Photochemical degradation kinetics and mechanism of short-chain chlorinated paraffins in aqueous solution: A case of 1-chlorodecane

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Short chain chlorinated paraffins (SCCPs) have attracted worldwide attention in recent years, due to their high production volume, persistent, bioaccumulative and toxic properties. In this study, 1-chlorodecane (CD) was selected as a model of SCCPs to explore its photochemical degradation behavior under UV irradiation. The results found that CD could be completely photochemically degraded within 120 min, and the *OH was found to be the main reactive species from both quenching experiments and electron paramagnetic resonance (EPR) results. However, the contribution of triple excited state of CD (3CD*) was still nonnegligible from the results with the absorption peak at 480 nm obtained by laser flash photolysis. Based on the identified intermediates as well as the data from theoretical chemical calculation, the detailed photochemical degradation mechanism of CD was tentatively proposed that CD firstly was excited and photo-ionized under UV irradiation, and the released CP in water could result in generating *OH. Then *OH initiates CD degradation mainly through the H-abstraction pathway, leading to the generation of several dehydrogenation radicals, which further generated alcohols or long chain intermediates through radical-radical reactions. The results will provide a comprehensive understanding of the degradation mechanism and environmental fates of SCCPs in water under UV irradiation.

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1. Introduction

Short chain chlorinated paraffins (SCCPs) are extensively used as adhesives, metal-working fluids, sealants, paints, and leather finishing agents as well as plasticizers and flame retardants in rubbers and polymers (Gao et al., 2016c). SCCPs are high production volume chemicals with annual global production of approximately 165000 t (Gluge et al., 2016). There are increasing concerns over SCCPs owing to their persistence, great potential for long-range atmospheric transport, bioaccumulation in food webs, high toxicity to aquatic organisms and potentially carcinogenic property (Du et al., 2018; Sun et al., 2017; Tomy et al., 1999; Zeng et al., 2011; Zhou et al., 2018). In addition, SCCPs could affect the human immune system and reproductive system (Feo et al., 2009). As such, SCCPs have been recognized as new persistent organic pollutants (POPs) in May 2017 by the Stockholm Convention. Moreover, the European Chemicals Agency also added SCCPs into the candidate list of substances of very high concern (Yuan et al., 2017).

SCCPs can be readily released into the environment during their production, metal, industrial use, storage, and carry-off from manufactured products. Therefore, in the past decades, SCCPs have been frequently detected in various aquatic ecosystems worldwide such as Spain, UK, Japan, Canada as well as China (Feo et al., 2009; Gao et al., 2012; Houde et al., 2008; Zeng et al., 2012). Furthermore, due to the incomplete removal by current wastewater treatment technologies, SCCPs are released into the aquatic environment where they are (bio) degraded, bioaccumulated or biotransformed. Several transformation products of some organic compounds are found to be more toxic or persistent than their parental compounds, and thus pose higher risks to the environment (Cui et al., 2011; Gao et al., 2016a; Gao et al., 2016b; Liu et al., 2014). Previous report found that CPs could be dechlorinated and chlorine rearranged in the plant tissues (Li et al., 2017). The thermal decomposition of CPs would generate high PAHs and Cl-PAHs, generally defined as unintentionally produced POPs (Xin et al., 2017). Moreover, chlorinated olefins could be formed during the metal drilling and drilling, and they possibly together with CPs
would accumulate in biota (Schinkel et al., 2018). Therefore, insight into the transformation products and degradation mechanisms is a necessary prerequisite to understand the environmental fate of an emerging organic compound in aquatic environments. However, even though SCCPs are high production volume chemicals, little information is available on transformation products and environmental fate in aquatic eco-systems.

