Review

Photo-degradation of chlorophenols in the aqueous solution

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Abstract

The review presents the chlorophenols photo-degradation kinetics and mechanism in the aquatic environment under UV–vis in the presence of hydroxyl radicals and singlet oxygen. The influence of experimental parameters e.g. pH, dissociation degree, presence of oxidants in solution, number and position of Cl atoms on the quantum yield and reaction rate constant of chlorophenols are discussed. Mechanisms of photolysis, reaction with hydroxyl radicals, singlet oxygen and secondary reactions for mono-, di-, tri-, tetra- and pentachlorophenol are proposed. The pathways for intermediate reactions e.g. dechlorination, oxidation, dimerization for chlorophenols are also presented.
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Contents

1. Introduction

Chlorophenols (CP) occurs in all components of the natural environment. They result from a variety of sources: the natural chlorination of organic material, biodegradation of phytodefensive chemicals, or the large-scale disinfection of drinking water [1–6]. Chlorophenols are weakly acidic, so in the aquatic environment they occur in both dissociated and undissociated forms. The main photochemical processes involving chlorophenols are: photo-dissociation, photo-isomerization, photo-substitution, photo-rearrangement, photo-oxidation and photo-reduction. In general, the photo-degradation of any substance in the natural environment is a superposition of reactions of several or all of these types, and its rate and quantum yield depend on a variety of factors. The maximum absorption level of the compound, wavelength of radiation, duration of radiation exposure and physical state of the compound undergoing the transformation process play central roles in determining the photochemical processes.

Because of the ubiquitous presence of chlorophenols in the natural environment and their toxic properties, understanding the kinetics and mechanisms of the process of photo-degradation of these compounds is critically important. The results of the investigations concerning this subject are presented below. Despite a great number of publications, however, some questions concerning the mechanisms of reaction during photo-degradation require further investigations.

2. Quantum yield of the photolysis

The quantum yield of a photochemical reaction depends on maximum light absorption of compounds undergoing the process, wavelength of the radiation, the properties of the solvent used [7] and the pH [8–10] of the solution. Boule et al. [9] point out the impact of chlorophenol speciation – dissociated or undissociated – on the quantum yield for photolysis of monochlorophenols upon 254 nm irradiation. Various papers show that photolysis of the anionic forms of these compounds results in a higher quantum yield than that of other molecular forms [10–13]. Some of the results concerning the quantum yield of photo-degradation of various chlorophenols have been taken from the literature and are presented in Table 1.

3. Kinetic study

The ability to undergo chemical transformation upon photon absorption is an intrinsic molecular property and may drastically differ among various compounds. Also, in the aquatic environment, the possibility of photo-induced transformation of the intermediate products of the primary reactions increases when the dissolved organic material has absorbed a high proportion of photons and can act as a potential photosensitizer. In the aquatic environment, singlet oxygen, superoxide ions, hydroperoxyl radicals, hydroxyl radicals and peroxy organic radicals may arise [14–28]. Under these circumstances photo-degradation processes may include direct photolysis and reactions with of reactive species. The kinetics and mechanism of these reactions is highly dependent on experimental conditions such as the wavelength of irradiation, pH of solution, concentration of dissolved oxygen and the presence of sensitizers. The kinetic results of chlorophenol transformation upon direct photolysis and reactions with •OH radicals and singlet oxygen are presented below.

3.1. Direct photolysis

The law describing light absorption in an aqueous environment is the Lambert–Beer law for liquid phase, expressed by the equation:

$$\log \left(\frac{E_\lambda^0}{E_\lambda^I} \right) = \varepsilon_\lambda c_i l \tag{1}$$

where E_λ^0 and E_λ^I are the light intensities, l the distance in the environment (optical path) [cm], ε the extinction coefficient [$M^{-1}\, cm^{-1}$] and c_i is the concentration [M] of component i.

The absorbance at wavelength λ is the product $\varepsilon_\lambda c_i l$.

The rate constant k for direct photolysis is defined by equation:

$$k = 2,3\phi_A^A I_0 \varepsilon_A l \tag{2}$$

where $\phi_{d,\lambda}$ is the quantum yield of the reaction, $I_{0,\lambda}$ the light intensity, ε_A the molar extinction coefficient of substance S at wavelength λ, and l is the optical path.

The results from Eq. (2) show that the rate of the direct photolysis of chlorophenols is proportional to the irradiation intensity.

Table 1
Quantum yields (ϕ) for chlorophenols, pH 7

| Compounds	ϕ	λ (nm)	Reference
2-Chlorophenol molecular form	0.03	296	[9]
2-CP anionic form	0.20	296	
3-Chlorophenol molecular form	0.09	296	[9]
3-CP anionic form	0.13–0.15	296	
4-Chlorophenol	0.25	296	[9]
	0.75	266	[10]
	0.44	266	[11]
4-Chloro-2-methylophenol	0.66	280	[12]
2,4,5-Trichlorophenol	5.9×10^{-2}	254	[13]
Pentachlorophenol	0.06	185–436	[8]

In the case of direct photolysis in a thin, near-surface layer the rate constant (k_d) is described by Eq. (3) [13]

$$k_d = 2, 3\phi_{d,\lambda} \int \varepsilon_\lambda(\lambda) I_{0,\lambda} \, d\lambda \tag{3}$$

where $\varepsilon_\lambda(\lambda)$ is the molar extinction coefficient of substance S at wavelength λ and $\int \varepsilon_\lambda(\lambda) I_{0,\lambda} \, d\lambda$ is the overlap integral of the radiation source and the absorption of substance A. In natural circumstances, dark processes initiated by photon absorption are insignificant. On the other hand, microbial degradations (dark processes) of photoproducts of polychlorinated phenols is rapid [29]. In this case, the dark processes play the main role.

Chlorophenols strongly absorb radiation wavelengths between 230 and 300 nm. Various studies show that the rate of photolysis of chlorophenols depends on the pH of the reaction environment [8,9,26,30,32–35] and on the structure of the molecule—particularly the positioning of the chlorine atom relative to the hydroxyl group [13,23,29,30,33,35,37–41].

Because chlorophenols partially dissociate in aqueous solutions, the reaction schemes of photo-transformation are as follow:

$$CP^- \xrightarrow{k_1 \, h\nu} product \, 1 \tag{4}$$

$$CP \xrightarrow{k_2 \, h\nu} product \, 2 \tag{5}$$
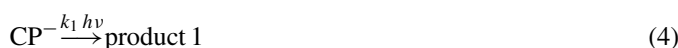
and the general kinetic equation for the photo-degradation reaction has the form:

$$\frac{-d[CP]_{tot}}{dt} = k_1[CP^-] + k_2([CP]_{tot} - [CP^-]) \tag{6}$$

or

$$\frac{-d[CP]_{tot}}{dt} = k_1 \alpha [CP]_{tot} + k_2(1-\alpha)[CP]_{tot} \tag{7}$$

where k_1, k_2 are the reaction rate constants for dissociated and undissociated chlorophenols, respectively, $[CP]_{tot}$ the total concentration of chlorophenol, $[CP^-]$ the concentration of dissociated molecules and α is the degree of dissociation, defined as

$$\alpha = \frac{1}{1 + 10^{(pK_a - pH)}} \tag{8}$$

From these considerations it may be concluded that the observed reaction rate is a sum of the reaction rates of the undissociated and dissociated forms of the compound. It is also known that the reactivity of these forms differs considerably. Observational analysis has regularly found that dissociated forms are more reactive than undissociated ones [36]. An increase in the reaction rate constant with increasing pH, was observed by Benitez et al. [8,36] and Shen et al. [34]. Photolysis rate constants for chlorophenols determined under some conditions are presented in Table 2.

