# Photochemical Degradation of 2,4,6-Trichlorophenol in the Brij 35 Micellar Solution: pH Control on Product Distribution

## W. Chu,* Y. F. Rao, C. Y. Kwan, and W. K. Choy

*Department of Civil and Structural Engineering, Research Centre for Environmental Technology and Management, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China*

Surfactants have been used for separating organic pollutants from contaminated soils in soil-washing process. The extracted pollutants can be effectively degraded upon UV irradiation in the presence of surfactant micelles. The photodecay rate of 2,4,6-trichlorophenol (2,4,6-TCP) by UV light at 253.7 nm and photonic efficiency of 2,4,6-TCP degradation reaction were investigated at different pH levels with the addition of nonionic surfactant solutions above the critical micelle concentration (cmc). A continual examination on intermediates at all pHs was conducted and photochemical processes induced the dechlorination of TCP to form di- and monochlorinated intermediates and phenol. An additional reaction was observed when the initial pH level was above neutral, at which chlorinated hydroquinones were the resulting intermediates through photohydrolysis process. Two reaction mechanisms, one at acidic and the other at basic conditions, were proposed and verified by the evidence presented in this study.

## Introduction

Chlorophenol compounds have received increasing interest in recent years in view of their environmental concerns as persistent, ubiquitous and potentially hazardous substances. Some of them such as 2-chlorophenol (2-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-TCP, and pentachlorophenol (PCP) have been listed among the priority pollutants by the U.S. EPA.[1] Among chlorophenol congeners, trichlorophenols have been widely used as a microbiocide, disinfectant, pesticide, and wood preservative,[2] which results in their being frequently detected in natural waters. Of particular attention has been 2,4,6-TCP because of its high toxicity and potential to be transformed to more toxic compounds under the action of natural factors.[3]

2,4,6-TCP has been subjected to various treatment processes such as UV/TiO$_2$,[4] Fenton's reaction,[5] UV/H$_2$O$_2$,[6] ion-induced radicals,[7] H$_2$O$_2$, and polyoxometallates.[8] The degradation products of 2,4,6-TCP treated with polyoxometallates or H$_2$O$_2$ were 3,5-dichlorocatechol, 2,6-dichlorobenzoquinone, dihydroxytrichlorobenzene and dichlorohydroquinone[8] and the products changed to 2,6-dichlorohydroquinone with trace quantities of 3,5-dichlorocatechol and 2,6-dichlorobenzoquinone in the UV/TiO$_2$ process.[4] These hydroxylated chemicals are the dominant end products of oxidation processes because of the formation of hydroxyl radicals. The degradation mechanisms rely on radical attacks, including chlorine substitution by the •OH radical and/or the hydroxylation of the aromatic ring. Oxidative treatment processes are undesirable because the daughter products may not be any less toxic than the starting compounds as those processes result in complicated chlorinated products; therefore, it is useful to investigate the transformation of TCP by other nonoxidative means that do not employ hydroxyl radical (•OH) attacks.

In general, the photodehalogenation of chlorinated aromatic compounds with a surfactant present proceeds through two mechanisms: the photochemical homolysis of a C−Cl bond and an electron transfer process.[9] In the homolysis process, upon to light absorption, aryl chloride (ArCl) will be excited to a singlet state $^1$ArCl, and then produce the triplet state $^3$ArCl through intersystem crossing (ISC).[10] The cleavage of the C−Cl bond generates an aryl radical, Ar•, and a chlorine radical, Cl•. Both radicals will abstract hydrogen from the hydrogen source (i.e., surfactant), leading to the formation of ArH and a chloride ion. In the electron transfer process, an electron donated from an electron source (i.e., surfactant) to an excited aryl chloride, ArCl*, produces an unstable aryl radical anion (ArCl•$^-$), which will eliminate chloride and leave an aryl radical. The aryl radical abstracts hydrogen from the hydrogen source, leading to the generation of the final product (ArH), similar to the former mechanism.

In this study, the photodegradation rate of 2,4,6-TCP by UV at 253.7 nm was examined with the surfactant dosage above cmc. In addition, the analysis of photoproducts distribution was conducted comprehensively and the reaction pathways were proposed.

## Experimental Section

**Materials.** Chlorophenols with a purity higher than 98% were bought from Riedel-deHaen. Phenol (99%) and 2,6-dichloro-hydroquinone (95%) were purchased from Wako Pure Chemical Industries Ltd. and Tokyo Chemical Industries, respectively. The commercial grade nonionic surfactant Brij 35 (polyoxyethylene(23) lauryl ether), with a formula of C$_{12}$H$_{25}$(OCH$_2$CH$_2$)$_{23}$OH and a molecular weight of 1200 g/mol, was purchased from ICI America Inc. From our previous experiment, the cmc of Brij 35 was determined to be $8.32 \times 10^{-5}$ M.[11] HPLC grade acetonitrile (ACN), HPLC-water and acetic acid were obtained from LAB-SCAN. The surfactant solutions, the stock solutions of 2,4,6-TCP and the reaction intermediates were prepared in deionized distilled water. All of the reagents were used as received.