Photochemical transformation is an important process influencing the environmental fate of aquatic pollutants. The current research focuses on the oxidative degradation of organic contaminants in the aquatic environment which is initiated by oxidizing radicals. The existing researches mainly focused on the oxidative degradation of organics in the water environment which may be subjected to attack by oxidizing radicals (An et al., 2014b; Fang et al., 2017a; Gao et al., 2014). For instance, photocatalytic degradation (Chen et al., 2016), Fenton and photo-Fenton reaction (El-Morsi et al., 2002) methods have been reported in the degradation of SCCPs in the aquatic environment, and mainly discussed the complexity of mixture CPs, it is very difficult to study their degradation behavior as a whole. Accordingly, the degradation mechanism of CPs has not been well explained in the literature, although only the longer chain products were reported. Therefore, in here, we chose 1-chlorodecane (CD) as a simplified model compound to investigate potential photochemical reaction mechanisms of SCCPs. Furthermore, the degradation mechanism and transformation pathways could track the degradation of pollutants and trace their attribution, to better explain the causes of these phenomena and to comprehensively evaluate the environmental behavior of compounds. Particularly, no report was focused on the direct photochemical transformation mechanisms of SCCPs in water solution. Hence, to precisely and comprehensively understand the fate of SCCPs in nature, the degradation of SCCPs under direct photolysis should also be clarified.

In natural aqueous systems, direct photolysis also plays an important role in the transformation of some organic pollutants. However, up to date, the direct photolysis of SCCPs has received relatively little attention, due to the lack of appropriate chromophores absorbing light (Feo et al., 2009). Therefore, in this study, a monochlorinated alkane, CD was selected as a simplified model compound to understand the photochemical degradation of SCCPs. The objectives of this study were to investigate the photochemical transformation kinetics under the UV irradiation in aqueous solution, and to identify its photochemical degradation by-products and propose its photolysis mechanism. Moreover, the photochemical transformation pathway and transient intermediates were further validated using theoretical calculation and laser flash photolysis (LFP) experiments. Photochemical investigations in this context may contribute to a better understanding of SCCPs behavior in the environment.

2. Experimental section

2.1. Chemicals and reagents

CD (purity 99.0%) and n-hexane (purity 95.0%) were purchased from J&K Chemical and ANPEL Laboratory Technologies (Shanghai), respectively. Reagents of GC grade (methanol, acetonitrile, hexane, dichloromethane) were purchased from Merck and CNW Technologies. Other chemicals and reagents were of analytical grade. Stock solution of CD was prepared in acetonitrile at concentration of 5000 mg L$^{-1}$ and kept at 20 °C.

2.2. Photodegradation experiments

A photo-reactor with a 1000 W high-pressure mercury lamp (Beijing Cel Sci-tech Co., Ltd., China) was used for all the photochemical degradation CD experiments. The lamp was inserted into the center of a cylinder reactor with Pyrex outer walls. The light was filtered through a quartz jacket (The wavelength was concentrated at approximately 254 nm), situating between the lamp and the reaction vessel, and through the quartz jacket containing circulating water which was used for maintaining a constant temperature of 20 ± 1 °C. The reaction solution was stirred to ensure complete mixing before the lamp was turned on. The homogeneous solution (5 mL) was sampled at specific time and extracted with hexane three times (5.0 mL each time). The liquid-liquid extraction process is presented in Fig. S1 and the recovery rates with approximately 67% were summarized in Table S1, the data of 1-CD concentrations and relevant wavelength (ranges) were provided in Tables S2 and S3, respectively. The hexane extracts were then combined and dehydrated with 0.2 g Na2SO4. The concentration of CD was measured on a HP-5 column (30 m x 0.25 mm ID, 0.25 m thickness) using GC equipped with a Flame Ionization Detector (GC-FID, Agilent 7890 B, USA). Injection temperature was 280 °C. Temperature of column oven was firstly hold on 60 °C for 5 min, then increased from 60 to 280 °C with a gradient of 15 °C min$^{-1}$, and hold 280 °C for 1 min, and the standard curve of standard sample shown in Fig. S2.

To identify the degradation products, 5 mg L$^{-1}$ CD solution was prepared, and the photochemical reaction time was terminated at 30 min 60 mL of the solution was extracted using hexane for three times (15 mL each time). The extracted solution was combined and dehydrated with Na2SO4, and then evaporated to approximately 10 mL with a rotary evaporator. Finally, the extract was concentrated and made up to 1.0 mL with nitrogen blow, and 0.5 mL of the extracted sample was directly analyzed by gas chromatography-mass spectrometer (GC-MS) with electron impact (EI) ionization (GC-EI-MS). Furthermore, in order to identify the possible hydroxylation products, 20 phenyl L double (trimethylsilyl) trifluoroacetamide (BSTFA) was selected as the derivative reagent for the experiment.

