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Photodegradation of 2,3,4,5-tetrachlorophenol in water/methanol mixture

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Abstract

The photodegradation of 2,3,4,5-tetrachlorophenol in water/methanol mixture using a low pressure 16 W mercury lamp was examined. The rate constants and quantum yields of the reaction were determined. The effect of pH on rate constants was also studied. The estimated first-order rate constants *k* for the phototransformation of 2,3,4,5-TeCP were found to be 6.48×10^{-3} min^{-1} (pH 2), 9.51×10^{-3} min^{-1} (pH 4.5) and 18.31×10^{-3} min^{-1} (pH 11). The determined quantum yield of TeCP reaction was 0.194 at pH 4.5.

The kinetic curves for formation of less chlorinated photodecomposition products are also presented. Analysis of the intermediates showed that hydroxylation of chlorophenols (CP) was involved in the oxidation during photodegradation. Finally, the pathway of photodecomposition of these compounds is proposed.

Keywords: 2,3,4,5-Tetrachlorophenol; Photodegradation; Rate constant; Quantum yield; Mechanism of reaction

1. Introduction

In recent years, chlorophenol (CP) compounds are the subjects of many studies due to their environmental significance as persistent and potentially hazardous substances. The majority of CPs is synthesized through various pathways, such as the natural chlorination of organic material, biodegradation of plant protecting chemicals or disinfections of drinking water [1–6]. In addition, chlorophenols such as 2,3,4,5-tetrachlorophenol are used as fungicides, in preservation of plants, kraft pulp mills, and sewage treatment. 2,3,4,5-Tetrachlorophenol is also one of the major dechlorination products formed during photolysis of pentachlorophenol. It is known, that in the natural environment CPs may decay via biodegradation and/or photodegradation [7,8]. Although, the kinetics and mechanisms of photodegradation of variety CPs are discussed in a large number of papers [9–12], the data on photodegradation of trichlorophenols and tetrachlorophenols, especially 2,3,4,5-tetrachlorophenol, are scare [13,14].

Recently advanced photochemical transformation, especially photooxidation, emerged as a powerful method for transforming pollutants into harmless substances [15–17]. There are various photochemical processes like photodissociation, photoisomerization, photosubstitution, photorearrangement, photooxidation and photoreduction in which chlorophenols may be involved. The kinetic and mechanism of these reactions strongly depend on the experimental conditions such as wavelength of radiation, pH of solution, concentration of oxygen dissolved and the presence of sensitizers [18–22]. Since dissociated compounds absorb irradiation more strongly than undissociated forms, the rate constants of photodegradation depend on the pH and dissociation degree of compounds [23,24]. The rate reactions depend also on the number of chlorine atoms in molecule and position of chlorine atom substitution [25].

Binary mixtures of water and amphiphilic solvent (molecules with both hydrophobic and hydrophilic groups) have a wide range of industrial applications. It is well known

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that water/alcohol mixtures exhibit an anomalous behaviour with respect to the properties of the two separate pure compounds [26,27]. Dynamical and structural properties of clusters of water/methanol solutions were subject of many papers [28–30].

The aim of this work was to study the mechanism and kinetic of photodegradation of 2,3,4,5-tetrachlorophenol in cluster of water/methanol solutions. Quantum yield and the rate constants are determined. The transformation mechanism is proposed on the basis of intermediate products analysis. The effect of pH on the kinetic of the reactions was also studied.

2. Experimental

2.1. Reagents and chemicals

All solvents, i.e. methylene chloride, methanol, HCl, NH_4OH were of the analytical grade. The 2,3,4,5-tetrachlorophenol (Supelco) was used without purification. Potassium ferrioxalate obtained by reaction of potassium oxalate with ferric chloride was crystallized three times and kept in the dark [31]. Triply distilled water was used for all experiments. The concentration of 2,3,4,5-TeCP was 0.875 $\mathrm{mmol\,l^{-1}}$ in water/methanol mixture (100:12.2, v/v). Characteristic of the solutions is given in Table 1.

The pH of studied solutions was adjusted with an automatic pH controller by adding HCl or NH_4OH solutions.

2.2. Photolysis experiments

Water/methanol solutions of chlorophenol were placed in quartz tubes and exposed to a radiation wavelength of 254 nm using low pressure 16 W mercury lamp. The samples were taken for further analysis every 15 min. The total experimental time was 200 min. Quantum yields were determined using potassium ferrioxalate actinometry [32]. Experiments were carried out at 25 °C.

Irradiated solutions were extracted with methylene chloride. The extraction was repeated three times. The methylene chloride extracts were mixed together, dehydrated, and evaporated under a nitrogen stream to volume of 0.5 ml. Qualitative and quantitative analyses, without derivatization, were performed using a Perkin-Elmer Clarus 500 gas chromatograph (GC) equipped with a quadrupole mass spectrometry (MS) detector, and a 30 m × 0.25 mm i.d. DB-5MS column with a film thickness of 0.25 μm. Quantitative analysis was performed using selected ion monitoring method (SIM), choosing two or three ions typical for each compound (Table 2).