**Batch Tests.** The experimental conditions were similar to our previous report. Two and a half millilmolar 2,4,6-TCP was applied as the initial concentration. The concentration of Brij 35 in the solution was set at 8 mM, which was above its cmc to ensure surfactant was present in the form of micelles rather than monomers. The solution was adjusted to the desired pH levels at about 2.5, 5.0, 7.0, 9.0, and 11.0 with 0.1 M sodium hydroxide and/or 0.1 M sulfuric acid, and the flask was filled

* To whom correspondence should be addressed. Fax: (852)23346389. E-mail: cewchu@polyu.edu.hk.

to the mark with distilled water. After the solution was stirred by a magnetic stirrer for 20 min, 5 mL of well-mixed solution was delivered to a number of 15 mL cylindrical quartz cuvettes and sealed with Teflon-lined caps to minimize the volatilization effect. These cuvettes were placed inside an RPR-200 Rayonet photochemical reactor equipped with a merry-go-round apparatus. The cuvettes were then irradiated by ten 253.7 nm phosphor-coated low-pressure mercury lamps with a total photon intensity of $1.5 \times 10^{-5}$ Einsteins $L^{-1}$ $s^{-1}$ determined by ferrioxalate actinometry.[12]

The initial concentration of the probe compound at time zero was determined from an unexposed sample. The illuminated samples were removed from the photoreactor at predetermined time intervals and analyzed by high-performance liquid chromatography (HPLC) with a ThermoQuest Hypersil ODS column, using a mobile phase of 2% acetic acid and ACN in the ratio of 60:40 at a flow rate of 1.5 mL/min. The 2,4,6-TCP and its reaction intermediates were identified and quantified by a Finnigan LCQTM DUO ion trap mass spectrometer operating in a negative mode at a capillary temperature of 225 °C and the coupled LC (equipped with a UV6000 LP detector), respectively. In this LC/MS system, however, the signal of chlorophenols in the MS part is weak. Thus, the information of those intermediates was collected mainly from the PDA-UV detector. To confirm the identification of the generated intermediates, the standards of 2,6-DCP, 2,4-DCP, 4-CP, 2-CP, 2,6-DCHQ and phenol were also injected into this system to make a comparison between the standards and intermediates. The detection limit of this method for parent compound and all intermediates is at ng/L level. Duplicate runs of each test were conducted and the variability was within 7%.

## Results and Discussion

**Effect of Initial pH on the Photodecay Rate of 2,4,6-TCP and Photonic Efficiency of 2,4,6-TCP Degradation.** The investigation on the effect of initial pH level on the photodegradation rate of 2,4,6-TCP by UV at 253.7 nm was conducted with the concentration of surfactant above cmc. Chu and Kwan (2003) have pointed out that the presence of surfactant micelle is an effective hydrogen source for the photoreduction.[13] In this case, photoreduction of 2,4,6-TCP is a dominant reaction pathway by the induction of hydrogen source resulting from surfactant. As demonstrated in Figure 1, the reaction rate and photonic efficiency ($\zeta$) as defined by $\zeta = R_0/I_0$ ($R_0$, the initial rate of 2,4,6-TCP degradation; $I_0$, incident light intensity) slightly decreases with the increase of pH level. This is likely attributed to the involvement of photoreduction via photodechlorination mechanism in such a system. It was proposed that the photodechlorination proceeds through photochemical homolysis and electron transfer, where the former involves the cleavage of a C−Cl bond, and the latter requires an electron donor to transfer electrons to the aryl halides.[14] In a solution with a pH level higher than the p$K_a$ of 2,4,6-TCP (i.e., 6.0), the predominant phenolate (anionic form of 2,4,6-TCP) may impede the electron transfer process because it is unfavorable for a negatively charged species to attract another electron.

**Reaction Mechanism and Intermediates.** The photolysis of 2,4,6-TCP in micellar solutions irradiated at 253.7 nm was conducted at pH values of 2.48, 4.94, 7.05, 9.02, and 11.01. The intermediates at the acidic (2.48 and 4.94) and neutral/basic pH levels (7.05, 9.02, and 11.01) were apparently different; therefore, the reaction pathways were divided into two major schemes (see Figure 2) according to the reaction pH in this study. Figure 3 shows the evolution of 2,4,6-TCP and its
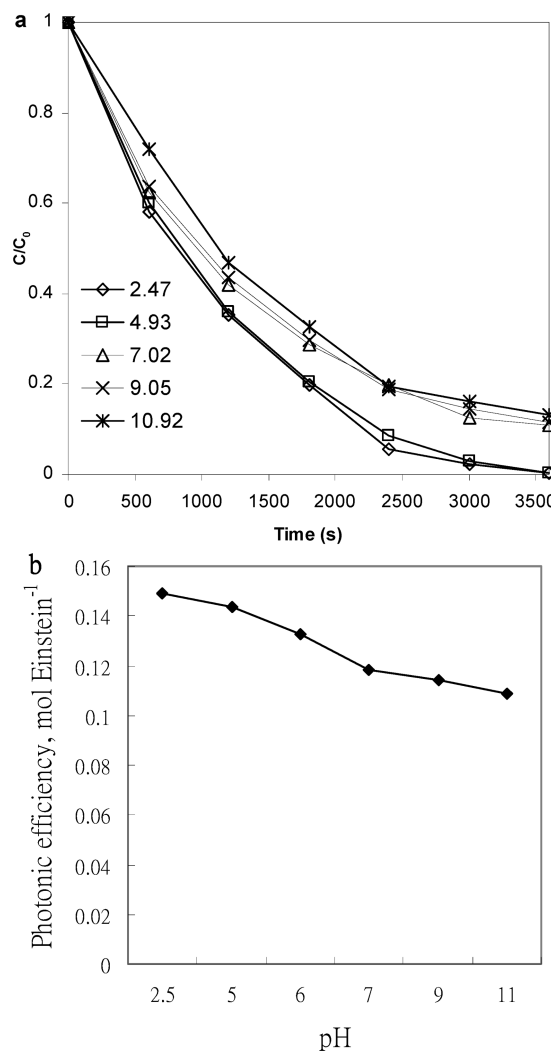