The UV--vis absorption spectra were measured using a UV--vis spectrophotometer (Hitachi UV-3010), and the total organic carbon (TOC) concentrations of the solutions were measured by using a Shimadzu TOC-5000A TOC analyzer. Chloride ions resulted from the cleavage of SCCPs during the irradiation were analyzed as follows: a 5 ml aliquot of irradiated solution was sampled at each 30 min reaction time and filled into polyethylene vials. The determination of chloride ions was performed using ion chromatography (ICS-900) based on DIN 38405 unit 19.

2.3. Detection of free radicals

Isopropanol (100 mM) was used to capture the hydroxyl radical (·OH) (Yang et al., 2010), while the H2O2 was used to release ·OH (Qin et al., 2018). The effect of oxygen (O2) was examined in ultrapure water (contains O2) and N2 aeration solution (2 L min$^{-1}$). In addition, 10 mM triethanolamine (TEOA) was added as the quencher of triple excited state (Broglia et al., 2005). K2Cr2O7 (50 µM) was used to quench hydrated electron (eaq) (Chen et al., 2005). On the other side, 10% acetonite was used to promote the generation of triple excited states (Latch et al., 2005). During the
reaction process, 5 mL solution was collected at different reaction time intervals (0, 30, 60, 90 and 120 min) to measure the concentrations of residual CD in the reaction solution using GC-FID.

The electron paramagnetic resonance (EPR) spectra were recorded on a Bruker EMXPlus-10/12 EPR spectrometer. Production of \( \cdot OH \) and \( \cdot O_2^- \) in the reaction mixtures was monitored using 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) as spin trapping agent, while \( \cdot O_2 \) was detected with 2,2,6,6-Tetramethylpiperidine (TEMP) as spin trapping agent. Aliquot 5 ppm CD spiked with 12.4 \( \mu L \) of 100 mM DMPO/TEMP was irradiated for 30 min, and the reaction samples were then diluted by 0.45 mL of water for \( \cdot OH/\cdot O_2 \) detection. Due to the facile disproportionation in water, formation of the \( \cdot O_2^- \) was examined in ethanol solution.

2.4. Laser flash photolysis (LFP) experiments

LFP was carried out using a Nd:YAG laser, and the 266 nm laser pulse with duration of 5 ns was used at the energy of 10–15 mJ per pulse. A xenon lamp was employed as detecting light source, and the laser and analyzing light beam passed perpendicularly through a 1 \( \times \) 10 mm slit and then to a 10 \( \times \) 40 mm quartz cell for the reaction. The transmitted light entered a monochromator equipped with an R955 photomultiplier. The output signal from the HP 54510 B digital oscillograph was transferred to a personal computer with an R955 photomultiplier. The output signal from the HP 54510 B digital oscillograph was transferred to a personal computer for further data analysis (Cheng et al., 2009b; Zhao et al., 2008). All of the measurements were carried out at 25 \( ^\circ \)C immediately after the preparation. For LFP, all anaerobic experiments were achieved by degassing with high-purity N2.

2.5. Computational methods

All quantum chemistry calculations in this work were performed with Gaussian 09 package (Frisch et al., 2009). The geometries and frequencies of the reactants, products, and transition states (TS) were carried out using the hybrid density functional M06–2X method (Zhao and Truhlar, 2008a, b) with 6-31 + G(d,p) basis set. Vibrational frequencies were calculated to ensure the stationary points and true energy minima. The solvent effect was considered by the continuum solvation model ‘SMD’ (Marenich et al., 2009). The minimum energy pathway (MEP) was obtained using intrinsic reaction coordinate (IRC) theory to confirm that each TS accurately connected the reactant with the associated product, and the flow chart of the photochemical degradation system listed in Fig. S3.