3.2. Kinetics of reactions with $^\bullet OH$ radicals

Hydroxyl radicals can be formed through various chemical reaction pathways, such as: (i) irradiation of H_2O_2; (ii) photol-

Table 2
Rate constants for direct photolysis of chlorophenols

Compounds	Rate constant reaction (min^{-1})	pH	Comments
2-CP	7.1×10^{-3}	3	$\lambda = 254$ nm, lamp intensity 60 W m^{-2} [34]
	7.7×10^{-3}	5	
	20×10^{-3}	7	
	101×10^{-3}	11	
2,4-DCP	3.6×10^{-3}	3	
	4.5×10^{-3}	5	
	28.6×10^{-3}	7	
	126×10^{-3}	11	
2,4,6-TCP	2.3×10^{-3}	3	
	6.3×10^{-3}	5	
	29.4×10^{-3}	7	
	36.3×10^{-3}	11	
PCP	0.16	3	Polychromatic radiation in the range from 185 to 436 nm, $\phi \times 10^3 = 200$ mol E^{-1} [8]
	0.19	5	$\phi \times 10^3 = 112$ mol E^{-1} [8]
	0.21	7	$\phi \times 10^3 = 52.5$ mol E^{-1} [8]
	0.26	9	$\phi \times 10^3 = 22$ mol E^{-1} [8]

ysis of ozone, either through the generation of singlet oxygen atoms which then react with water to generate $^\bullet OH$; (iii) photolysis of Fe^{3+} or polyoxometallates [42]; (iv) Fenton type reaction of Fe^{+2}, Cu^{+1} or Ti^{+3}; (v) radiolysis of water [43]. The hydroxyl radicals can be also formed by the radiolysis of water in the presence of N_2O (Eq. (9))

$$N_2O + e_{aq}^- \rightarrow N_2 + {}^\bullet OH + OH^- \tag{9}$$

In the case of natural water, present protonic forms of nitrate and nitrous ions are a sources of hydroxyl radicals [44]. The organic matter dissolved in aquatic environment, especially humic acids, absorbed a large portion of photons, and formation of hydroxyl radicals can also occur. Hydroxyl radicals can react with organic substances by: electron transfer, $H^\bullet$ abstraction, or $^\bullet OH$ addition to an aromatic ring [45,46]. The present paper discusses results of kinetic investigations of the reactions of chlorophenols with hydroxyl radicals, generated by adding H_2O_2 to irradiated aqueous solutions of these compounds [14,23–26,34,35,40,47–64].

The reaction of chlorophenols and hydroxyl radicals is described by a second order reaction model [35,56,64] or as a pseudo-first order reaction [23,40,58].

The rate constant for the reaction of hydroxyl radicals with 3-chlorophenol (3-CP), determined with pulse radiolysis by Savel'eva et al. [64], at a pH equal to 9, was $k(OH + CP) = 0.72 \times 10^{10}$ M^{-1} s^{-1}. Kochany and Bolton [35], applying a technique of spin trapping with detection by electron paramagnetic resonance (EPR) spectroscopy, examined the rates of reaction for mono- and dichlorophenols with $^\bullet OH$ radicals generated by irradiation of H_2O_2. A 150 W mercury–xenon lamp was used as the light source, while the pH of the solution

Table 3
Rate constants for the reaction of •OH radicals with chlorophenols using spin trapping technique with EPR detection, pH = 7 [35]

Compound	Rate constant (10^{10} M$^{(1}$ s$^{(1)}$)	
	With a Pyrex filter	Without a Pyrex filter
2-CP	1.65	1.69
3-CP	0.86	0.84
4-CP	2.82	2.65
2,4-DCP	3.10	2.95
3,5-DCP	0.78	0.72

was held at 7. To exclude the influence of direct photolysis as a possible side reaction, they have performed a series experiment using a Pyrex filter, which eliminates light radiation for $\lambda < 300$ nm. Obtained results were analyzed within following kinetic model:

$$H_2O_2 \xrightarrow{\phi N_a} 2 \, {}^{\bullet}OH \tag{10}$$

$$ {}^{\bullet}OH + DMPO \xrightarrow{k_2} DMPO - OH \tag{11}$$

$$ {}^{\bullet}OH + S \xrightarrow{k_3} products \tag{12}$$

$$S \xrightarrow{\phi' N_a'} products \tag{13}$$

where N_a and N' are the rate of photon absorption by H_2O_2 and substrate (S), ϕ and ϕ' are corresponding quantum yields, k_2 the rate constants of the reaction of •OH with DMPO, k_3 the rate reaction of •OH with chlorophenols.

On applied a steady-state analysis of the above mechanism they obtained correlation:

$$\frac{R_0^0}{R_0} = 1 + \frac{k_3[S]_0}{k_2[DMPO]_0} \tag{14}$$

where $[S]_0$ and $[DMPO]_0$ are initial concentration, R_0^0/R_0 is the inverse initial rate ratio, R_0^0 is the value initial rate of formation of DMPO–OH (R) when $[S] = 0$. R_0 is initial rate of formation of DMPO–OH. For all calculation, they assumed that $k_2 = 4.3 \times 10^9$ M^{-1} s^{-1}.

The results obtained (Table 3) show that rate constants for the reaction of •OH radicals with monochlorophenols $\{k_3(OH+CP)\}$ and 2,4-DCP and 3,5-DCP range from 0.78×10^{10} M^{-1} s^{-1} for 3,5-DCP to 3.10×10^{10} M^{-1} s^{-1} for 2,4-CP with the use of a filter and range from 0.72×10^{10} M^{-1} s^{-1} for 3,5-DCP to 2.95×10^{10} M^{-1} s^{-1} for 2,4-CP without the use of a filter. Considering the few differences between reaction rate constants of chlorophenols under conditions with and without filters, the authors saw little influence of photolysis on the rate constant of this reaction. It was also found, that the reactivity of this reaction decreases in the following order: 4-CP > 2-CP > 3-CP, and 2,4-DCP demonstrated higher reactivity in comparison with 3,5-DCP. It was also observed that the alkalinity of the reaction environment caused an increase in the reaction rate constant. De et al. [56] investigating UV/H_2O_2 photo-oxidation of 2-CP and 4-CP using a UV dosage of 24 W/L showed that the reaction rate between monochlorophenols and

•OH radicals amounted to 0.91×10^{10} M^{-1} s^{-1} for 2-CP and 1.07×10^{10} M^{-1} s^{-1} in the case of 4-CP. They showed that the conversion of monochlorophenols also increased with increasing of the initial concentrations of H_2O_2. On the other hand, it was observed that the conversion of substrate depended on the initial concentration of chlorophenols. The rate of degradation increase almost linearly with the increase of initial concentration of substrate. The values of the reaction rate constants suggest that the reaction rate is controlled by diffusion [55,59].