**Figure 1.** (a) Photodecay rate of 2,4,6-TCP in 8.17 mM Brij 35 solution at varied pH level;(b) photonic efficiency of photodecay reaction in 8.17 mM Brij 35 solution at varied pH level.

intermediates during the photolysis process at typically acidic (2.48) and neutral/basic (11.0) pH levels.

For the acidic pH range (Figure 3A), the mass balance (aromatic ring) curve intercepted the total intermediate curve at 3600 s. This indicated that 2,4,6-TCP was completely transformed at that time, at which, the mass balance was solely contributed by the presence of various intermediates. Then, they would be degradable at a later stage as shown in the trend curve. In general, the total intermediate curve increased initially, and then declined because of the accumulation and degradation of primary and secondary intermediates. The mass balance curves for all acidic pH tests showed a continuous decline, whereas no additional and/or significant peaks were observed in the mass spectra. Hence, benzene, the end product from phenol reduction,[15] is likely to be responsible for the decline in the curve, but it degraded rapidly and could not be detected because the photodecay rate coefficient of benzene is very close to that of phenol (i.e., about $3 \times 10^{-4}$ $s^{-1}$, data not shown). In addition, the rupture of the aromatic ring or ring contraction may also be responsible for the decline.[16] Unlike the intermediate curve measured under acidic conditions, the intermediate curve measured under neutral to basic conditions increased slowly and continuously throughout the time course. This behavior suggests that intermediates degraded at a slower rate than that measured under acidic conditions. This is because the decay rate of 2,4,6-
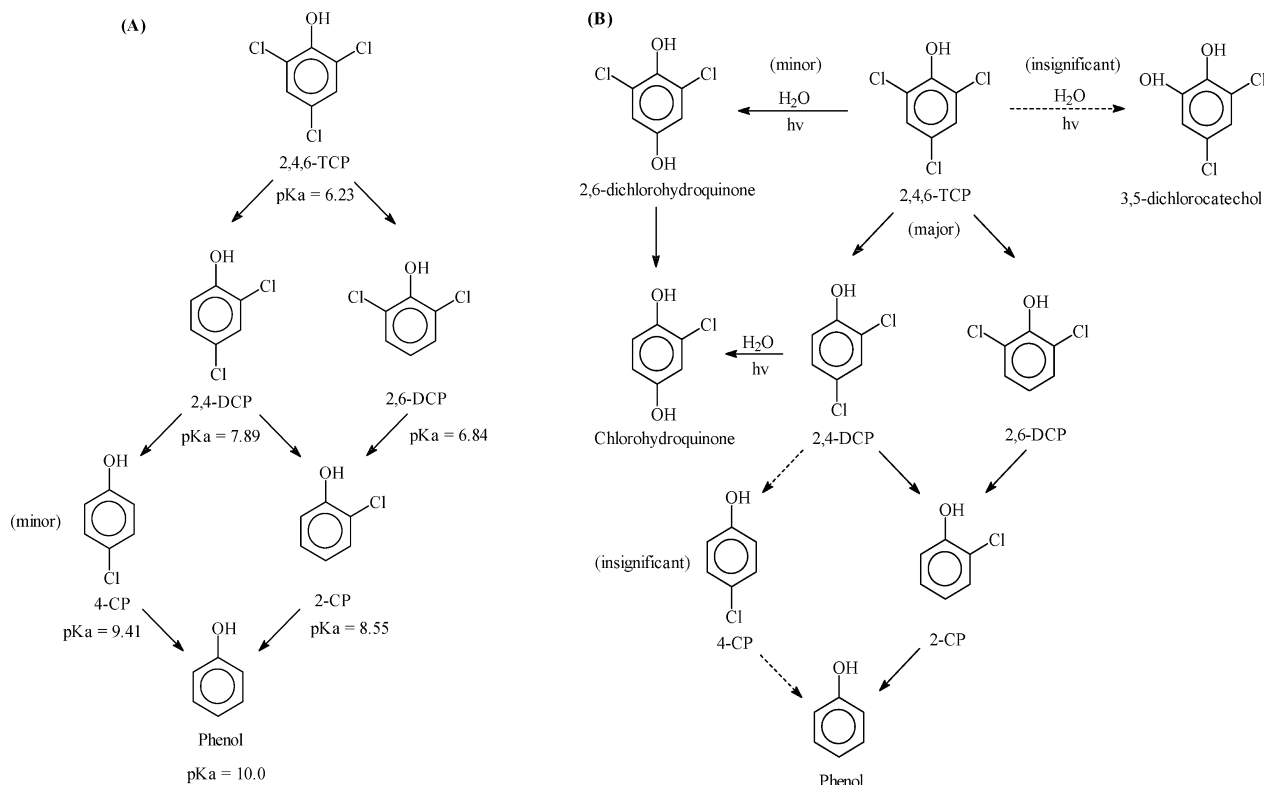
**Figure 2.** Proposed reaction pathways for (A) acidic pH and (B) neutral/basic pH levels.
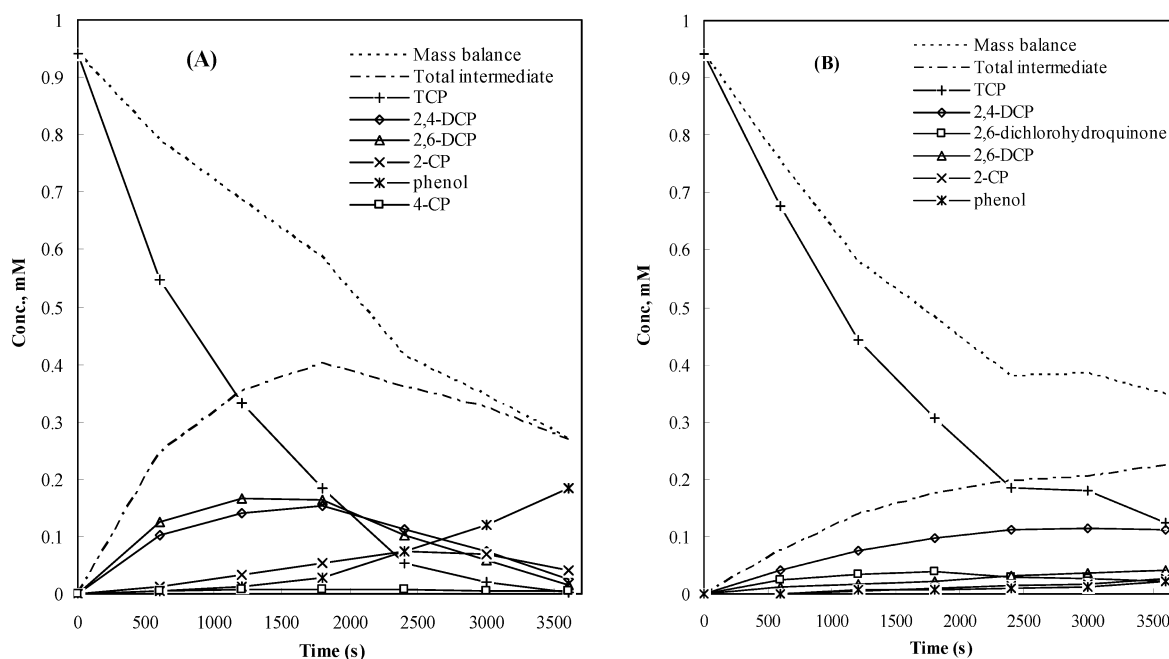