3. Results and discussion

3.1. Photochemical degradation kinetic

Before the photochemical experiment, the effect of co-solvent on the photochemical degradation of CD was tested, and the results show the photo-degradation depending on the use of co-solvent (Fig. S4). Due to the fact that acetone is also acted as a sensitiser to accelerate the photo-degradation of SCCPs by photosensitization (Koh and Thiemann, 2001), experiments were carried out in inert co-solvent (acetoneitrile) to minimize the co-solvent effect on the degradation mechanism. The UV/vis absorption spectrum of CD in the water was characterized. As shown in Fig. S5, the absorption spectrum of CD showed a weak overlap (250–300 nm) with that of sunlight reaching the Earth’s surface (\( \lambda > 290 \) nm). Our experimental results confirmed this hypothesis (Fig. 1a). That is, in the control, little loss of CD was observed (<5.8%), indicating that the photochemical degradation of CD was nearly negligible without UV irradiation. In contrast, under UV irradiation, 90% of CD was photochemically degraded within 60 min, and all of CD with an initial concentration of 5 mg L\(^{-1}\) was completely removed within 120 min. This suggests that the photochemical degradation of CD proceeded quickly under UV irradiation. Furthermore, the photochemical degradation curves of CD fit well with the pseudo-first-order kinetics equations (in the insert of Fig. 1a), and the rate constant was obtained as 0.028 min\(^{-1}\), with the half-time of 24.4 min. To further evaluate the photo-chemical transformation of CD, the dechlorination efficiencies were also determined. As shown in Fig. 1b, the concentration of chloride ion (Cl\(^-\)) increased with the concentration of the chloride ion increased over time, and the dechlorination efficiency reached approximately 85% within 120 min irradiation, at which CD was photochemically degraded completely. This indicated the dechlorination efficiency was lower than the degradation efficiency of CD under UV irradiation due to the bond energy of C–Cl bond is higher than that of C–Cl bond (Koh and Thiemann, 2001), illuminating that the dechlorination could be easier to occur than the cleavage of C–Cl bond. It could be inferred that several reactions consuming the chlorine may occur in the system, resulting in the lower dechlorination efficiency. Therefore, it is necessary to further study the transformation mechanism of CD in this system to better illustrate the phenomenon.

3.2. Contributions of different reactive species

To investigate the main reactive species and their contribution to photochemical degradation of CD, specific scavengers experiments were designed, and the degradation kinetics curves with and without the addition of scavengers are summarized in Fig. 2 and Table S4. The degradation of CD was obviously suppressed in the presence of *OH scavenger (isopropanol addition). The rate constant reduced notably from 0.028 to 0.006 min\(^{-1}\), indicating *OH...
contributed to CD degradation efficiency of 58.0% and the photochemical degradation of CD was mostly induced by *OH. With the addition of the scavenger of triplet excited state (TEOA), the rate constant was decreased to 0.014 min\(^{-1}\), suggesting that 25.8% of the contribution was originated from the triplet excited state. Furthermore, excluding \(\text{O}_2\) from the solution by bubbling \(\text{N}_2\) could slightly decrease the rate constant to 0.019 min\(^{-1}\), which is 1.47 times lower than that of rate constant without any scavenger added. This indicates that the oxygen-containing reactive species such as \(\text{O}_2^-\) and/or \(\text{O}_2\) only contributed to 9.4% of CD degradation. In addition, quenching \(e_{\text{aq}}\) produced under UV irradiation by adding \(\text{K}_2\text{Cr}_2\text{O}_7\) decreased the rate constant to 0.017 min\(^{-1}\), implying that \(e_{\text{aq}}\) also involved in the photochemical degradation of CD, but the contribution only of 6.8%. Therefore, *OH and triplet excited state were believed as the main reactive species in the photochemical degradation of CD.