Antonaraki et al. [23], Apak and Hügul [24], Hugül et al. [58] and Shen et al. [34] obtained another kinetic model for this reaction. At relatively high ratios of oxidant-to-CP, these authors used the pseudo-first order to describe the reaction of chlorophenols with •OH radicals. The investigations found that H_2O_2 concentration influenced the rate of photo-oxidation for some chlorophenols at wavelengths 240–570 nm (exhibiting the maximum quantum efficiency at 250 nm) [58]. Due to the range of radiation wavelengths used, both direct photolysis and hydroxyl radical reactions occur within the reaction system. The chlorophenol/H_2O_2 mole ratios were 1:1, 1:4, and 1:8. They observed that the reaction rate constant decreased when ratios were 1:4 and 1:8 for the examined compounds, in the following order: 2,4,6-TCP > 2,4-DCP > 2-CP. The rate constants for the 1:4 chlorophenol to H_2O_2 ratio was 4.86×10^4 s^{-1} for 2,4,6-TCP, 4.56×10^4 s^{-1} for 2,4-DCP and 3.10×10^4 s^{-1} in the case of 2-CP. A similar correlation between reaction rate constants and the number of chlorine atoms in the chlorophenol molecule was presented by Sundstrom [65]. On the other hand, for 1:1 chlorophenol/oxidant mole ratios rate constants decrease in the order: 2,4,6-TCP > 2-CP > 2,4-DCP. These data may suggest that the reaction is accelerated not only an increase in the number of chlorine atoms in a molecule, but also by the chlorophenol to oxidant ratio. Investigations by Ghaly et al. [40] under similar irradiation conditions (200–600 nm) for photo-degradation of 4-CP under UV in the presence of H_2O_2 show that the addition of H_2O_2 causes an increase in the degradation rate when the H_2O_2 concentration increases over the interval 0.005–0.02 mol/l and for 0.05 mol/l. However, the effect of hydrogen peroxide was negative for concentrations higher than 0.02 mol/l, for which the 4-CP degradation rate was even lower than that obtained from the direct photolysis. A strong relationship between pH and rate constant was also observed. De et al. [56] presented similar results. They found that the initial substrate concentration, e.g. *ortho*- and *meta*-chlorophenols to H_2O_2 molar ratio of around 0.02 gave a maximum substrate conversion. Yue and Legrini [66], investigating the 4-CP oxidation by advanced oxidation process using UV/H_2O_2, postulated that the kinetics of the photo-oxidation of dissolved organics depends on the initial concentration of the parent organic compounds. Reaction rate constants for photo-oxidation reactions of some chlorophenols are presented in Table 4.

Antonaraki et al. [23] investigated the photo-oxidation of chlorophenols in the presence of H_2O_2 using irradiation with $\lambda > 320$ nm (the conditions of the experiments precluded direct photolysis), a concentration of H_2O_2 at 30% (v/v), an initial concentration of substrate of 1×10^{-3} M and pH 1. They observed that rates of decomposition

Table 4
The pseudo-first order rate constants (k) of chlorophenol with hydroxyl radicals

Compounds	k	Unit	Comments
2-CP	0.0341	min^{-1}	$\lambda = 254$ nm, pH 7 [33]
2-CP	1.86	s^{-1}	$\lambda = 250$ nm, CP/H_2O_2 mole ratio 1:1 [58]
2-CP	3.10	s^{-1}	$\lambda = 250$ nm, CP/H_2O_2 mole ratio 1:4 [58]
4-CP	0.15	min^{-1}	$\lambda = 200–600$ nm [40]
2,4-DCP	0.0792	min^{-1}	$\lambda = 254$ nm, pH 7 [33]
2,4-DCP	1.62	s^{-1}	$\lambda = 250$ nm, CP/H_2O_2 mole ratio 1:1 [58]
2,4-DCP	4.56	s^{-1}	$\lambda = 250$ nm, CP/H_2O_2 mole ratio 1:4 [58]
2,4,6-TCP	0.0347	min^{-1}	$\lambda = 254$ nm, pH 7 [33]
2,4,6-TCP	2.60	s^{-1}	$\lambda = 250$ nm, CP/H_2O_2 mole ratio 1:1 [58]
2,4,6-TCP	4.81	s^{-1}	$\lambda = 250$ nm, CP/H_2O_2 mole ratio 1:4 [58]

of CPs calculated from the first-order reaction model decrease for monochlorophenols in the order 3-CP > 4-CP > 2-CP, for dichlorophenols: 3,5-DCP > 2,5-DCP > 3,4-DCP > 2,3-DCP > 2,4-DCP > 2,6-DCP and for trichlorophenols: 3,4,5-TCP > 2,3,5-TCP > 2,4,5-TCP > 2,3,6-TCP > 2,3,4-TCP > 2,4,6-TCP.

In the presence of UV radiation, hydrogen peroxide photo-dissociates to form $^\bullet$OH free radicals, which attack the benzene ring and undergo very rapid and effective substitution reactions to form oxygenated intermediates.

3.3. Reactions with singlet oxygen

Singlet oxygen ($^1O_2$) is the first excited state of molecular oxygen. As a moderately reactive electrophile, it oxidizes numerous electron-rich organic substances. The method most frequently used for producing singlet oxygen in the laboratory is photo-sensitization. Eosin [67], rose bengal [20], methylene blue [68] metallophthalocyanine [69] are usually used as a photo-sensitizers. Both continuous irradiation and pulsed excitation studies have made much use of this method of singlet oxygen generation. Singlet oxygen can be directly generated by absorption of the output at 1065 nm of a pulsed Nd-glass laser by oxygen dissolvent under pressure in 1,1,2-trichlorotrifluoroethan [70]. Singlet oxygen in natural waters can be produce in oxic aqueous solutions of an appropriate sensitizer that absorbs light and transfers the energy to dissolved triplet oxygen. The dissolved organic matter is a primary sensitizer responsible for singlet oxygen formation.

Reactions of phenols with singlet oxygen are well known, but most of the research concerns mechanisms and kinetics of reactions of singlet oxygen with phenols in non-aqueous solutions, and therefore cannot be used to predict these reactions in the aqueous environment. It is supposed that $^1O_2$ interacts with organic substances forming endoperoxides and, via a mechanism resulting in one- or two-electron transfer, a superoxide radical or hydrogen peroxide, respectively, is formed. It has been shown that the reaction of $^1O_2$ with phenol derivatives proceeds mainly according to mechanisms of physical quenching or electron transfer [20,67]. Quenching of $^1O_2$ by water is a first-order reaction, quenching by a probe substance is a second-order reaction.

The reaction of a compound (S) with $^1O_2$ follows the scheme:

$$^1O_2 + S \xrightarrow{k_1\ h\nu} {}^3O_2 + S^*$$

(15)

or

$$^1O_2 + S \xrightarrow{k_2\ h\nu} products$$

(16)

where k_1 is the rate constant of a second-order reaction of physical quenching of $^1O_2$ by the substance under investigation, k_2 the rate constant of a second-order reaction between $^1O_2$ and the substance under investigation.

When chlorophenols dissociate in water, a full description of the kinetics of photo-oxidation, similar to that of previously discussed reactions, should take into account forms of occurrence of the compound in an aqueous environment. Thus, the rate constant k_2 of the reaction is the sum of the rate constants of the reactions of both forms of the compound, the molecular and the dissociated

$$k_2 = (1 - \alpha)k_{CP} + \alpha k_{CP^-}$$

(17)

But simultaneously, assuming a pseudo-first order model of the reaction, we get the equation

$$\frac{d[CP]}{dt} = k_{obs}[CP]$$

(18)

where

$$k_{obs} = k_2[^1O_2]$$

(19)

For various chlorophenols, Tratnyek and Holgně [20] determined the rate constants for reactions of singlet oxygen with dissociated and undissociated forms of these compounds at wavelengths above 520 nm. Rose bengal was used as a sensitizer for formation of $^1O_2$. Their results show significant differences in the rates of the discussed reactions. Undissociated molecules react more slowly with singlet oxygen (Table 5). The stability of the transition states of phenol or phenolate and singlet oxygen determines the rate of photo-oxidation. The electronic interaction takes place between the calculated lowest unoccupied molecular orbital (LUMO) of singlet oxygen, located at -0.98 eV, and the calculated highest occupied molecular orbital (HOMO) of phenolate at -2.69 eV and of phenol located at -9.81 eV. An increase in the difference between the energy of the LUMO of singlet oxygen and the energy of the HOMO of the organic substrate results in weaker electronic interaction. Gerdes et al. [71] explains how in this way phenol is less reactive than

