Various forms of distributed 2,4-D are shown in Table 1, and the estimated annual agricultural use of 2,4-D is outlined in Table 2.

Farmers rely profoundly on the use of herbicides and pesticides to maximize crop yields. This dependence on 2,4-D and other herbicides by the agricultural industry will not decline, guaranteeing the continued application of these compounds in large amounts (millions of pounds per year). The present rate of total herbicide application in the United States by the farming industry is 650–780 million lb/yr. Commercial and industrial use averages 125 million lb/yr, and homeowner use was estimated to be 74 million lb/yr in 1995.³ This massive reliance

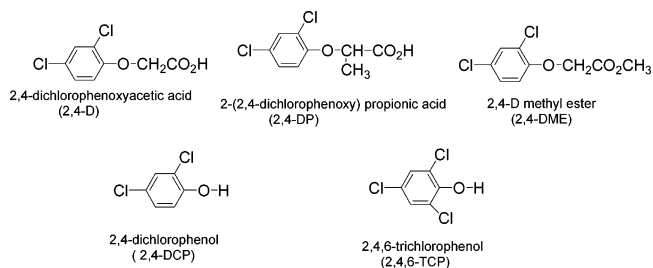


Figure 1. 2,4-D and derivatives and chlorinated phenols 2,4-DCP and 2,4,6-TCP.

TABLE 1: Chemical Numbers, Forms, and Abbreviations of 2,4-D Used in Herbicidal Applications

030001	2,4-dichlorophenoxyacetic acid	2,4-D
030019	dimethylamine salt of 2,4-D	DMA
030063	2-ethylhexyl ester of 2,4	2-EHE
030053	butoxyethyl ester of 2,4-D	BEE
030035	triisoproamine salt of 2,4-D	TIPA
030025	isopropylamine salt of 2,4-D	IPA
030016	diethanolamine salt of 2,4-D	DEA
030004	sodium salt of 2,4-D	Na
030066	isopropyl ester of 2,4-D	IPE

on herbicides has led to measurable herbicide levels in natural bodies of water, which supply the human population with fresh drinking water.^{4–6} An additional concern is the undesirable and often more toxic and/or persistent intermediates formed in the natural degradation pathways of herbicides and pesticides that can accumulate in the ecosystem in even higher concentrations.^{7–11}

Because herbicides and pesticides exhibit some degree of water solubility, much of the contamination of natural waterways originates from agricultural field runoff, which is considered to be a nonpoint source of pollution. 2,4-D readily dissolves

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TABLE 2: Agricultural Use of 2,4-D in 1997²

crops	percent use in United States
pasture	42 (~17 000 000 lbs)
wheat	21 (~8 300 000 lbs)
corn	10. (~3 900 000 lbs)
soybeans	8.0 (~3 200 000 lbs)
fallowland	5.8 (~2 300 000 lbs)
others (hay, sugarcane, barley, rice, etc.)	11

and dissipates in surface waters. Herbicides can also be transported through the atmosphere during airborne application or via volatilization and redeposition through air currents and rainfall.¹² When herbicides reach the water supply, natural degradation processes, such as UV light degradation or biodegradation from microorganisms, may initiate the breakdown of the compounds. The persistence of the compounds varies according to many factors in the water environments: UV light, concentration of organics, level of microorganisms, oxygen level, temperature, and so forth.^{13–16} The half-life of 2,4-D can be as short as 4–10 days; however, 2,4-D and/or its natural degradation products may persist for several weeks. Even though natural degradation processes take place, measurable levels of herbicides are frequently detected.

Human exposure to 2,4-D is most likely to occur to workers who spray the herbicide and to those who live near spray sites because of the drift associated with the application process. The majority of 2,4-D is sprayed from the air, making the spread of the herbicide inevitable. Although the toxicity risks of 2,4-D are not completely known, the World Health Organization has established a guideline value of 30 $\mu\text{g/L}$ for drinking water. No guideline value has been established for 2,4-DCP, the major breakdown product of 2,4-D, but the United States Environmental Protection Agency (EPA) has posted a notice on its deadly acute toxicity when it is in its molten state¹⁷ entitled “Chemical Advisory and Notice of Potential Risk: Skin Exposure to Molten 2,4-Dichlorophenol (2,4-DCP) Can Cause Rapid Death.”

The U.S. EPA has established maximum contaminant levels (MCL) and health advisory levels (HAL) for many common herbicides.¹⁸ The concentrations of herbicides are regularly monitored to realize the extent of the contamination and to comply with the established levels. For example, the herbicide contamination in the Mississippi River and its tributaries has been documented over the past several years. The total herbicide concentration in the Mississippi River at Baton Rouge from 1991–1997 ranged from 3 to 10 $\mu\text{g/L}$.¹⁹ The concentration of the herbicides showed variation in seasonal cycles and was usually highest in the herbicide application season. Because measurable levels of herbicides are continually detected in natural waters, it is clear that herbicide usage has surpassed the ability of the ecological systems to degrade these organic contaminants.^{20–24}