**Figure 3.** Typical concentration changes of 2,4,6-TCP and its degradation products upon UV irradiation at 253.7 nm in 8 mM Brij 35 micelles, at (A) acidic pH (2.48) and (B) medium-to-high pH (11.01) levels. The total intermediate curve is the sum of all individual intermediates. The mass balance (aromatic ring) curve is the combination of 2,4,6-TCP and the total intermediate curves.

TCP and the subsequent degradations of its intermediates are comparatively slower at higher pH levels. The details of reaction kinetics will be discussed later.

One interesting observation was that the intermediates that were detected in the two different pH ranges were different. At acidic pH levels, five major intermediates including 2,4-DCP, 2,6-dichlorophenol (2,6-DCP), 2-CP, 4-CP, and phenol were identified, whereas 2,4-DCP, 2,6-DCP, 2-CP, phenol, and 2,6-dichlorohydroquinone (2,6-DCHQ) were the dominant inter-

mediates found at neutral/basic pH levels. The evolution profiles of these intermediates at measured pH ranges suggest the degradation pathways of 2,4,6-TCP in a UV/surfactant process in Figure 2.

At acidic pH (Figure 2A), the decay mechanism is mainly dechlorination through either the homolysis of a C−Cl bond or via the electron transfer process upon UV absorption. The results are consistent with a mechanism in which hydrogen atoms are abstracted from the surfactant hydrocarbon followed by chlorine

detachment from the aromatic ring. Because photodechlorination may occur at either the para or ortho site, two dichlorophenol isomers can be produced as described in eqs 1 and 2



$$(1)$$



$$(2)$$
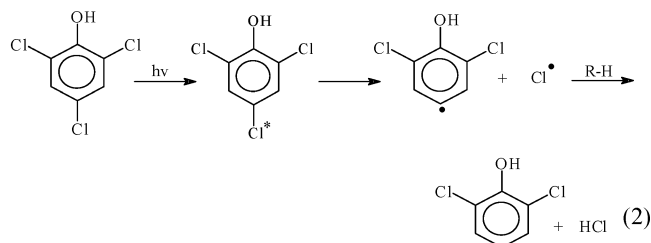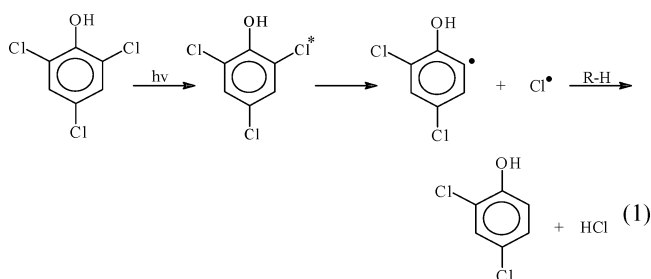
2,4-DCP can subsequently undergo secondary photodechlorination at the ortho- and para-chlorine positions to form 4-CP and 2-CP, respectively. Further decay of 2,6-DCP results in the formation of 2-CP. Regardless of the sources of monochlorophenols, the two isomers were capable of being further dechlorinated to phenol, the last detectable compound, as the end product.

At neutral/basic pH levels, the formation of 2,6-DCHQ suggested that another side pathway must exist. Because one significant difference between the two environments is the hydroxyl ion concentration, the photohydrolysis mechanism likely accounts for the production of 2,6-DCHQ, in which the chlorine atom at the para site of the aromatic ring is replaced by a hydroxyl group.[17] Similar observations of photohydrolysis have been reported previously; for example, catechol was formed when 2-CP was irradiated in water at a pH of above 7, in which catechol resulted from the water nucleophilic displacement of chloride from a singlet excited state of 2-CP.[18,19] The OH substitution of the chlorine atom at the para site was found to be more preferable than the ortho site. The yield of 2,6-DCHQ (para-substitution), therefore, was much higher than that of 3,6-dichlorocatechol (ortho-substitution), which was already close to the detecting limit in the solution. Hydroxylation at the ortho site may experience a more steric strain than that at the para position. Similar suggestions have also been made elsewhere.[7,20] Another possibility is that the dissociated 2,4,6-TCP ion (at a higher pH) is the preferred reaction species for the photohydrolysis process, rather than the molecular form of 2,4,6-TCP ion (at a lower pH). The details will be discussed in a later section.

It should be noted that photodechlorination is still likely to be the dominant mechanism in the overall surfactant/UV reaction, because the highest yield of 2,6-DCHQ observed at pH 11.01 was about 4.12% (of the original 2,4,6-TCP). A trace amount of chlorohydroquinone (CHQ) was also detected in the solution. It came from either the photodechlorination of 2,6-DCHQ or from the subsequent photohydrolysis of 2,4-DCP at a para position.

**Effects of Initial pH on Intermediate Yield.** The change of pH during photolysis process was monitored, and is illustrated in Figure 4. It is noted that there is a general drop of pH with
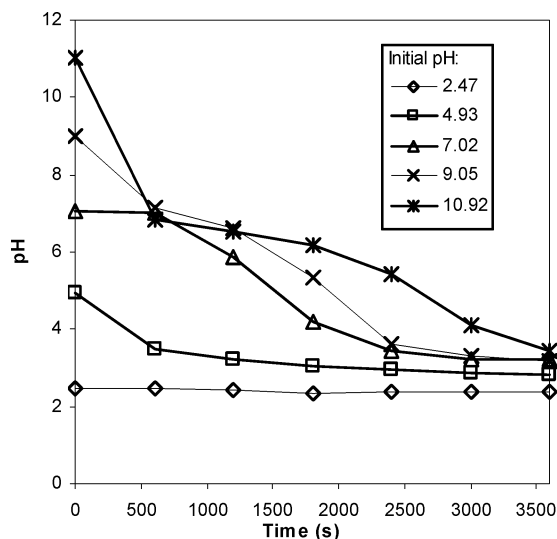


**Figure 4.** Variation of pH in reaction solution during the photodegradation of 2,4,6-TCP in 8.17 mM Brij 35 solution.

the time span. The drop in the pH of the solution was mainly due to the production of excess protons and chlorides from surfactant (the hydrogen source) and from 2,4,6-TCP, respectively, via photodechlorination. The Cl radical abstracts a hydrogen to form HCl and then dissociates to $H^+$ and $Cl^-$ (see eqs 1 and 2). Another important observation was that the solution's pH levels quickly dropped below 7 after 1000 s of reaction even for the neutral/basic cases. This suggests that the photohydrolysis mechanism was significant only at the commencement of the process. Compared to the photodechlorination mechanism, the photohydrolysis can only be considered a minor mechanism, justifying the lower formations of 2,6-DCHQ and CHQ.