Table 5
Rate constants for the reaction singlet oxygen with chlorophenols ($\lambda > 520$ nm) [20]

Compounds	pK_a	k_{CP} ($M^{-1}\,s^{-1}$)	k_{CP^-} ($M^{-1}\,s^{-1}$)
2-CP	8.55	$9.2 \pm 9.4 \times 10^6$	$1.92 \pm 0.1 \times 10^8$
3-CP	9.12	$5.4 \pm 1.0 \times 10^6$	$1.60 \pm 0.02 \times 10^8$
4-CP	9.41	$6.0 \pm 3.6 \times 10^6$	$1.93 \pm 0.04 \times 10^8$
2,4-DCP	7.89	$5.1 \pm 4.7 \times 10^6$	$1.70 \pm 0.03 \times 10^8$
2,4,6-TCP	6.23	$1.7 \pm 0.7 \times 10^7$	$1.67 \pm 0.07 \times 10^8$
PCP	4.70	$0.2 \pm 5.5 \times 10^6$	$9.36 \pm 0.36 \times 10^7$

phenolate during this process. The rate of reaction is also affected by substitution of a chlorine atom in the molecule. Tratnyek and Holgně [20] have also shown that the reaction rate constants of the dissociated chlorophenols decrease in the following order: 4-CP > 2-CP > 2,4-DCP > 3-CP > 2,4,6-TCP > PCP, and those of the undissociated chlorophenols in the order: 2-CP > 4-CP > 3-CP > 2,4-DCP > 2,4,6-TCP > PCP. Ozoemena and Kuznetsova [69] studied photosensitised transformations of polychlorophenols at wavelengths above 600 nm, finding that the contribution of the type II (singlet oxygen-mediated) mechanism to the relative efficiency of the photosensitised photo-oxidation of phenol, decreased from phenol to 4-CP, TCP and PCP, whereas, the type I (photo-induced electron transfer process to give the primary radicals) increased. The results obtained for PCP show that the electron transfer from the excited sensitizer to the substrate in its unionised form is responsible for enhanced sensitizer photodegradation.

In summary, the cited papers indicate that combinations of hydrogen peroxide and UV irradiation increase the photodegradation rate of chlorophenols when compared with UV irradiation alone. In the case of UV/H_2O_2, the initial ratio of chlorophenols to oxidant is important. Independently of the reaction conditions e.g. the presence of hydrogen peroxide or singlet oxygen in solution [20,34], the rate of photo-degradation of chlorophenols is higher in alkaline solution [23,50]. This is due to higher concentrations of more reactivity, dissociated forms. Reactions rate depend on the number and position of chlorine atom in the molecule. It was found that the contribution of the types I or II mechanism in photosensitised photo-oxidation depended on structure molecule. The role of chlorine atom substitution will be discussed in detail in the next chapter.

3.4. The influence of the number and position of Cl atom on the photo-degradation rates of CPs by direct photolysis, UV/H_2O_2 and UV/$^1O_2$ reactions

The various papers indicated the important of the chlorine positions on chlorophenol isomers in the kinetics of chlorophenol photo-degradation [9,13,23–25,33–36,56,58,72–74]. It is well known that the OH group is a very strong activator as well as *ortho*- and *para*-directing in electrophilic aromatic substitution. Therefore a direct •OH radical attack on electron rich positions should be expected. Halogen substituents are slightly deactivating but are also *ortho*-, *para*-directing in this reaction. The inductive effect of the hydroxyl group, due to the electronegativity of oxygen, is the withdrawal of electrons. For the nucleophilic substitution the Cl group directs to the *para*-position in this reaction. In the case of radical reactions, a nucleophilic radical will react preferentially at the *ortho*- and *para*-positions if the substituent is π-acceptor, and at the *meta* if it is a π-donor. The opposite situation occurs for an electrophilic radical. Cassady et al. [75], in their investigations of chlorophenols and methylchlorophenols with the use of Fourier transformation ion cyclotron resonance mass spectrometry (FTMS), suggest that the relative positions of the chloro- and hydroxyl groups may have greater effects on photo-dissociation than the methyl group position.

3.4.1. Direct photolysis

Boule et al. [9] found that during direct photolysis the dechlorination rate of 4-CP and 2-CP is faster than 3-CP. Kuo [76] observed that the reaction rate for direct photolysis upon irradiation at λ < 300 nm decreases in the order: 2,4-CP > 4-CP > 2-CP. Shen et al. [34] on the basis of results obtained under similar conditions, found rate constants during direct photolysis decrease in the order: 2,4-CP > 2-CP > 2,4,6-TCP. These results indicated that the *para-* and *ortho*-positions are more active in direct photolysis. The increased occurrence of *para*-position in comparison with *ortho*-position in this reaction is explained by the intermolecular hydrogen bonding between the *ortho*-positioned Cl atom and a hydrogen from the hydroxyl group. In the case of *ortho*-substituted chlorophenols, hydrogen bonds may be formed internally between Cl and OH as well as externally between molecules of chlorophenol and water. Bazyl et al. [73], Akai et al. [77], Ahn et al. [78,79] and Feng [80] described the molecular structures of phenol chloroderivatives and their complexes with water.

The citied paper indicated that the structure of compounds, especially of a position of the chlorine atom relative to the hydroxyl group, determines the reactivity of chlorophenol in direct photolysis. The chlorine atom is photo-reactive more in *ortho*- and *para*-position than in meta-position.

3.4.2. Reaction with •OH radicals

Antonaraki et al. [23], investigating the effect of the position of substitution of the chlorine atom on the reaction rate, found that the rate of photo-oxidiation of monochlorophenols (for λ > 320 nm) by the •OH radicals decreases according to the order: 3-CP > 4-CP > 2-CP. Some authors [23,72] observed also that the presence of two chlorine atoms in the *meta*-position in a molecule (3,5-DCP) – if compared to a chlorophenol with chlorine atoms in two *ortho*-positions (2,6-DCP) in a molecule – increases the rate of the reaction. A similar phenomenon was observed for trichlorophenols. Trichlorophenols with two chlorine atoms in the *meta*-position reacted faster than trichlorophenols having only one chlorine atom in the *meta*-position. This means that for mono-, di- and trichlorophenols, the initial rate of the reaction is affected more by the position of the substituted chlorine atoms than by the number of these atoms in the molecules. A similar correlation was observed by Tang and Huang [81] for the reaction of chlorophenols with H_2O_2 in the absence of a radiation source. In the case of observed reactions of •OH radicals with PCP, Mills and Hoffmann [82] saw that the addition of •OH radicals at the *ortho*-position was more favourable than at *para*-position. It may be concluded that the increase in the number of substituted chlorine atoms on the ring blocks favourable positions susceptible to the hydroxyl attack, what means a decrease in the degradation rate with an increased number of chlorine atoms in the molecule.

Another relationship was observed by Shen et.al. [34], Hugül et al. [58], and Moza et al. [72] during the photolysis of chlorophenols in the presence of H_2O_2. Shen et al. [34] and Hugül et al. [58] conducted their investigations using a

254 nm wavelength, thus their results concerning the kinetics are the consequence of two reactions: the direct photolysis of chlorophenols and the reactions with the $^{\bullet}OH$ radicals formed from H_2O_2. Hugül et al. [58] showed that the rate constant under these conditions decrease in the order: 2,4,6-TCP > 2,4-DCP > 2-CP. This correlation was obtained for a 1:1 and 1:8 chlorophenol/H_2O_2 mole ratio. Moza et al. [72] showed that TCP photo-degradation is faster than either MCP or DCP. Moza et al. [72], and Schuler et al. [61,83] observed also that the *ortho-* and *meta*-positions in substituted phenols were more active in reactions with $^{\bullet}OH$ radicals. Such behaviour was caused by the strong +M effect of the OH-group. On other hand, Shen et al. [34] for the same compounds found decreasing rate constants in the order 2,4-DCP > 2,4,6-TCP > 2-CP for pH = 7, but under other conditions (7 < pH > 7) the rate constant decreases in the order 2,4-DCP > 2-CP > 2,4,6-TCP. The presented conflicting orders of photo-degradation rates may be caused by the irradiation source (mono- or polychromatic), geometric arrangement of irradiation or scavenging effects.