To further confirm the roles of the main reactive species in this study, more experiments on *OH and triple excited state were carried out. Firstly, when 10% (volume fraction) acetone was introduced into solution as a triplet state sensitizer in the system, an extremely high rate constant (0.054 min\(^{-1}\)) was achieved. The acceleration was similar with the observation in the previous study (Koh and Thiemann, 2001), further confirming the contribution of the triplet excited state in this system. Moreover, the addition of \(\text{H}_2\text{O}_2\) also resulted in an increase of the rate constant to 0.058 min\(^{-1}\) due to that *OH was found to be released in the UV/\(\text{H}_2\text{O}_2\) system (Parker et al., 2017), which would increase the concentration of *OH in this system. Therefore, these results further confirmed the above assumption that *OH was mainly responsible for the photochemical transformation of CD under UV irradiation, and the excited triplet state was also involved. Furthermore, EPR technology was further used to doubly confirm the main reactive species involved in this reaction system. As shown in Fig. 3, four characteristic peaks of a 1:2:2:1 quartet pattern were detected under UV irradiation (Fig. 3A), and a significant increasing trend was obtained with the degradation progress of CD under UV irradiation, proving the generation of *OH. Furthermore, the EPR spectra also observed six characteristic peaks of the DMPO-*OH spin adducts in the ethanol solution (Fig. 3B), and there was a clear increase of these peak intensities but not as much as the DMPO-*OH spin adducts. This indicated that both \(\text{OH}\) and \(\text{O}_2^-\) play an important role in the photochemical degradation of CD, and the contribution of *OH was greater than that of \(\text{O}_2^-\). As well known, TEMP could trap singlet oxygen, resulting in the spin adduct TEMPO (Qu et al., 2018). From Fig. 3C, a 1:1:1 triplet signal characteristic of TEMPO radical was not increased as the reaction time increases, demonstrating that \(\text{O}_2\) was not existent in this reaction system. But during 30 min UV irradiation, the intensity of the TEMPO and DMPO-*OH peaks changed slightly, while the formation of DMPO-*OH spin adducts was significantly induced. These spin-trap experiments revealed that *OH contributed mainly to the photochemical transformation of CD, and the contribution of \(\text{OH}\) was greater than that of \(\text{O}_2^-\). In comparison to other studies, the contribution of *OH is almost negligible under UV irradiation during the photochemical transformation of emerging organic pollutants such as halogenated organic compounds (Czaplicka, 2006; Fang et al., 2013, M.K. Kim and O’Keefe, 2000; Pera-Titus et al., 2004), preservative parabens and antiviral drug acyclovir (An et al., 2014a) reported in our early works. However, in the UV/chlorine system, *OH was formed because of the presence of \(\text{HOCl}\) and \(\text{OCl}^-\) (Fang et al., 2017b; Zimbron and Reardon, 2005). For instance, some organic contaminants, such as trichloroethylene, nitrobenzene and 1-chlorobutane, have been proved to be oxidized by the UV/chlorine system, in which *OH could be formed (Feng et al., 2007; Wang et al., 2012; Zimbron and Reardon, 2005). Surprisingly, in this study, it was found that *OH could be generated only with UV irradiation without the addition of extra chlorine. Chlorine in the system could be generated potentially from the photochemical dechlorination of CD with the initial of the excited triplet state of CD (3CD*) or the
3.3. Transient absorption measurements of CD

As shown in Fig. 5, the UV–vis spectrum of CD shows an absorption peak at 255 nm. Therefore, the laser of 266 nm can be employed as the excitation light source to investigate the photoytotic kinetics and mechanism of CD. As shown in Fig. 4, the new intermediate with absorption peak at 240 nm was formed. In addition, this transient specie was formed and increased within the short lifetime scale of nanoseconds, followed by a rapid decay (Fig. S7). From the linear dependence of the intensities of this peak on the concentration of CD (Fig. S8), the pseudo-first-order decay rate constant was determined as 1.68 × 10^10 M^{-1} s^{-1} (in Table S5). The data was further confirmed by the experimental results of photochemical degradation kinetics as followed. In addition, two characteristic peaks at 480 nm and a wide band in 600–800 nm region have been observed in CD solution under excited by UV irradiation. According to the results from early laser flash photolysis studies, the maximum absorption at 480 nm was attributed tentatively to the excited triplet states (Cheng et al., 2009a), and the absorption peaks in the region 600–800 nm may be corresponded to hydrated electron (e_{aq}) (Cheng et al., 2009b; Zhao et al., 2010).