The breakdown of 2,4-D represents a pathway where a toxic intermediate, 2,4-dichlorophenol (2,4-DCP), is formed in the hydrolysis of the herbicide. 2,4-DCP is also a problematic industrial contaminant because it is formed from phenolic compounds when water undergoes chlorination treatment. Although 2,4-D is believed to be only mildly toxic to birds and aquatic life, the major breakdown product, 2,4-DCP, is likely a

more toxic compound and often more resistant to oxidative degradation. Other natural metabolic pathways of 2,4-D lead to compounds such as 2,4-dichloro-5-hydroxyacetic acid and 4-chlorophenoxyacetic acid.²⁵ The monitoring of herbicides/pesticides in natural bodies of water obviously requires an awareness of the natural breakdown products and toxicities associated with the degradation pathways.^{26,27}

Advanced Oxidation Processes for Environmental Remediation

The unequivocal reliance on herbicides will necessitate water treatments that eliminate the dangers of exposure to the herbicides and the products of their natural transformations. Conventional water treatment plants utilize the processes of mechanical removal, filtration, activated sludge, and chlorination to clean wastewaters. Unfortunately, these processes are typically not effective in remediating industrial organic contaminants such as herbicides. In fact, the chlorination process often increases the toxicity of organic compounds through the formation of chlorinated hydrocarbons and aromatics.^{28–31} A large research effort is focused on alternative remediation strategies that can effectively clean waters contaminated by anthropogenic chemicals.^{32–35} Because the breakdown of organic compounds can lead to the formation of substances equally or more toxic than the parent compounds, effective remediation processes must also address the need for transformations to nontoxic compounds or to mineralization (formation of CO_2 and inorganics substances) of the contaminants.³⁶ These realizations have led to detailed research on advanced oxidation processes (AOPs).^{37–47} Advanced oxidation technologies that utilize non-chlorine oxidants in the remediation of industrial chemicals show great promise as part of the water treatment process.

Advanced oxidation processes are defined as technologies that employ the highly reactive hydroxyl radical as the main oxidative species for the breakdown of organic contaminants such as herbicides. The hydroxyl radical can be formed by a number of methods in aqueous systems: high-frequency ultrasound waves, γ rays or high-energy electrons, TiO_2 and UV light, H_2O_2 and UV light, O_3 and UV light, the Fenton reaction ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$), and various combinations of these processes. Some of the processes require gases and others require surfaces for the production or reaction of hydroxyl radicals. Many of the strengths and weaknesses of these processes have been assessed, leading to a better understanding of their practical implementation potentials.^{35,47–55} At the same time, many details of the oxidation mechanisms are still not known, and the exact mechanisms involved may depend on the advanced oxidation process(es) used. Even so, great potential exists in these processes and possibly even more in combining of certain oxidation technologies to meet the remediation needs.^{38,44,56} The oxidative degradations of 2,4-D and related chlorinated aromatic compounds have been explored using the advanced oxidation processes of TiO_2 photocatalysis, high-frequency sonolysis, and radiolysis. A brief description of each of these three processes follows.

TiO_2 Photocatalysis. In the TiO_2 photocatalysis of aqueous solutions, UV light is used to excite an electron from the metal oxide to form an electron–hole pair, where the hole is a localized oxidizing site. The photogenerated electron can be scavenged by dissolved oxygen gas. Organic species may undergo oxidation directly at the hole surface. The hole can also undergo charge transfer with an adsorbed water molecule or hydroxide surface-bound species, ultimately forming the

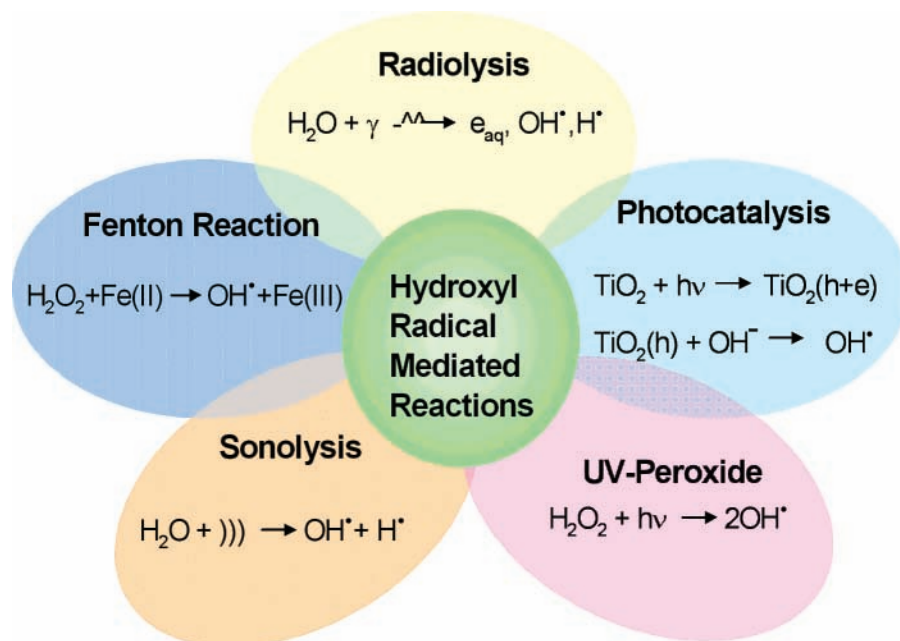
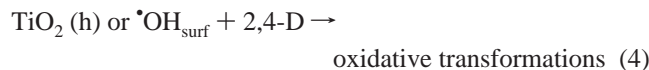


Figure 2. Advanced oxidation technologies.

hydroxyl radical as the oxidant. These reactions are depicted in eqs 1–4.