3.4.3. Reaction with singlet oxygen

Tratnyek and Holgně [20], investigating reactions of chlorophenols with singlet oxygen using rose bengal as a sensitizer, observed that the *ortho-* and *meta*-positions in monochlorophenols molecules were more active in reactions with singlet oxygen, independent of the presence of dissociated or undissociated forms. They also showed that increasing the number of chlorine atoms caused a decrease in the rate of the reactions.

Ozoemena and Kuznetsova [69], studying photosensitization transformations of polychlorophenols by radiation above 600 nm, suggested that negative inductive effects (when halogen substitution occurs on an aromatic ring) result in an electron-withdrawing effect from the benzene nucleus, deactivating it for an electrophilic attack by singlet oxygen. This electron withdrawal decreases the contribution of the type II pathway as the number of halogen substitutes increases. However, in the case of polychlorophenols, the electron-withdrawing effects of chlorine substituents cause a reduction in the electron-donating ability of the substrate while the electron–acceptor ability is increased substantially.

Generally, cited papers indicate that independent of reaction type the number and position of chlorine atoms strongly influence the kinetic and mechanism of the photo-degradation of chlorophenols. The position of substituent chlorine atoms in the molecule is a very important determinant of the reaction kinetics. In the case of direct photolysis, the favourable positions are *para-* and *ortho-* that are the result of inductive and mesomeric effects from OH and Cl groups. When hydroxyl radicals are generated upon irradiation the presence of a chlorine atom in *meta*-position in monochlorophenols increases the reaction rate between CP and $^{\bullet}OH$. In the case of polychlorophenols addition of hydroxyl radicals at the *ortho*-position is more favourable than at *para*-position. Such behaviour was caused by the strong +M effect of the OH-group. Additionally for polychlorophenols, the steric effects are very important.

3.5. Kinetics of secondary reactions

In various papers [8,13,21,23,34,39,82–90], authors examined the secondary reactions of stable intermediate products resulting from photo-degradation. It is suggested that few quinones, being intermediate products of photo-degradation of chlorophenols, may be water photo-oxidizing agents during irradiation by the visible or UV light range. The postulated mechanism involves reaction of the quinone triplet state or the cation radical with water to produce a hydroxylating intermediate [21,73,74]. For example, Rossi et al. [84] studied the UV photolysis ($\lambda = 254$ nm) of chlorohydroquinone and proposed a mechanism of action involving the formation of two radical anions or their protonated forms.

3.6. Kinetics of reactions in natural waters

The presented results, cited from literature, mostly represent the results of laboratory investigations. Nevertheless, the kinetics of the photo-degradation processes in the aquatic environment, under natural circumstances, depend not only on the concentration of dissolved oxygen, pH of the solution, and molecule structure, but also on the presence of metal ions or sensitizers such as dissolved organic matter [7,31,63,85,91–109]. The rate constants under such conditions, are the rate constants observed for reactions including direct photolysis, $^{\bullet}OH$ radical and singlet oxygen reactions, and recombination reactions. In the natural environment, sensitized transformations proceed at the same time as with direct photolysis under the action of solar light [77,110–113]. The active reaction intermediates participating in the transformation of chlorophenols may be excited sensitizer molecules or their fragmentation, hydrolysis products, the solvated electron and hydroxyl radicals. Additionally, under aerobic conditions the products of interaction between the excited sensitizer molecule, solvated electron and singlet oxygen, or superoxide radical could be involved. The presence of $^1O_2$ in solar irradiated natural waters was reported in numerous papers [12,63,96–98]. The basic photosensitizer responsible for the presence of this oxygen state in natural waters is dissolved organic matter. Consequently, the kinetics of the reaction is affected by the concentration of $^{\bullet}OH$ radicals [59,63], singlet oxygen [96,97], and photosensitisers, e.g. humics and quenching substances [91,93–107].

Experiments with samples of natural water [92–104] showed that phenolic pollutants readily photo-degrade in natural waters, and the photo-degradation follows a mechanism different than in samples lacking humic and fulvic acids and dissolved organic matter. Vialaton and Richard [103], investigating 4-Cl-2-MP photo-degradation of in water by natural summer sunlight, observed that the transformation rate of 4-Cl-2-MP was higher for samples in natural, rather than purified water. Canonica et al. [93–95], showed that phenolic contaminants are easily photo-degraded in natural waters and they claimed that the reaction mainly involved excited triplet states of humic and fulvic acids. They suggested also that 4-Cl-2-MP was oxidized to a radical by reacting with an excited triplet state. In natural waters, photosensitized reactions dominate during photo-degradation.

Mille and Crosby [100], investigating the processes of photo-degradation using solar light in seawater, revealed that the rate of reaction is affected by interactions between the substrate and chlorine ions. Photo-oxidation, photonucleophilic substitution and photoreduction were all observed. Tetrachloromuconic acid was identified as an unstable photoproduct of the ring-fission reaction.

Hwang et al. [98,99] studied sunlight photo-degradation of chlorophenols in water from a river estuary assuming a first order reaction model. They showed that the photolysis rate of chlorophenols with two or three chlorine atoms in a molecule is higher than those for phenol and monochlorophenol.

4. Mechanisms for photo-degradation of chlorophenols in an aqueous environment

Various papers present the results of investigations aimed at identifying both stable and intermediate products from the photo-degradation of chlorophenols. These investigations were usually conducted with the use of the high performance liquid chromatography (HPLC), gas chromatography (GC/MS), and spectroscopy methods: UV–vis, FT-IR, NMR and EPR. Some of the proposed mechanisms of reaction for selected chlorophenols are presented below.

4.1. 2-Chlorophenol

The chlorine atom in the *ortho*-position is strongly electro-attractive. Boule et al. [9] proved that an attack of oxygen and hydroxyl radicals on the *ortho*-position of 2-chlorophenol irradiated with 254 nm light yields unstable 1,2-benzosemiquinone and HCl. Next, depending on the form of the compound, pyrocatechol or cyclopentadienyl carboxy acid are formed (Fig. 1). The authors indicate that pyrocatechol is a product of the photo-degradation of undissociated molecules. They suggest also that photo-degradation of the 2-chlorophenol anionic form leads to cyclopentadienic acid, which dimerizes according to the Diels–Alder reaction. Presence of the C=C=O group in the products of the photo-degradation of 2-CP by UV light from a super-pressure mercury lamp in low-temperature argon matrices was confirmed with the FT-IR method by Akai et al. [77].
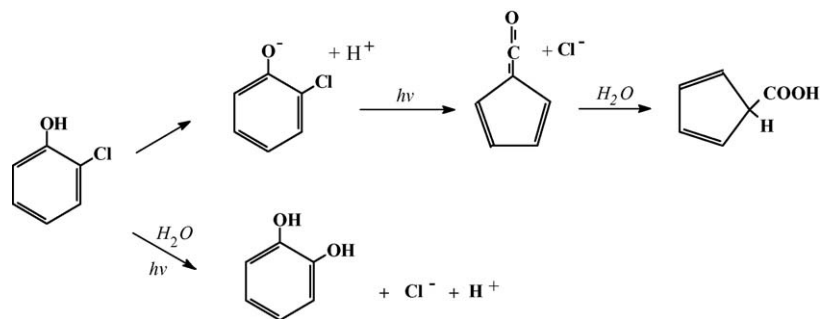
4.2. 3-Chlorophenol

For 3-CP, irradiation with UV light, independently of the form of the compound, leads to the main products—resorcinol and Cl$^-$ ions [9,38,58,100]. Boule et al. [9] explained the mechanism of formation of the resorcinol by polarization of the C–Cl bond and heterolytic scission of a molecule of water with the concerted formation of Cl$^-$ and resorcinol. Czaplicka [74] investigated the photolysis of 3-CP, identified resorcinol and 3-chloro-1,4-benzenediol in solution irradiated for 2 h at 254 nm.