The discrepancies in pH drop at different initial pH levels may imply reaction pathways are varied at different scales, making it interesting to investigate the yields of intermediates under different initial pH levels. Six major intermediates including 2,4-DCP, 2,6-DCP, 2-CP, 4-CP, phenol, and 2,6-DCHQ were therefore examined and compared in Figure 5.

The initial formation of 2,4-DCP (see Figure 5A), followed the precise order from low (faster) to high (slower) pH levels. The concentration of 2,4-DCP at acidic pH ranges (2.48 and 4.95), however, reached a peak at 1800 s, then decreased dramatically. This was because 2,4-DCP was transformed to the secondary intermediates of 2-CP or 4-CP with higher decay rates, where the principle of the lower the pH the higher the decay rates was analogous to the decay of 2,4,6-TCP. Similar trends were observed for another intermediate, 2,6-DCP, as shown in Figure 5B. The sharp increases in [2,4-DCP] and [2,6-DCP] at the beginning of the process implied they were the primary intermediates, which is consistent with the proposed reaction pathways (Figure 2).

The decay of the two primary intermediates resulted in the formation of 2-CP and 4-CP. The 2-CP was apparently dominant in all reaction solutions, while the yield of 4-CP is comparatively low under acidic conditions and undetectable in the neutral/basic pH ranges (see Figures 5C and 5D). Interestingly, the concentration of 4-CP reached a plateau during the time course, it was interesting to find that the [4-CP] concentration was maintained at a constant throughout the reaction, indicating that the generation rate (from 2,4-DCP) and the decay rate (to phenol) of 4-CP were about the same. This ruled out the possibility that the undetectable [4-CP] in the neutral/basic pH ranges was due to the faster decay of 4-CP. The domination of
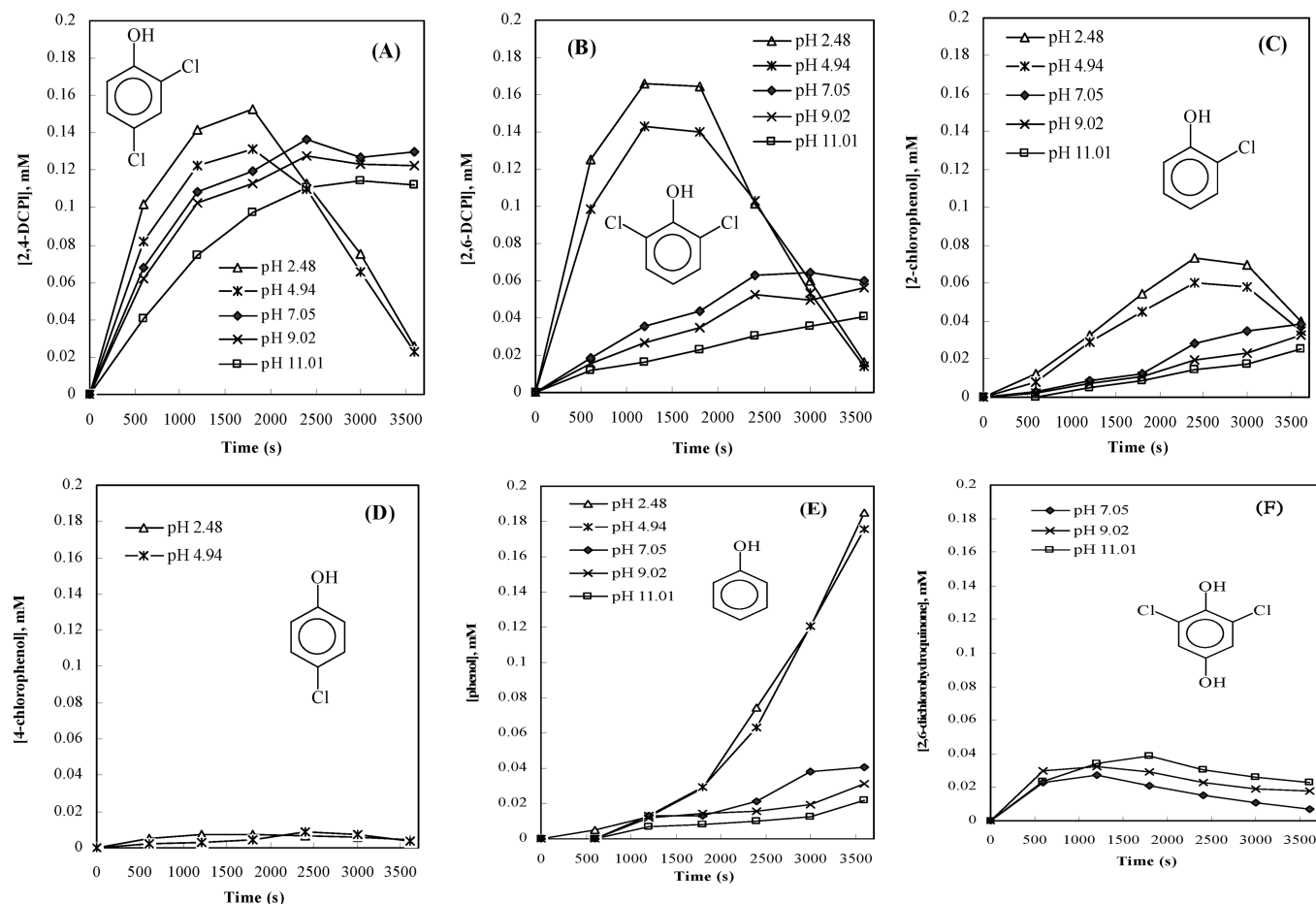
**Figure 5.** The impact of initial pH on the yield of each of the following photoproducts: (A), 4-DCP, (B) 2,6-DCP, (C), 2-CP, (D) 4-CP, (E) phenol, and (F) 2,6-dichlorohydroquinone.