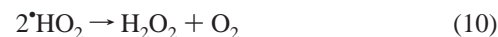
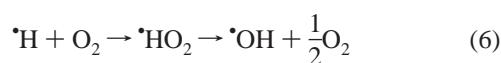
Equation 4 relays both oxidation pathway options, direct oxidation by the photogenerated holes and $\cdot\text{OH}$ -mediated oxidation. The preferred oxidation route is highly compound-dependent. Those species that adsorb strongly to TiO_2 , highly polar compounds, are more likely to oxidize via the photogenerated holes.

Although semiconductors other than TiO_2 are also able to act as photocatalysts, TiO_2 is the most widely studied photocatalyst in connection with oxidative degradation reactions. Over the past two decades, scores of papers have assessed the process of TiO_2 photocatalysis in the remediation of organic pollutants.^{40,48,57–62} The findings of many of the studies implicate the adsorption ability of compounds to the TiO_2 surface to the likelihood or rate of oxidation.^{54,63–65} Some studies have linked the size of the TiO_2 particles to their activity,^{66–68} and other papers have reported the effect of salts,⁶³ metals,^{69–71} intermittent light exposure,⁷² and other solutes or conditions on the oxidative ability of the TiO_2 process.^{73–75}

Most of the published findings that deal with the destruction of organic pollutants by TiO_2 photocatalysis verify the suitability of TiO_2 as a photocatalyst. Its inert properties, low cost, and effectiveness have sparked continued research in the field. Although the majority of the papers report that compounds are quickly degraded via this photocatalytic oxidation, some compounds have been found to be rather resistant. The ability of TiO_2 photocatalysis to mineralize organic compounds in practical time frames has been proven in many of the reported experiments.^{76,77} Even so, the fact remains that some compounds, such as cyanuric acid and carbon tetrachloride, show resistance to photocatalytic degradation.^{78,79}

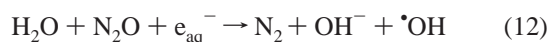
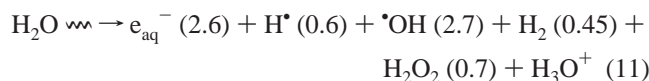
High-Frequency Ultrasound. When high-frequency ultrasound waves are introduced into an aqueous solution, bubbles rapidly form and develop through rarefaction/compression cycles. Upon the buildup of a certain pressure (critical bubble size), the bubbles collapse inwardly. This ultrasound-induced implosion process is known as cavitation. Very high temperatures and pressures accompany the implosion of the cavitation bubbles, forming microscopic areas of extremely high energy. Pressures as high as 1000 atm and 5000 K have been attained.^{80,81}

High-frequency sonolysis can induce the degradation of organic compounds by two main avenues. Upon collapse of the cavitation bubble, vaporized volatile compounds are destroyed via pyrolytic or combusive reactions because of the extreme temperature and pressure conditions. Small molecular weight hydrocarbons and other volatile compounds form intermediates and products that mirror pyrolysis or combustion reaction products.⁸² The second type of reaction pathway consists of the chemical processes at the interface of the bubble, induced by hydrogen atoms and hydroxyl radicals formed from the homolysis of water, promoted by the implosion conditions. Reactions 5–10 summarize the main reactive species produced by the high-frequency ultrasound in an O_2 -saturated aqueous solution. Solute molecules that do not vaporize but diffuse into or near the bubble are likely to undergo radical attack by $\cdot\text{OH}$ or $\cdot\text{H}$. The concentration of hydroxyl radicals at the interface is believed to be as high as 1×10^{-2} M upon bubble collapse.⁴⁷



Effective degradation reactions in high-frequency sonolysis are limited to the inside of the collapsing cavitation bubble and the interface of the bubble. Molecules that are hydrophobic or volatile are most likely to undergo pyrolysis-type reactions because they can enter the hydrophobic interior of the bubbles during cavitation.^{83,84} Because compounds that are hydrophilic or nonvolatile will not enter the hydrophobic cavitation bubbles, their reactivity will be $\cdot\text{OH}$ -mediated at the bubble surface.⁸⁵ Solutes that are present in these environments are very effectively degraded.^{51,82–84,86–89} Conversely, highly hydrophilic compounds that are dispersed in the bulk solution (not attracted to the bubble interface), such as low-molecular-weight carboxylic acids, degrade at extremely slow rates, indicating a lack of $\cdot\text{OH}$ activity in the bulk solution.⁸⁵ Because hydrophilic compounds are formed in the intermediate and final steps of the oxidation reactions of organic compounds, high-frequency ultrasound is a poor process to achieve complete mineralization of organic compounds.^{38,90,91}

γ Radiolysis. The radiolytic oxidation of organic solutes in aqueous solutions involves the use of ionizing radiation from sources such as high-energy electron beams or cobalt-60, which emits γ rays. The ionizing radiation forces the ejection of electrons from the water molecules, and the subsequent formation of the primary radicals $\cdot\text{OH}$ and $\text{H}\cdot$, as well as the highly reactive aqueous electron, ensues. Equation 11 shows the species resulting from the radiolysis of water and their G values, the number of species formed per 100 eV of energy.⁹²



Various scavengers of the aqueous electron, such as $\text{O}_2(\text{g})$ or $\text{N}_2\text{O}(\text{g})$, render the conditions of the aqueous solution oxidative (eq 12). If $\text{N}_2\text{O}(\text{g})$ is utilized as the scavenger of the $e^- (\text{aq})$, then the highly reactive hydroxyl radical constitutes 90% of the primary radicals in the solution.⁹³ The hydroxyl radical is the powerful oxidant in radiation remediation, with no interference from other extraneous sources such as catalysts, surfaces, UV light, or extreme heat. Because the hydroxyl radical is the only oxidative species involved in solute transformations, radiolysis is particularly useful for mechanistic studies on the role and reactivity of this species.