4.3. 4-Chlorophenol

In a neutral or acid environment, 4-CP does not dissociate. Svetlichnyi et al. [112], using UV laser excitation, confirmed a photodissociation of the C–Cl bond in 4-CP. Cleavage of the C–Cl bond in 4-CP through predissociation and photodissociation leads to a triplet state. The photodissociation of the C–Cl bond in the $S_2(\pi\sigma^*)$ state may also result from direct dissociation if the rate constant for this process is greater than 10^{11} s$^{(1}$. A 4-hydroxyphenyl radical is the resultant product of this reaction. The authors claim that the increase in the rate of the photochemical reaction, resulting from the presence of a chlorine atom in the *para*-position of the phenyl rings, proves that the first stage of the 4-CP photoreaction is the C–Cl bond cleavage, and subsequently the decomposition of the intermediate ionic or radical forms occurs. The main product of the reaction is hydroquinone. This hypothesis is in agreement with quantum chemistry theory. Some authors [18,111,113,105] propose the mechanism of 4-CP degradation in an aqueous environment consists of carbenes formation, which reacts with oxygen atoms to yield 1,4-benzoquinone (Fig. 2). Durand et al. [11], investigating the reaction mechanism in water solutions with laser flash photolysis confirmed that the carbene 4-oxocyclohexa-2,5-dienylidene is formed from 4-CP by the loss of HCl. This species reacts with oxygen to form 1,4-benzoquinone-*O*-oxide, which subsequently yields 1,4-benzoquinone. The carbene also undergoes a reaction with water and coupling reactions to produce 1,4-hydroquinone and polyhydroxybiphenyls, respectively. Tseng [102] shows that at the first stage of the reaction the 4-chlorodihydroxycyclohexadienyl radical is formed, which is subsequently transformed to hydroquinone. For the dissoci-
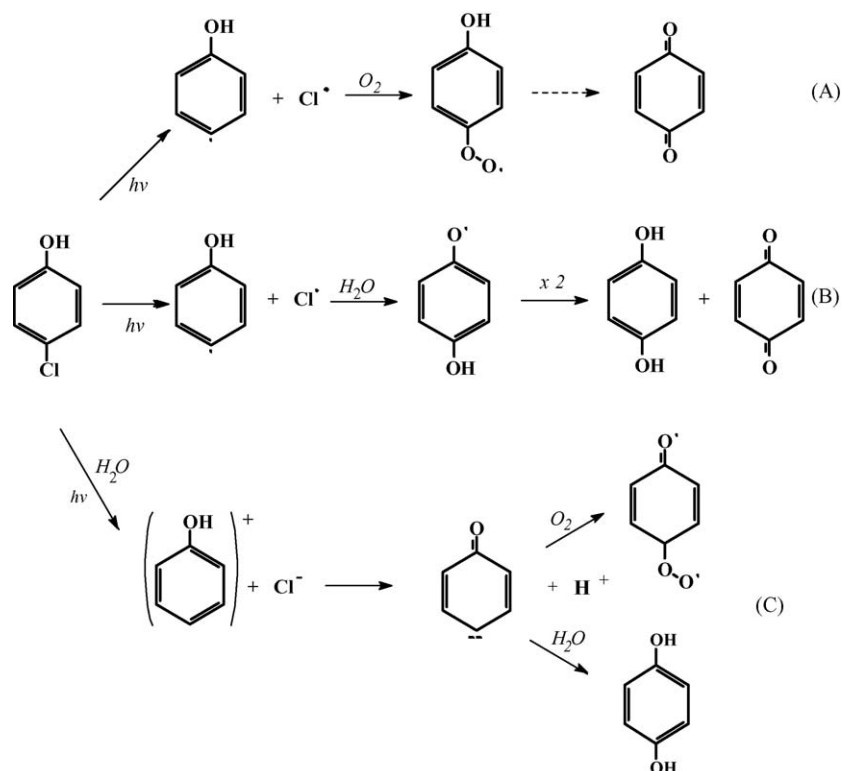

Fig. 1. Photo-degradation pathways of 2,4-CP.

Fig. 2. Mechanisms of the aqueous photoreactions of 4-CP according to Lipczynska-Kochany and Bolton (A) [18], Boule et al. (B) [9] and Grabner et al. [113].

ated form, the main reaction pathway leads to the formation of 2-hydroxy-1,4-benzoquinone.

Some authors [33,56,71,111] also report the formation of benzoquinone, 2-hydroxy-1,4-benzoquinone, hydroquinone, dihydroxybiphenylenes, 2,4-dihydroxy-5-chlorobiphenyl, and a few polihydroxybiphenylenes during photo-oxidation by •OH radicals and singlet oxygen. Phenol and biphenyldiol were identified as products of complete dechlorination in reactions with a UV/H$_2$O$_2$ combination [33]. The presence of biphenyldiol, identified as 4,4′-dihydroxybiphenyl, was noted only in experiments at a pH equal to 9.5.

4.4. 4-Chloro-2-methylphenol

Photolysis of 4-Cl-2-MP in 280 nm light yields methyl-*para*-benzoquinone [12]. Canonica et al. [91–94] suggest that 4-Cl-2-MP in natural water solutions is oxidized to proper radicals in interactions with the excited triplet state. The opening of the ring occurs via the subsequent addition of a hydroperoxyl radical/superoxide anion, rearrangement and formation of hyperoxide. In natural waters, photosensitised reactions are of greater importance than direct photolysis.

Jeffrey et al. [114], using electron spin resonance spectroscopy coupled with DMPO, showed that UV irradiation of 4-Cl-2-MP yields free radicals. Analysis of the spectra proved formation of substituted semi-quinone anion radicals, formed by substituting an OH group for the chlorine atom. In the presence of oxygen, hydroquinones were oxidized to the corresponding semiquinone radicals. Indirectly, this gave evidence of the initial presence of a carbon-centred aryl radical formed by chlorine

loss. Stabilization of the semiquinone radicals with increasing alkalinity of the solution was also noted.

4.5. 2,4-Dichlorophenol

Direct photolysis of 2,4-DCP in the aqueous environment leads to formation of 4-chlorocyclopentadienyl carboxy acid, chlorohydroquinone or 4-chloro-1,2-benzenediol (Fig. 3) [67,87,115]. These products were identified using NMR and FT-IR methods.

Pandiyan et al. [41], investigating the photolysis of 2,4-DCP using GC/MS, identified monochlorophenol as the main product. Hirvonen et al. [33] investigating photo-oxidation reactions using UV/H$_2$O$_2$ methods for wavelenght $\lambda = 254$, observed the formation of numerous hydroxylated intermediates such as: trichlorohydroxybiphenyl, tetrachlorodihydroxybiphenyls, tetrachlorotrihydroxybiphenyl and dichlorobenzenediols. The authors suggested that the presence of dichlorobenzenediol in solution after photo-oxidation is the result of a hydroxyl group attached to the aromatic ring without dechlorination. The chloro-hydroxybiphenyls are formed by dimerization of organic radicals or from their reactions with the parent chlorophenols.