2-CP in the solution was, therefore, expected because that 2-CP was the common intermediate from the dual sources of 2,4-DCP and 2,6-DCP photodecay, whereas the generation of 4-CP was limited to the sole decay of 2,4-DCP. In addition, the constrained yield of 4-CP might also be due to the steric effect at the ortho-position, whereas the photodechlorination is easier at the para-position. A similar effect was also observed for the generation of 2,4-DCP and 2,6-DCP at acidic conditions. Though 2,4,6-TCP has two ortho-chlorines and one para-chlorine on its aromatic ring, the yields of 2,4-DCP and 2,6-DCP are similar (see panels A and B in Figure 5). Judging from the probability of dechlorination on the above sites, the photodechlorination at para-site is likely preferred. One more factor which can rationalize the domination of photodechlorination at para-site is the formation of intramolecular hydrogen bonding (O−H···Cl) and a stable 5-membered ring[21,22] as described in eq 3.

$$(3)$$
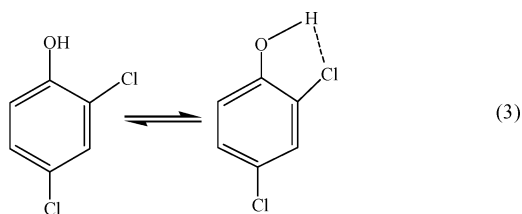
In Figure 5E, the exponential increase of [phenol] in the acidic ranges suggested that phenol is the tertiary degradation product, while simultaneously a significant [2-CP] drop was observed in Figure 5C. The low yield of phenol in the neutral/basic conditions, on the other hand, was due to the slow accumulation of 2-CP.

It was previously mentioned that a special hydroxylated intermediate, 2,6-DCHQ, was identified in high pH ranges as a product of photohydrolysis but was absent in an acidic situation (Figure 5F). The dissociated 2,4,6-TCP ion (at a high pH) may be more susceptible to photohydrolysis than the neutral form. This was because the increase in the spin density on the ring enhances the negative polarization of the chlorine atoms,[17] and therefore promotes the substitution process. Similar suggestions were made for the photohydrolysis of 3-chlorophenol and 3,5- and 3,4-dichlorophenols, where the anionic forms of these compounds had higher quantum yields than that of molecular forms.[17] In addition, the rate of photohydrolysis would increase with an increase in hydroxide ions, which are abundant at a higher pH. Because of unfavorable charge interactions, hydroxide would be expected to attack in the para-position on the ring, as far away as possible from the negative charge on the phenolate anion. This leads to the formation of 2,6-DCHQ rather than the catechol product. The yield of 2,6-DCHQ would decrease at a later stage because of the formation of the dechlorinated product, CHQ (see Figure 5F). Although photohydrolysis was a minor mechanism and could only be observed in neutral/basic conditions, it competed with the para-dechlorination process in transforming 2,4,6-TCP. The result rationalized a significantly lower yield of 2,6-DCP at neutral/basic pH ranges than at acidic pH levels.

## Conclusion

The effect of pH levels on the photodegradation rate of 2, 4, 6-Trichlorophenol (2,4,6-TCP) by UV light at 253.7 nm and

product distribution was investigated in the Brij 35 micellar solution. The increase of pH level was found to exert a negative influence on the reaction rate and photonic efficiency because the predominant phenolate (anionic form of 2,4,6-TCP) may impede the electron transfer process through which photo-dechlorination proceeds in the basic range. At acidic pH levels, five major intermediates including 2,4-DCP, 2,6-DCP, 2-CP, 4-CP, and phenol were identified, whereas 2,4-DCP, 2,6-DCP, 2-CP, phenol, and 2,6-dichlorohydroquinone (2,6-DCHQ) were the dominant intermediates found at neutral/basic pH levels. Two different reaction mechanisms were proposed at acidic pH and neutral/basic pH levels, accordingly. Evolution of each intermediate at different pH levels was also studied, which may further verify the proposed mechanisms.

## Acknowledgment

## Literature Cited

(1) Keith, L. H.; Telliard, W. A. Priority pollutants: a prospective view. *Environ. Sci. Technol.* **1979**, *13*, 416–424.

(2) *Environmental Health Criteria 93. Chlorophenols Other than Pentachlorophenol*; World Health Organization: Geneva, Switzerland, 1989.