Advanced Oxidation Processes and 2,4-D

An investigation of the use of high-frequency ultrasound in the remediation of herbicide 2,4-D and its main breakdown product 2,4-DCP was reported.⁸⁵ Although the strength of this technology clearly lies in its ability to degrade a wide array of nonpolar compounds adequately, its deficiency in achieving the complete mineralization of organic contaminants was confirmed. Upon subjecting aqueous, O_2 -saturated 2,4-D and 2,4-DP (2-(2,4-dichlorophenoxy)propionic acid, Figure 1) solutions to sonolysis, quick degradation of the herbicides took place. The decay of the herbicides follows a pseudo-first-order decay with degradation lifetimes of 12 and 11 min for 2,4-D and 2,4-DP, respectively. Figure 3 shows the decrease of 2,4-D upon exposure to high-frequency ultrasound and the small amount of 2,4-DCP that is detected and subsequently degraded. A key observation in the degradation of 2,4-D is that no significant buildup of 2,4-DCP occurs, which demonstrates the main strength of the sonolytic

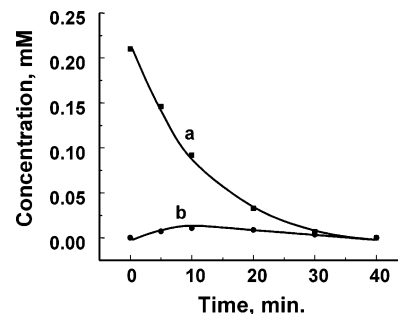


Figure 3. Sonolysis of a 0.22 mM 2,4-D solution using $\text{O}_2(\text{g})$. The breakdown of (a) 2,4-D (■) and (b) formation/degradation of the intermediate 2,4-DCP (●) (reprinted from ref 85).

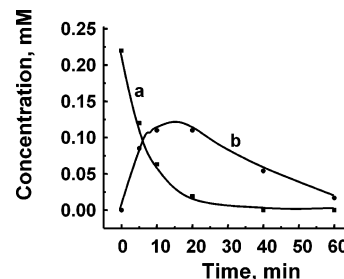


Figure 4. Photocatalysis of a 0.24 mM 2,4-D solution with an O_2 -sparged system. The breakdown of (a) 2,4-D (■) leads to the longer-lasting (b) 2,4-DCP (●) with a lifetime (20 min) more than twice that of 2,4-D (8 min) (reprinted from ref 44).

degradation process. Toxic organic intermediates are often absent, unlike the situation in many other oxidative and hydrolytic degradation processes.

Whereas the sonolytic degradation lifetimes for 2,4-D, its derivatives, and its early breakdown products are very similar and relatively short (~ 10 – 12 min), the decrease in total organic carbon (TOC) occurs at a remarkably slow rate. Mineralization of the model compounds (2,4-D, 2,4-DCP, 2,4-DP, and 2,4,6-TCP) was typically less than 50% after 4–5 h of exposure to high-frequency ultrasound. After subjecting a 0.20 mM 2,4-D solution to high-frequency ultrasound for 5 h, only about a 50% reduction in the total organic carbon was observed. As indicated in our previous study,⁸⁵ low-molecular-weight organic acids (e.g., oxalic acid) accumulated in solution during sonolysis, and their degradation occurred at an extremely slow rate. Being polar in nature, these short-chain carboxylic acids are repelled from the hydrophobic bubble surface during sonolytic cavitation, which decreases the probability of their interaction with hydroxyl radicals. The resistance of highly polar compounds to sonolytic oxidation leads to a very slow mineralization process of organic compounds.

The photocatalytic degradations of 2,4-D and other model compounds were carried out using TiO_2 Degussa (P25). UV illumination was done by placing a medium-pressure mercury lamp set inside a copper sulfate filter tube close to the solution cell. A different pattern of reactivity emerged for the chlorinated aromatic compounds in the photocatalytic studies. Herbicide 2,4-D was transformed to oxidation products during photocatalysis, and the initial degradation rate was relatively fast (lifetime = 8 min), slightly faster than the one observed in the sonolysis experiments. Similarly, the degradation lifetime for herbicide 2,4-DP (2-(2,4-dichlorophenoxy)propanoic acid) was $6(\pm 1)$ min. However, the clear difference in comparison with the sonolysis experiment can be seen in the plot of the formation of chemical intermediate 2,4-DCP, which accumulates during the photocatalysis of both 2,4-D and 2,4-DP solutions and remains in solution for a substantial period of time. The