4.6. 2,4,6-Trichlorophenol

Two hundred and fifty four nanometers irradiation of 2,4,6-TCP in aqueous solution leads to dechlorination. The main photoproducts were identified as dichlorophenol and monochlorophenol [41]. Antonaraki et al. [23], showed that in the configuration UV/H$_2$O$_2$ for $\lambda > 320$ nm the main products of
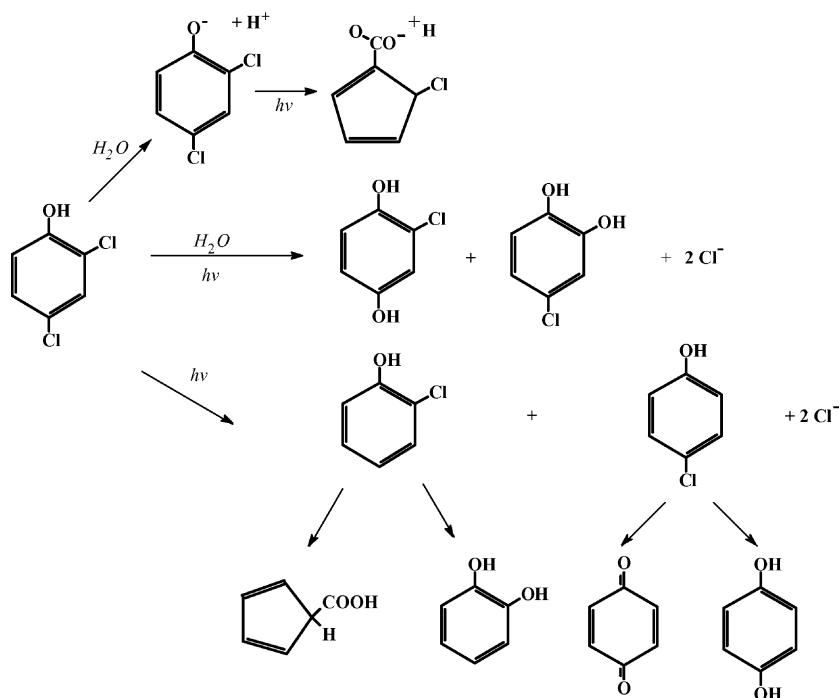
Fig. 3. Photo-degradation pathway of 2,4-DCP [115].

2,4,6-TCP photo-degradation are: 2,6-dichlorobenzoquinone, 2,6-dichlorohydroquinone, 3,5-dichlorocatechol, dihydroxytrichlorobenzene, trihydroxydichlorobenzene. On the other hand, photo-oxidation under conditions of 254 nm wavelength and the presence of H_2O_2 leads to different products, depending on pH levels [33]. At a pH of 2.5, the trichlorobenzenediol, tetrachlorotrihydroxybiphenyls, tetrachlorotetrahydroxybiphenyls and compounds probably pentachlorinated phenoxyphenol with a molecular mass 356, were identified.

4.7. 2,4,5-Trichlorophenol

Skurlatov et al. [13] studying the photo-degradation of 2,4,5-TCP showed the influence of irradiation on mechanisms of reaction. In the case of photolysis at $\lambda = 254$ nm, they identified primary products such as: organic acid, 2,5-dichlorohydroquinone and, in trace quantities, 2,4- and 2,5-dichlorophenols. The formation of dichlorobenzoquinone in this reaction was explained as a result of non-radical oxidation by singlet oxygen with subsequent detachment of the Cl^- ion in the four-position, and also of a reaction via a charge-transfer precursor. The complex precursor is supposed to interact through a complete one-electron transfer to yield a superoxide anion radical and a phenoxy radical or result in an endoperoxide, a back reaction resulting in the quenching of $^1O_2$, or a combination of these mechanisms.

In comparing the results of experiments in aerobic and anaerobic conditions, Skurlatov et al. [13] showed also that oxygen or its activation products are not involved in direct photolysis of polychlorophenols. They showed that in near UV light, not only the occurrence of heterolytic decomposition of the compound, accompanied by formation of the Cl^- ion, but also homolytic

cleavage of the C–Cl bond with release of a chlorine atom and free alkylphenoxy radicals takes place. The primary products of both direct and indirect photolyses show clear electron–donor properties. On the basis of obtained results the following scheme of reactions was proposed: (i) hydrolysis accompanied by formation of the Cl^- ion and (ii) homolytic C–Cl bond cleavage to form chlorine and carbon-centred phenoxy radicals. Skurlatov et al. [13] indicated the possibility of formation of polychlorinated dioxins and dibenzofuranes in direct photolysis of 2,4,5-TCP.

4.8. Pentachlorophenol

Some authors show that the direct photolysis of pentachlorophenol in distilled water gives numerous degradation products such as: tetra-, tri-chlorophenols [78], chlorinated hydroxybenzenes [13,47] (Fig. 4a and b), 2,3-dichloromaleic acid [82], dichlorocyclopentenedione, and polychlorinated dibenzodioxins and furans (Fig. 5). Skurlatov et al. [13] studying the photolysis of PCP by solar irradiation, identified tetrachloro-, 2,3,5-trichloro-, and 2,4-dichlorohydroquinones and trace amounts of 4,5-dichloro-4-cyclohexene-1-one, 5-chloro-4-cyclohexene-1-one, 2,3,5-TCP, 2,3,6-TCP, and 2,5-DCP in solution following reaction. Hong et al. [88] investigating the photolytical transformation of PCP in water by a high-pressure mercury lamp (1.2 and 0.6 kW) observed the formation of terta-, tri- and dichlorophenols as typical reductive-products in the successive dechlorination of these compounds and oxidation products such as tetrachlorocatechol and tetrachlorohydroquinone. They also identified hexachlorobenzene, pentachlorobenzene and 1,2,4-trihydroxytrichlorobenzene. The
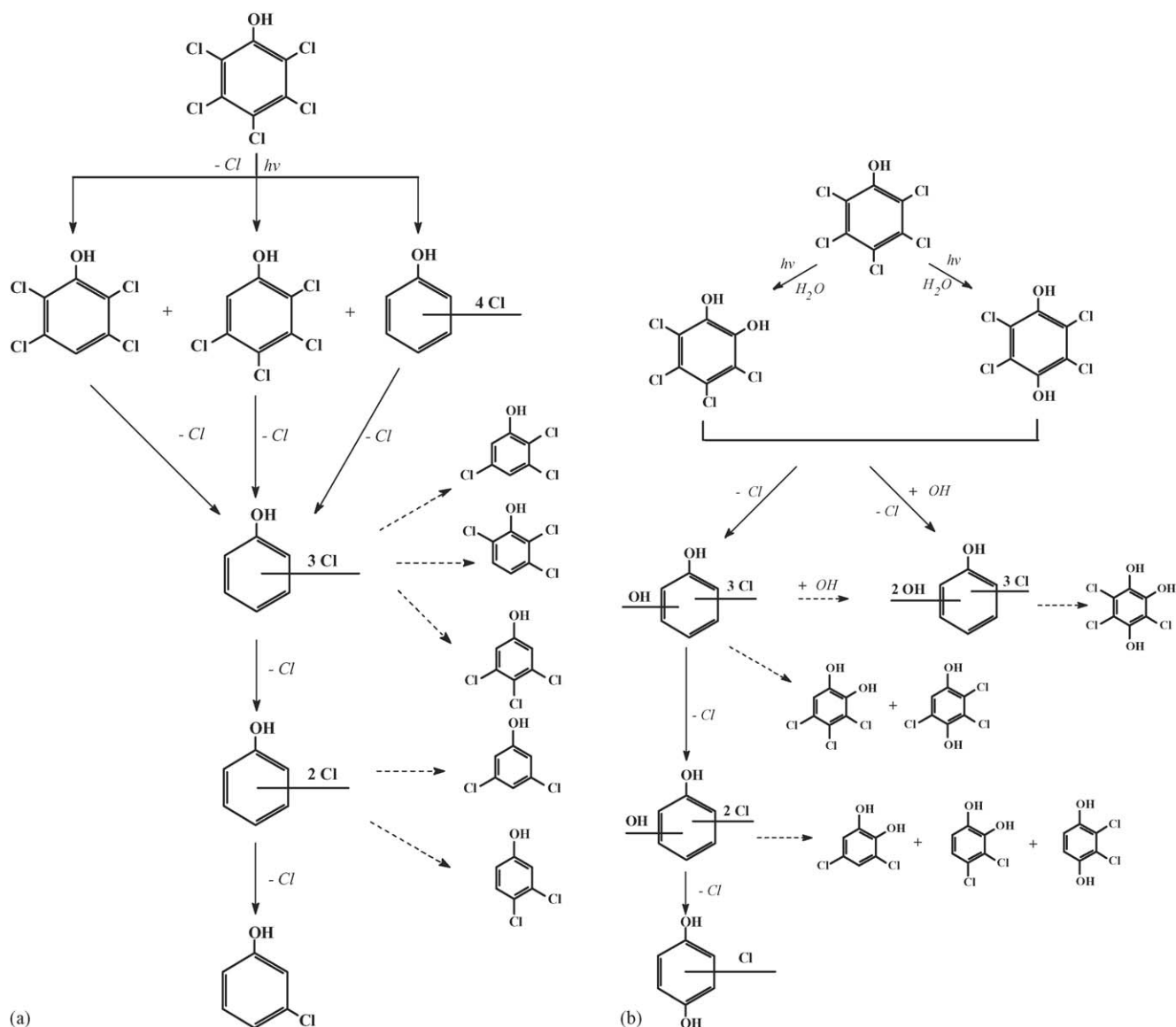
Fig. 4. (a) Photodechlorination of PCP, (b) formation of hydroxychlorobenzenes during photo-degradation of PCP.