(3) Svenson, A.; Kjeller, L. O.; Rappe, C. Enzyme-mediated formation of 2,3,7,8-tetrasubstituted chlorinated dibenzodioxins and dibenzofurans. *Environ. Sci. Technol.* **1989**, *23* (7), 900–902.

(4) D'Oliveira, J.-C.; Minero, C.; Pelizzetti, E.; Pichat, P. Photodegradation of dichlorophenols and trichlorophenols in TiO₂ aqueous suspensions: kinetic effects of the positions of the Cl atoms and identification of the intermediates. *J. Photochem. Photobiol., A* **1993**, *72* (3), 261–267.

(5) Tang, W. Z.; Huang, C. P. The effect of chlorine position of chlorinated phenols on their dechlorination kinetics by Fenton's reagent. *Waste Manage.* **1995a**, *15* (8), 615–622.

(6) Hirvonen, A.; Trapido, M.; Hentunen, J.; Tarhanen, J. Formation of hydroxylated and dimeric intermediates during oxidation of chlorinated phenols in aqueous solution. *Chemosphere* **2000**, *41* (8), 1211–1218.

(7) Ma, H. M.; Wohlers, J.; Meierhenrich, U.; Bernecker, A.; Suling, V.; Thiemann, W. Analysis of oxidative degradation products of 2,4,6-trichlorophenol treated with air ions. *Anal. Chem.* **2001**, *73* (14), 3506–3510.

(8) Antonaraki, S.; Androulaki, E.; Dimotikali, D.; Hiskia, A.; Papaconstantinou, E. Photolytic degradation of all chlorophenols with polyoxometallates and H₂O₂. *J. Photochem. Photobiol., A* **2002**, *148* (1–3), 191–197.

(9) Chu, W.; Jafvert, C. T.; Diehl, C. A.; Marley, K.; Larson, R. A. Phototransformations of polychlorobiphenyls in Brij 58 Micellar solutions. *Environ. Sci. Technol.* **1998**, *32* (13), 1989–1993.

(10) Bunce, N. J.; Kumar, Y.; Safe, S. Photochemisrty of chlorinated biphenyls in iso-octane solution. *J. Chem. Soc., Perkin Trans.* **1978**, *2* (9), 880–884.

(11) Choy, W. K.; Chu, W.; Kwan, C. Y. Photochemical Degradation of 2,4,6-Trichlorophenol in the Presence of a Nonionic Surfactant: pH Control on Reaction Kinetics. *J. Environ. Eng.* **2007**, *133* (6), 641–645.

(12) Horspol, W. M. *Aspects of Organic Photochemistry*; Academic Press: New York, 1976.

(13) Chu, W.; Kwan, C. Y. Reactor Design and Kinetics Study of 4,4′-Dichlorobiphenyl Photodecay in Surfactant Solution by Using a Photosensitizer and Hydrogen Source. *Water Res.* **2003**, *37* (10), 2442–2448.

(14) Chu, W.; Jafvert, C. T. Photodechlorination of polychlorobenzene congeners in surfactant micelle solutions. *Environ. Sci. Technol.* **1994**, *28*, 2415–2422.

(15) Moulton, W.; Wade, C. Notes-Reduction of phenols to aromatic hydrocarbons. *J. Org. Chem.* **1961**, *26* (7), 2528–2529.

(16) Boule, P.; Guyon, C.; Lemaire, J. Photochimie et environnement VIII- Comportement photochimique de dichlorophenols en solution aqueuse diluee. *Chemosphere* **1984**, *13* (5–6), 603–612.

(17) Boule, P., Guyon, C., Tissot, A., Lemaire, J. Specific phototransformation of xenobiotic compounds: Chlorobenzenes and halophenols. In *Photochemistry of Environmental Aquatic Systems*; Zika, R. G., Cooper, W. J., Eds.; ACS Symposium Series; American Chemical Society, Washington, D.C., 1987; Vol. 327, p 10–26.

(18) Shi, Z.; Sigman, M. E.; Ghosh, M. M.; Dabestani, R. Photolysis of 2-chlorophenol dissolved in surfactant solutions. *Environ. Sci. Technol.* **1997**, *31* (12), 3581–3587.

(19) Puma, G. L.; Yue, P. L. Effect of the radiation wavelength on the rate of photocatalytic oxidation of organic pollutants. *Ind. Eng. Chem. Res.* **2002**, *41* (23), 5594–5600.

(20) Tang, W. Z.; Huang, C. P. Photocatalyzed oxidation pathways of 2,4-dichlorophenol by CdS in basic and acidic aqueous solutions. *Water Res.* **1995b**, *29* (2), 745–756.

(21) Brune, B. J.; Koehler, J. A.; Smith, P. J.; Payne, G. F. Correlation between adsorption and small molecule hydrogen bonding. *Langmuir* **1999**, *15*, 3987–3992.

(22) Koll, A.; Parasuk, V.; Parasuk, W.; Karpfen, A.; Wolschann, P. Theoretical study on the intramolecular hydrogen bond in chloro-substituted *N,N*-dimethylaminomethylphenols. I. Structural effects. *J. Mol. Struct.* **2004**, *690*, 165–174.