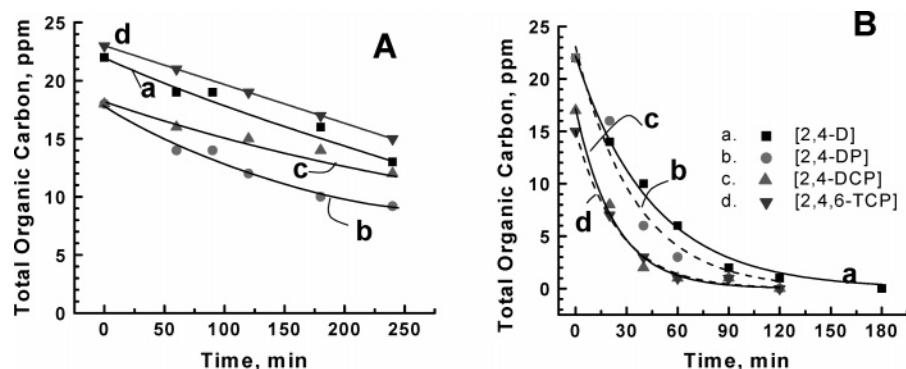


Figure 5. (A) Change in total organic carbon content (TOC, ppm) of model compound solutions when subjected to 640-kHz ultrasonic waves in an O₂-sparged system over a 4-h period. (B) Change in TOC (ppm) of model compound solutions using TiO₂ photocatalysis over 3 h (500 mg/L solution and CuSO₄ filter solution). (a) 2,4-D; (b) 2,4-DP; (c) 2,4-DCP; and (d) 2,4,6-TCP (reprinted from ref 44).

TABLE 3: Degradation Lifetimes of Chlorinated Aromatic Compounds⁴⁴

compound	degradation lifetime, (± 1) min (and reaction rates, min ⁻¹)			
	sonolysis	sonolysis + UV photolysis	TiO ₂ photocatalysis	combined sonolysis and photocatalysis
2,4-dichlorophenoxyacetic acid (2,4-D)	12 (0.083)	11 (0.091)	8.0 (0.13)	6.6 (0.15)
2,4-dichlorophenol (2,4-DCP)	11 (0.091)	11 (0.091)	20.0 (0.050)	7.7 (0.13)
2-(2,4-dichlorophenoxy)propionic acid (2,4-DP)	11 (0.091)	10 (0.10)	6.2 (0.16)	5.9 (0.17)
2,4,6-trichlorophenol (2,4,6-TCP)	12 (0.083)	10 (0.10)	18 (0.056)	8.2 (0.12)

formation/breakdown of 2,4-DCP during the photocatalysis of 2,4-D is shown in Figure 4.

The photocatalytic degradation lifetime of 2,4-dichlorophenol, determined by a separate photocatalysis experiment, was 20 min, more than twice the degradation lifetime of 2,4-D. Another model compound, 2,4,6-trichlorophenol, was also less prone to photocatalytic degradation than the herbicides with a calculated lifetime of 18 min. These experiments clearly demonstrate that certain organic compounds, which show a higher degree of resistance to TiO₂ photocatalysis, tend to accumulate in solutions. Such longer persistence of chemical intermediates in a water treatment process can be problematic, especially if they are more toxic than the parent compounds, as is the case with 2,4-DCP.

Whereas TiO₂ photocatalysis is slow in its ability to break down chlorinated phenols efficiently, it is quite powerful in its ability to induce complete mineralization. During the first hour of photocatalysis, the toxicity of the solution is problematic. As soon as 2,4-DCP is oxidized to more polar compounds, further oxidation to the point of mineralization is fairly rapid. All four compounds transformed by TiO₂ photocatalysis were completely mineralized in 2–3 h, compared to the incomplete mineralization noted in the sonolysis experiments, which was less than 50% during the same period. (Figure 5A) The change in total organic carbon in the photocatalytic breakdown of the model compounds is illustrated in Figure 5B.

A simultaneous sonolysis/photocatalysis was employed to realize the complementing benefits of the two advanced oxidation processes utilizing four chlorinated aromatic compounds (2,4-D, 2,4-DP, 2,4-DCP, and 2,4,6-TCP).⁴⁴ One setup was devised for both processes to allow for separate and combined sonolysis/photocatalysis experiments. During the combination experiments, the solutions contained suspended TiO₂ particles and were subjected to UV light and high-frequency ultrasound at the same time. For all four model

compounds, the oxidative degradation was enhanced when photocatalysis and sonolysis were carried out simultaneously. The degradation lifetimes of all of the compounds decreased as compared to the lifetimes obtained in either of the individual photocatalysis or sonolysis experiments, in at least an additive fashion. The results are summarized in Table 3. Furthermore, no accumulation of toxic intermediates was detected.

γ radiolysis is a particularly valuable technique for gaining information about and an understanding of hydroxyl radical-mediated processes.⁹⁴ In the wide array of studies involving the oxidative remediation of organic compounds in water, the reported kinetic data relays only some of the essential information of the processes because intermediates generated in the breakdown may still be problematic.^{95–97} In addition, it is clear that some advanced oxidation processes, especially those using Fenton-type chemistry, involve species other than just the hydroxyl radical.^{98,99} A complete understanding of the reaction mechanisms and intermediates that form in the degradation pathways of these compounds is needed to address the contamination problems fully and optimize the oxidation processes. γ radiolysis provides a means to set the \cdot OH-mediated reactions apart from other types of reactions.

Herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) undergoes efficient degradation when subjected to oxidative conditions of γ radiolysis because it is highly susceptible to attack by the hydroxyl radical.⁹⁶ Some of the intermediates formed in the OH \cdot -mediated oxidative breakdown of 2,4-D include 2,4-DCP, 4-chlorocatechol, 2-chlorohydroquinone, hydroxylated 2,4-dichlorophenols, 4,6-dichlororesorcinol, 2,4-dichloroanisole, 1,2,4-trihydroxybenzene, and small amounts of unidentified compounds. The most prevalent intermediate formed during the early course of the breakdown is 2,4-dichlorophenol, which was also the case in the photocatalysis and sonolysis experiments. Figure 6 shows the formation of 2,4-dichlorophenol as the concentration of 2,4-D decreases over time when a 0.20 mM

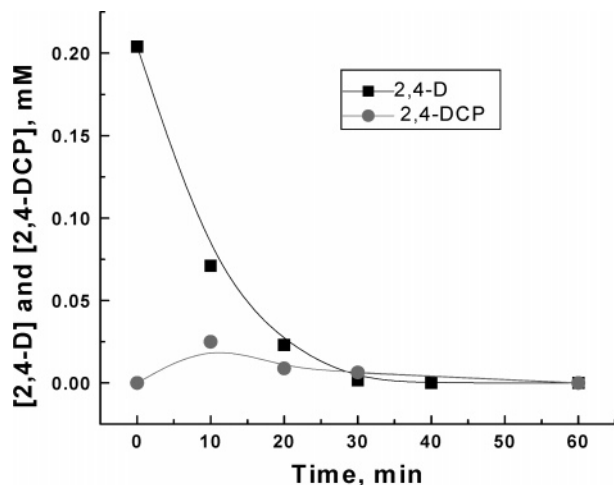


Figure 6. Radiolytic degradation of a 0.21 mM aqueous, N_2O -saturated 2,4-D solution and the formation and subsequent degradation of 2,4-DCP (reprinted from ref 85).

aqueous solution is subjected to γ radiolysis. Total organic carbon (TOC) analyses were performed on the aqueous solutions at various times during the radiolysis and indicate that most of the organic carbon remained in the solution well after 2,4-D and 2,4-DCP were completely consumed. This verified the presence of other later organic intermediates formed in the degradation of 2,4-D. After 4 h, approximately 60% mineralization was achieved.

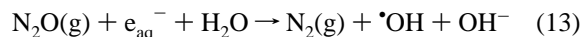
As depicted in Figure 6, radiolytic degradation leads to only a small accumulation of 2,4-DCP. More specifically, at the 5–10 min mark in the radiolysis, approximately 10 ppm of 2,4-DCP was detected when a 46 ppm solution of 2,4-D was irradiated. From a mechanistic viewpoint, the formation of this intermediate indicates a site specific for $\bullet OH$ addition to the 2,4-D ring. Most of the other identified intermediates seen in the product analyses resulted from the $\bullet OH$ attack on the intermediate, 2,4-DCP, and were not a direct result of hydroxyl radical attack on 2,4-D. These intermediates appeared after the formation of 2,4-DCP.

The reactivity of the hydroxyl radical with 2,4-dichlorophenol (2,4-DCP) shows some similarities to that of 2,4-D. 2,4-DCP is efficiently degraded in γ radiolysis experiments, indicating that the hydroxyl radical is comparably effective in attacking the chlorinated phenol. The lifetime of 2,4-DCP, upon irradiation with a dose rate of 5.3 krad/min, is somewhat longer than that of 2,4-D, with a half-life of 13 min compared to 9 min for 2,4-D. The difference in the calculated lifetimes is explained, at least in part, by the ineffective reaction of the hydroxyl radical at carbon 1 of 2,4-DCP, which reforms the reactant after the collapse of the initial addition adduct. Intermediates formed in the $\bullet OH$ -mediated degradation include hydroxylated 2,4-dichlorophenols (such as 4,6-dichlororesorcinol), 4-chlorocatechol, and 2-chlorohydroquinone.

More definitive experimental information on the initial hydroxyl radical attack on the ring of 2,4-D was obtained using O-18 labeled water in the γ radiolysis experiments.¹⁰⁰ A 2,4-D solution in O-18 labeled water (87% $H_2^{18}O$) was subjected to γ rays, and O-18 labeled hydroxyl radicals, in addition to the O-16 hydroxyl radicals from unlabeled water, were generated.

Mass spectral data revealed the presence of the two expected isotopomers of 2,4-dichlorophenol from the $^{18}OH/\bullet OH$ reactions with 2,4-D. The labeled 2,4-DCP intermediate was calculated to be present at $38 \pm 4\%$. Half of the reactive hydroxyl radicals were formed from the labeled water, and half were formed from the reaction of the aqueous electrons with nitrous oxide gas, as

shown in eq 13. The oxygen atoms of the hydroxyl radicals formed from the nitrous oxide scavenging of aqueous electrons originated from the nitrous oxide molecules, not the water molecules. The ^{18}O content of the water solvent was 87%, making the concentration of ^{18}OH about 43%.



Within experimental accuracy, all of the phenolic oxygens of 2,4-DCP, the major product of the reaction between 2,4-D and $\bullet OH$, originated from hydroxyl radicals. Consequently, the bond between aromatic carbon 1 and the oxygen of the ether is broken in the initial $\bullet OH$ -mediated transformation of 2,4-D. These experimental results are summarized in Figure 7.