authors showed that the dechlorination of PCP occurred mainly at the *ortho*-position under these conditions. Similar conclusions follow from the work of Mills and Hoffmann [82]. They claim loss of the chlorine atom in the PCP molecule, under anaerobic conditions, is mainly in *ortho*- and *para*-positions. On other hand, Skurlatov et al. [13] suggested that the hydroxyl radicals generated from the photolysis of PCP in water could attack a molecule to yield photo-oxidation products such as chlorocatechols and chlorohydroquinones. The formation ratio tetrachlorocatechol to tetrachlorohydroquinone indicates that the addition of OH radicals at the *ortho*-position was more favourable than at *para*-position. Similar results were obtained by Benitez et al. [8] during studies of the photo-degradation of PCP by polychromatic light emitting from 185 nm up to 436 nm. Crosby and Wong [104] proposed the photo-nucleophilic substitution of hydroxide for chlorine as the first step in PCP decomposition.

During UV irradiation of a PCP solution, Crosby and Wong [104] identified octachlorodibenzodioxin in the solution after

reaction. From investigations of the pentachlorophenol photolysis in water by 254 nm light [116], it follows that PCDDs and PCDFs arise in reactions, among which there are only two toxic congeners. The authors maintain that only hepta- and octachlorinated PCDDs and PCDFs are formed upon UV irradiation. The process scheme proposed by the authors is shown in Fig. 5. Formation of dioxins from PCP photo-degradation was also confirmed by some authors [13,88,117].

Hirvonen et al. [33] studied the degradation of PCP in aqueous solution by the $^\bullet$OH radicals generated by 254 nm photolysis in combination with H_2O_2. Hydroxylated chlorophenols e.g. tetrachlorocatechol, tetrachlorohydroquinone and dimeric intermediates were found as transient intermediates in the degradation.

Terzian et al. [62], investigating interactions of hydroxyl radicals with PCP with pulse radiolysis using optical detection, revealed that a pentachlorophenoxyl radical can be formed via a homogenous reaction of the azide radical with pentachlorophe-
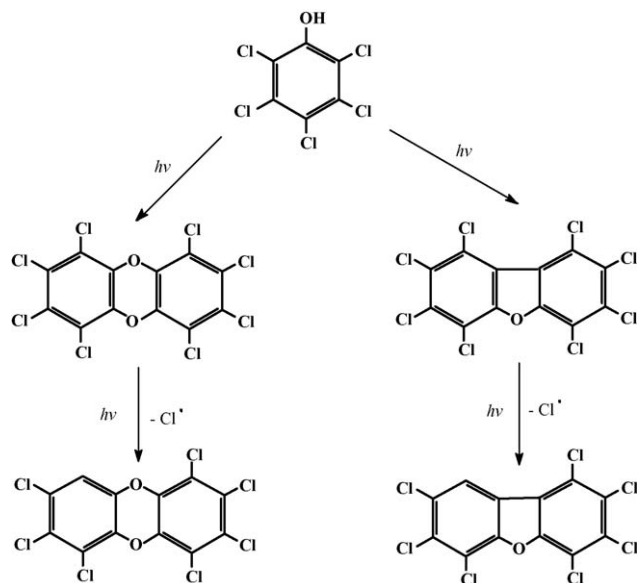
Fig. 5. Photochemical formation of PCDDs and PCDFs during the UV irradiaton of PCP in water [116].

nolate. The azide radicals react with aromatic substances via direct electron transfer.

5. Summary

The authors of the works cited prove that for all chlorophenols, the cleavage of the C−Cl bond occurs at the first stage of the reaction, as a result of the heterolytic and/or homolytic scission. In all cases, the authors concluded that direct photolysis leads to dechlorination products.

The rate constants of direct photolysis depend on the pH and degree of dissociation of the compounds. Rate constant increases result from higher concentration of dissociated forms, which absorb radiation more strongly than undissociated forms. Reaction rates depend on the number of chlorine atoms in a molecule and the position of chlorine atom substitution.

In the case of direct photolysis, *para*- and *ortho*-positions are more favourable to the cleavage of the C−Cl bond than the *meta*-position. The favourable *para*- and *ortho*-positions are a result of the inductive and mesomeric effects of OH and Cl groups.

The papers indicate that in direct photolysis of trichlorophenols and PCP, PCDDs and PCDFs are formed.

The photo-oxidation reaction, independent of $^\bullet$OH radical generation methods, is much faster than direct photolysis. The reaction rate constants suggest that the reaction rate is controlled by diffusion. In the case of $^\bullet$OH radicals, under conditions of irradiation of wavelengths absorbed by CP, the *ortho*- and *meta*-positions in substituted phenols were more active in reactions with $^\bullet$OH radicals. In reactions of $^\bullet$OH radicals during irradiation with wavelengths, which are not absorbed by chlorophenols, the presence of chlorine atoms in the *meta*-position leads increases in rate reaction.

The products of photo-oxidations of chlorophenols are mainly chlorobenzenediols. A direct $^\bullet$OH radical attack on positions rich in electrons should be expected. Similarly to direct

photolysis, the position of substitution for the $^\bullet$OH radical is dependent on the inductive and mesomeric effects of the groups.

Considering the effect of particular factors on the mechanism and kinetics of the processes, one should note that some of the proposed mechanisms require further confirmation.

Acknowledgements

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