To further verify the existence of CD* and e_{aq}, the quenching experiments were further carried out using LFP. The results of quenching experiment were shown in Fig. S9 (N_{2}-saturated), Fig. S10 (O_{2}-saturated) and Fig. S11 (TEOA), respectively, and the transient absorption spectra obtained from 266 nm LFP together with TEOA, N_{2}-saturated and O_{2}-saturated solution and 5 ppm CD was recorded respectively in Fig. 5 at 9 ns after laser pulse. As shown in Fig. 5, the species with the absorption peak at 480 nm disappeared completely in presence of TEOA as a CD* quencher, compared with that without TEOA. Hence, the transient absorption peak at 480 nm was confirmed the formation of CD*, and the decay rate coefficient of CD* was determined as 1.44 × 10^11 M^{-1} s^{-1} (in Table S6, Fig. S11), which indicated CD* was extremely unstable under UV irradiation and it would be consumed quickly (Fig. S12). In addition, the absorption spectrum of e_{aq} was first checked and compared using the oxygen-bubbled and nitrogen-bubbled solution, because e_{aq} could react with O_{2} leading to the formation of O_{2}^{-} and/or O_{2}. According to the early result of EPR, the O_{2} in this system was negligible, so the active species from this reaction should be mainly O_{2}^{-}. Seen from Fig. 5, after bubbling oxygen in CD solution, the absorption peak in the 600–800 nm range decreased markedly, and the absorption intensity reduced to one fifth of that observed in the aqueous solution. In contrast, the absorption intensity at this range increased around twice in the nitrogen-bubbled solution. Thus, the results doubly confirmed the formation of e_{aq} during the photoionized directly of 1-chlorodecane under UV irradiation, and may be the original of above-mentioned reactive species of O_{2}^{-}.

Overall, from the transient absorption measurements of CD, it could be found that hydrated electrons and excited states could be formed, indicating that both hydrated electrons and excited states play positive roles in the photochemical degradation of CD. These results further confirmed the correctness of the quenching experiments discussed above.

3.4. Photodegradation mechanism of CD

As discussed above, OH was believed as one of the dominant reactive species besides CD in the photochemical degradation of CD. Thus, the detailed degradation pathways of OH-initiated transformation of CD were first modeled using quantum chemistry. As illustrated in Fig. S13, all four different kinds of reaction pathways were considered, and three H-abstraction (H_{ab1}, H_{ab10}, H_{ab6}) and one Cl-abstraction (Cl_{ab}) pathways were obtained. The potential energy surface diagram (PES) and the transition state structure of these four possible pathways are all shown in Fig. 6. It could be found from the calculation results that Cl-abstraction...
pathway was an endothermic process with a positive $\Delta G$ (33.32 kcal mol$^{-1}$), while all three H-abstraction pathways were exothermic process with negative $\Delta G$ ($-23.12$ to $-20.79$ kcal mol$^{-1}$). These data indicate that Cl-abstraction pathway was less spontaneous than H-abstraction pathways. Moreover, the highest energy barrier ($\Delta G^{\ast}$) of 39.94 kcal mol$^{-1}$ was also observed for Cl-abstraction pathway, which was higher by at least 29 kcal mol$^{-1}$ than three H-abstraction pathways. Therefore, Cl-abstraction pathway can be completely ruled out from the degradation mechanism due to the highest energy barrier and highly endothermic process, and that means Cl atom of CD was very difficult to be abstracted by *OH radicals. Furthermore, this finding indicates *OH cannot react with CD directly through the Cl-abstraction pathway, and *OH as well as its precursor HClO in solution only can be generated from the initial photoionization and/or photoexcitation pathways, further confirm the correctness of our proposed above-mentioned mechanisms in Equations (1)–(5).

For H-abstraction pathways, the calculated $\Delta G^{\ast}$ of $\text{H}_{\text{abs}6}$ was obtained as 8.85 kcal mol$^{-1}$, which was slightly lower than $\text{H}_{\text{abs}}1$ (9.65 kcal mol$^{-1}$) and $\text{H}_{\text{abs}10}$ (10.41 kcal mol$^{-1}$). These imply that $\text{H}_{\text{abs}6}$ may be the most favorable pathway for CD degradation, and *OH could easily abstract H atom from the middle C atom of CD. Of course, other two H-abstraction pathways still can be abstract H atom from other position although much slowly than the middle C atom of CD. However, all three pathways can be lead to the formation of dehydrogenation radical *CD(-H)c, and can be further generated alcohols with hydrolytic dissociation or long chain products through radical-radical polymerization reaction although the middle C atom were much important than other two C atom of CD.