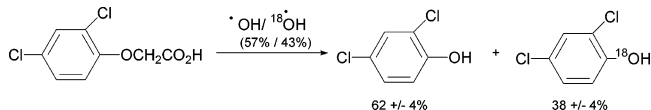


Figure 7. Reaction of labeled and unlabeled hydroxyl radicals with 2,4-D (reprinted from John Wiley, ref 100).

Mechanistic Details of the $\bullet OH$ Reaction with 2,4-D: Computational Studies

In the hydroxyl radical transformations of 2,4-D, the single most prevalent intermediate in the reaction, regardless of the technique used to form the $\bullet OH$, is 2,4-dichlorophenol.^{96,101–106} The formation of this intermediate implies a high degree of selectivity for $\bullet OH$ addition to the 2,4-D ring. It is envisioned that an $\bullet OH$ attack at C_1 (Figure 8) of the aromatic ring followed

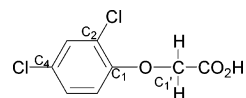


Figure 8. 2,4-D and the specific sites of reactivity.

by the loss of an alkoxy radical or anion to form 2,4-DCP takes place. Alternatively, hydrogen abstraction from the methylene carbon, followed by trapping of the ensuing radical and breaking of the $C_1'-O$ bond, by analogy to the mechanism proposed in an earlier study by Li and Jenks, is also possible.¹⁰⁷ These two pathways differ by which C–O bond, C_1-O or $C_1'-O$, is broken.

Results of the experiments using the O-18 labeled water discussed above clarify the site of $\bullet OH$ attack on 2,4-D. The hydroxyl radicals formed from the labeled water were incorporated into the structure of the intermediate 2,4-DCP. It can therefore be concluded that the formation of 2,4-DCP proceeds via hydroxyl radical addition to the ring in the first step of the mechanism, followed by the loss of the alkoxy group. No hydroxylated intermediates of 2,4-D were detected in any of the experiments.

The experimental work of the $\bullet OH$ reaction with 2,4-D was complemented by computational studies.¹⁰⁰ The suitable level of theory chosen for the work was Becke3LYP/6-31G* using the Gaussian 98¹⁰⁸ series of programs, where the geometries of all of the reaction species were optimized. Energies from the CPCM calculations were corrected for zero-point energies using the results of the gas-phase calculations.

The computed reaction energies of 2,4-D and the hydroxyl radical to form the various reaction intermediates are depicted in Figure 9. Both the gas-phase energies and the energies from the solvent cavity model used to model the aqueous environment are shown in Figure 9. The results of these calculations suggest that all of the hydroxyl radical addition reactions to the aromatic

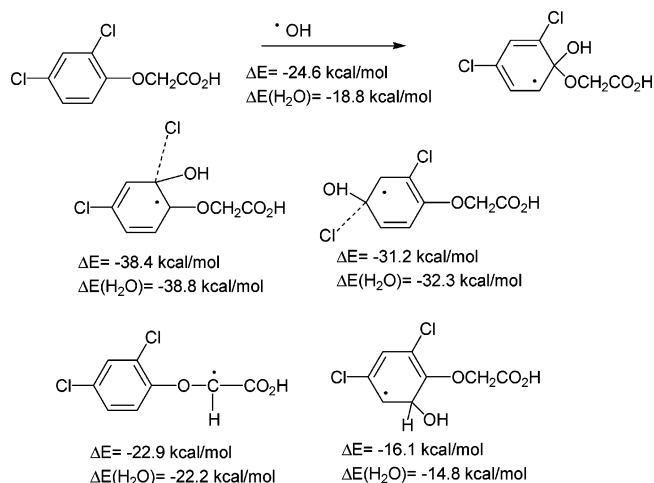


Figure 9. Energies (gas phase and water continuum model) of the radical intermediates formed from hydroxyl radical attacks on 2,4-D using B3LYP/6-31G* (reprinted from John Wiley, ref 100).

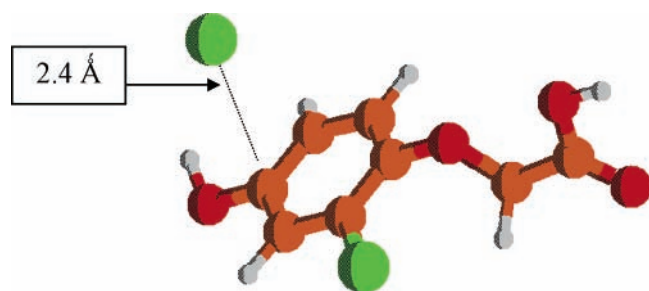


Figure 10. π complex formed by $\cdot\text{OH}$ addition at carbon 4 of the aromatic ring (reprinted from John Wiley, ref 100).

ring of 2,4-D, as well as the hydrogen abstraction reaction, are energetically favorable. The ipso attacks (at carbons 1, 2, and 4 of the aromatic ring) are preferred over attacks at the unsubstituted positions of the ring by a significant margin. This is consistent with the observation that no hydroxylated 2,4-D intermediates were identified in the experimental work.^{85,96}

Further computational studies on the three substituted positions on the 2,4-D molecule indicated that two different types of reaction pathways were found, one for attack at the chlorine-substituted positions, C₂ and C₄, and the other for attack at the oxygen-substituted C₁. The reaction of $\cdot\text{OH}$ at C₁ leads to the formation of a σ -type adduct, which is 24.6 kcal/mol lower in energy than the separated species. The newly formed C₁–O bond length is 1.45 Å, whereas that of C₁ and the ether oxygen is 1.40 Å. Scans of both the C–O bond lengths show that the $\cdot\text{OH}$ attack at carbon 1 of the ring is barrierless in the gas phase.