The concentration changes of CD during the UV-light-driven photochemical degradation were experimentally monitored by GC. The degradation kinetics of CD by UV-light-driven photochemical degradation were detected and identified with a GC. Fig. S14 shows the gas chromatogram of CD at different irradiation times. After 30 min of UV irradiation, the concentration of CD decreased approximately 60%. Simultaneously, three degradation intermediates peaks ($\text{P}_1$ with $t_R = 11.37$ min, $\text{P}_2$ with $t_R = 11.68$ min, $\text{P}_3$ with $t_R = 12.02$ min) were detected. All of them increased as the reaction time continued. Furthermore, these three possible intermediates were identified and confirmed using GC-EI-MS, and total ion current (TIC) and mass spectra are all shown in Figs. S15 and S16, respectively. The possible structures and retention times of the products were proposed as show in Table S7. The product A corresponds to the hydrolytic product (1-decanol) by the Cl removing pathway at Cl 17 position from parental compound. Other two longer carbon chain length products, product B (1-pentadecanol) and product C (1-heptadecanol) were also found through H-abstraction by *OH attack and then radical-radical reaction pathway. This formation mechanism of the long-chain products were different from the study of (Koh and Thiemann, 2001), that short chain fragments combined to long-chain products through radical-radical polymerization reaction although the middle C atom were much important than other two C atom of CD.

Fig. 6. At the level of M062X/6-31 + G(d,p), the potential surface diagram of the substitution reaction of CD (CD) and *OH was calculated, and the key length unit was (Å).
The concentration of organic carbon was also investigated during the photochemical degradation process of CD (Fig. S17). The mineralization rate of CD in the aqueous was only obtained as 4.96% within 120 min, although the CD could be degraded completely at the same period. This suggests that the degradation intermediates were very persistent, and could not be fully mineralized under UV irradiation. One reason may be explained that the relatively few *OH was generated in this system. As discussed above, *OH was generated only from the reaction of Cl atom cleaved from CD, and the amount of *OH was out of reach the condition for the mineralization of CD and its transformation intermediates. Another possibility was that the degradation intermediates like 1-pentadecanol and 1-heptadecanol were harder to absorb light than the parental CD, and then more difficult to react with *OH. Therefore, these reasons result in the low mineralization, further leading to the persistent of CD and its degradation intermediates in aquatic environment.

Overall, it can be concluded that, during the *OH-initiated direct photochemical degradation of CD in water, it might be produced some persistence and bioaccumulation intermediates, and are exposed to the aquatic organisms for their entire life span, and then possible result in high biological accumulation. Thus, the aquatic toxicities of these photochemical transformation intermediates as well as parent compound CD should not be ignored. Of course, high *OH concentrations can be produces easily under some extreme conditions, which might be a potential ability to achieve the complete mineralization of CD and its intermediates. The results get from this work will gain in-depth understanding on the free radical reaction kinetics and degradation mechanism of SCCPs with similar structures.

3.5. Extrapolation of results to SCCPs in environmental systems

In this work, CD was chosen as a model compound to investigate the photo-degradation pathways of the SCCPs homologous. In fact, SCCPs are complex mixture in environmental systems, and the physical and chemical properties of homologues vary greatly with the content of chlorine and the number of carbon atoms. The increase of carbon chain length could lead to strong increases in $K_{OW}$.

To further identify the mineralization of these intermediates, molecules within certain micelles formed by the insoluble CPs in water. In addition, there might be some potential photochemical degradation products at a low concentration, which were not been detected in this study.

Based on all the evidence presented both from calculation and experiments, the photochemical degradation mechanism of CD (CD) in aqueous solution was proposed in Fig. 7. In the route I, the absorption of UV light promotes CD to photo-excited, and part of the CD was photoionized directly by UV light to produce $e_{aq}$ and the ionized CD (CD$^{+}$), which was consistent with the result of previous research (Cheng et al., 2009b). Part of CD in the ground state was excited to electronically excited singlet (1CD$^*$), and then to electronically excited triplet states (3CD$^*$). 1CD$^*$ was unstable and it was not detected in the study. And the formation of 3CD$^*$ was confirmed at 480 nm wavelength with 266 nm LFP (Fig. 4). However, both CD$^*$ and 3CD$^*$ were unstable in solution, and they would further decompose. CD$^*$ would occur to generate H$^*$ and CD(-H), while the 3CD$^*$ decompose to generate CD(-Cl) and the excited active substances, and the released Cl$^*$ in the aqueous could form the *OH under UV irradiation. Thus *OH was believed as the main reactive species in this photochemical degradation system and then could promote further decomposition of CD. As seen from the route (II), the free radicals of *CD(-H) and *CD(-Cl) forming from above mentioned occurred radical-radical reactions, which would break the carbon chain, or the addition of polymerization. In the route (III), there were two reaction pathways occurred under *OH-initiated: H-abstraction and Cl-abstraction (Clabs) pathway respectively based on our above calculated results. For H-abstraction pathways, H$^*$ may be the most favorable pathway for CD degradation, and *OH could easily abstract H atom from the middle C atom of CD, leading to the formation of dehydrogenation radical *CD(-H)$_{16}$, while for the Cl-abstraction pathway, dechlorination was not easy to happen as compared with H-abstraction reaction based on our above calculated results. Therefore, Cl only could be generated from the photoexcitation pathways. However, both *CD(-H)$_{16}$ and *CD(-Cl)$_{15}$ were unstable in aqueous solution, and could further produce alcohols (product A) or long chain products (product B and product C) through radical-radical reactions.

To further identify the mineralization of these intermediates, the proposed photochemical degradation mechanism of 1-chlorodecane.
and corresponding decreases in water solubility, although the increase of chlorine content did not cause pronounced changes in water solubility and octanol-water partition coefficient (Kow) (Gluge et al., 2013). Thus, for the shorter SCCPs (within five chlorine atoms), due to higher water solubility and lower Kow value, they might be more easily partitioned into the aqueous phase, and have a rapidly photo-degradation (Muir et al., 2000; Zeng et al., 2013). For higher chlorination SCCPs (the number of chlorine atoms n(Cl) > 5), the photo-degradation rate of SCCPs might decrease as the number of chlorines increased, due to steric hindrances (Czaplicka, 2006; Pera-Titus et al., 2004). As such, this may have a potential harm to aquatic ecological environment and it should not be ignored in future studies.

Although the laser flash photolysis experiment was carried out at 266 nm, it might have no apparent overlap with sunlight, which might be work under some extreme conditions such as UV-based advanced oxidation processes. Otherwise, the experiment mainly indicated that triple excitation state played an indispensable role for the photo-degradation of SCCPs and it provided necessary basis for photochemical degradation of SCCPs homologues. Dissolved organic matter (DOM) is usually existed in the natural water environment, and the •OH, singlet oxygen (O182), and DOM triplet states (3DOM) can be generated under solar radiation, which have been proved to play a very important role in the degradation of halogenated compounds (Chen et al., 2012, Akkanen et al., 2004). Similarly, •OH and triple excited states were very important for SCCPs photochemical degradation, in view of this work for CD mechanism of speculation, which was different from the research by Koh and Thiemann, (2001). They did not point out that •OH could rapidly increase the photo-degradation of SCCPs, which may be due to its over-amplification of acetone as a triple excited state and neglect of hydroxyl.

In sum, CD as a simple model provides a certain reference value for the possible degradation pathway of SCCPs. In addition, it also shown that the homologues of CD might be degraded in deep oxidation systems, natural water bodies and extreme weather conditions.

4. Conclusions

This paper mainly reported the photochemical degradation kinetics, mechanisms and fate of CD as the model of SCCPs under UV irradiation based on the combination of theoretical and experimental results. The major findings are listed as following:

1) CD could be completely photochemically degraded within 120 min, with first-order kinetic rate of 0.028 min-1 and half-time was 24.4 min. •OH was believed as the main reactive species with the contribution of 58% to promote the photochemical degradation of CD.

2) It was found that •OH could easily abstract H atom from the middle C atom of CD, to form the dehydrogenation radical •CD-H by theoretical calculation, and 3CD was observed using LEP indicated that triple excited states, as a transient intermediate was mainly formed with the absorption peak at 480 nm.

3) The photochemical degradation mechanism of CD was proposed. CD firstly was photoinduced excitation and photoinitiation, and the free radicals of •CD-(H) and •CD-(Cl) occurred by radical-radical reactions, which was further generated alcohols or long chain products (like 1-pentadecanol and 1-heptadecanol) through radical-radical reactions.

4) For shorter SCCPs (the number of chlorine atoms n(Cl) < 5), the reaction rate could increase as the increase of chlorine atoms; however, for higher chlorination SCCPs (the number of chlorine atoms n(Cl) > 5), the photo-degradation rate might decrease.

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Appendix A. Supplementary data

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References