In contrast, no such σ -type intermediate was located for the attack of $\cdot\text{OH}$ at either C₂ or C₄. Instead, the computed results showed that the initial product of the hydroxyl radical approach to C₂ or C₄ of 2,4-D is a π complex, exemplified in Figure 10. The reaction energy in the formation of this complex is –38.8 kcal/mol, even more exothermic than the formation of the σ -type intermediate discussed above. The calculated carbon–chlorine bond length is \sim 2.4 Å, significantly longer than a normal carbon–chlorine bond length of \sim 1.7 Å, indicating that only a weak interaction of the chlorine radical and the aromatic system persists with this π complex.¹⁰⁹

Although the attack of the $\cdot\text{OH}$ at C₂ or C₄ seemed reasonable by the computed energy values shown in Figure 9, none of the products of $\cdot\text{OH}$ attack on C₂ or C₄ of 2,4-D were detected in the experimental studies.^{85,96} A more complete analysis of the reaction pathway was deemed necessary. Thus, the pathways

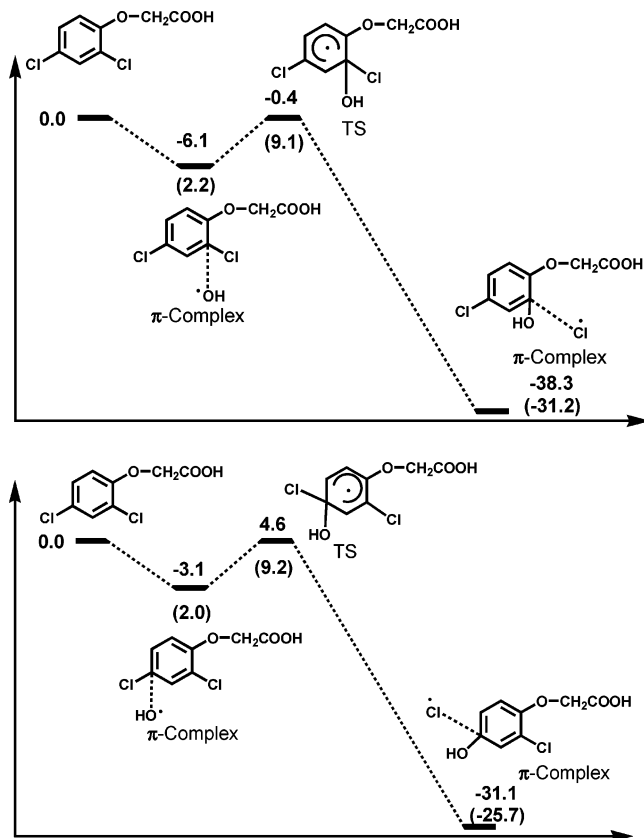


Figure 11. Energy profiles ($\Delta E + \text{ZPE}$ and ΔG , in parentheses) in the $\cdot\text{OH}$ additions on carbon 2 (top) and carbon 4 (bottom) of the aromatic ring (gas-phase values) (reprinted from John Wiley, ref 100).

leading to the formation of the π complexes were studied in more detail. The results of these calculations are summarized in Figure 11. Free-energy values were also determined and are shown in parentheses in Figure 11.

According to the computational data, the reaction pathways for the $\cdot\text{OH}$ attack at C₂ and C₄ involve barriers of 5.7 and 7.7 kcal/mol, respectively. In comparison to these attacks at carbons 2 and 4, the hydroxyl radical addition at C₁ was determined to be barrierless. Similarly, the hydrogen abstraction from the side-chain methylene carbon (reaction energy of –22.9 kcal/mol in the gas phase) indicates a thermodynamically competitive reaction with the $\cdot\text{OH}$ attack at C₁. Upon a more detailed inspection of the reaction pathway, a significant activation barrier of 3.5 kcal/mol was computed for this reaction as well. Therefore, the kinetic data favors the $\cdot\text{OH}$ addition at carbon 1 of the 2,4-D molecule, the barrierless reaction, as the first step in the mechanistic pathway, which coincides with the experimentally generated data.

Concluding Remarks

Although an intense need exists to discover more effective herbicides that can be used at lower application doses with fewer undesirable environmental consequences, the reality of the present situation dictates an enormous reliance on millions of pounds of herbicides each year in the U.S. alone. The emergence of these compounds in natural soils and water supplies further substantiates the heavy reliance on herbicides and pesticides in today's world. The detection of anthropogenic compounds in waters also indicates a burden beyond the remediation power of nature. Oxidation by means of the powerful hydroxyl radical has been shown to be effective in the breakdown of herbicide 2,4-D and many similar compounds. Certain advanced oxidation

processes and combinations of the technologies have proven to be more effective than others in the various steps of herbicide degradation. The need for the determination of mechanistic details cannot be underestimated because remediation processes must address the existence of many types of organic compounds and the degradation compounds formed in their oxidative pathways. If the reaction sequences involved in the oxidative degradations are not understood, then effective and efficient water remediation technologies will be difficult to devise.

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