Table 1
Characteristic of 2,3,4,5-tetrachlorophenol solution

Parameter	Value
Concentration of 2,3,4,5-TeCP ($\mathrm{mmol\,l^{-1}}$)	0.875
Ratio in solution water/methanol (v/v)	100:12.2
pH	4.5
Concentration of oxygen dissolvent ($\mathrm{mg\,O_2\,l^{-1}}$)	8.56

Table 2
Characteristic ions (*m*/*z*) used for selected ion monitoring of photodegradation of 2,3,4,5-TeCP products

Compounds	$[M]^+$	Other
2,3,4,5-TeCP	232(100)	230(81), 234(51), 194(21), 168(110), 131(38)
2,3,5-TCP	196(100)	162(25), 160(39), 132(19), 97(54)
2,4,5-TCP	196(100)	198(89), 162(11), 132(28), 99(20), 97(42)
2,3,6-TCP	196(100)	200(30), 198(96), 160(23), 131(20), 97(23)
3,5-Dichlorophenol	162(100)	164(64), 99(31), 63(25)
3-Chlorophenol	128(100)	130(33), 100(18), 65(34)
3,4,5-Trichlorocatechol	212(100)	214(99), 216(27), 178(33), 148(23), 113(38), 85(18)
Tetrachloromethoxybenzene	246(100)	231(48), 203(69), 131(30)
3,4,6-Trichloro-2-methoxyphenol	226(100)	228(65), 230(20), 213(99), 183(47), 147(36), 119(35)
2,5-Dichloro-1,1′-biphenyl	222(100)	224(50), 152(99), 93(21), 75(27)

The concentration of Cl^- ions was determined using a combined ion selective electrode (Corning Company). The pH of solutions was measured during experiments.

3. Results and discussion

3.1. Kinetics studies

Chlorophenols strongly absorb radiation wavelengths between 230 and 300 nm. The photodecomposition of CPs in aqueous solution irradiated at 254 nm may include reactions such as direct photolysis, oxidation or dimerization reactions. The obtained kinetic curves of TeCP photolysis are given in Fig. 1.

Because chlorophenols partially dissociate in aqueous solutions, the reaction schemes of photodegradation are as follows:

$$\mathrm{ArCl{-}O^-} \xrightarrow{k_1} \text{product 1} \tag{1}$$

$$\mathrm{ArCl{-}OH} \xrightarrow{k_2} \text{product 2} \tag{2}$$

Thus, the general kinetic equation for the photodegradation reaction is defined as

$$\frac{-\mathrm{d}[\mathrm{ArCl{-}OH}]}{\mathrm{d}t} = k_1[\mathrm{ArCl{-}O^-}] + k_2([\mathrm{ArCl{-}OH}] - [\mathrm{ArCl{-}O^-}]) \tag{3}$$

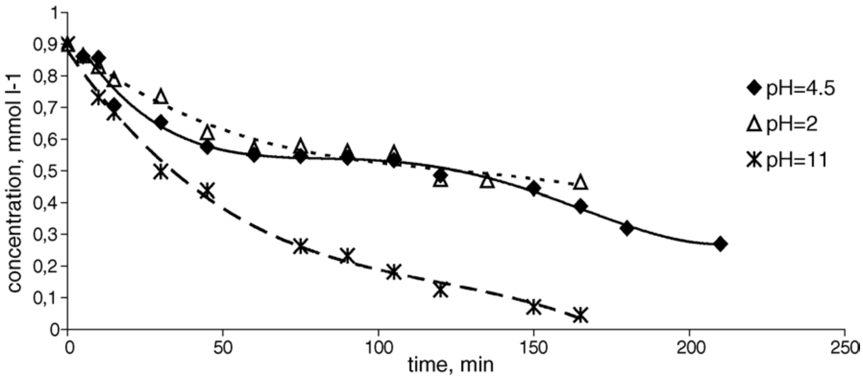

Fig. 1. The kinetics curves of photodegradation of 2,3,4,5-TeCP.

or

$$\frac{-\mathrm{d[ArCl{-}OH]}}{\mathrm{d}t} = k_1\alpha[\mathrm{ArCl{-}OH}] + k_2(1-\alpha)[\mathrm{ArCl{-}OH}] \tag{4}$$

where k_1, k_2 are the rate constants for dissociated and undissociated chlorophenols, respectively; [ArCl–OH] total concentration of chlorophenol, $[\mathrm{ArCl{-}O^-}]$ the concentration of dissociated molecules, and α is the degree of dissociation, defined as:

$$\alpha = \frac{1}{1+10^{(\mathrm{p}K_\mathrm{a}-\mathrm{pH})}} \tag{5}$$

Based on these assumptions, 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. Thus, the photolysis reaction rate constant (k) is a pseudo-first-order approximation. The rate constants determined according to the first-order reaction model was $9.51 \times 10^{-3}\,\mathrm{min}^{-1}$ at pH 4.5. The correlation between reaction rate and reaction time is shown in Fig. 2. Since, there is no reported data on the photolysis reaction rate constants of TeCP in aqueous or water/methanol solutions, therefore the obtained results were compared with data for other polychlorophenols. The rate constant of the photodegradation of 2,4,6-TCP in water was reported to be $2.3 \times 10^{-3}\,\mathrm{min}^{-1}$ at pH 3 [33], whereas the pentachlorophenol photolysis rate in the acidified water (pH 3) was $0.16\,\mathrm{min}^{-1}$ [23]. The photolysis rate constant under similar conditions (water/methanol mixture) was $1.99 \times 10^{-3}\,\mathrm{min}^{-1}$ [12]. This comparison indicates that the obtained data are in good agreement with previous studies.

The determined quantum yield of TeCP reaction was 0.194. The reported quantum yield for chlorophenols varied from 0.13 to 0.57, which depends on the number and position of substituted chlorine atoms and conditions of radiation [23,24]. For example Benitez et al. [23] reported that quantum yield for the photolysis of pentachlorophenol in water at pH 5 was 0.32, whereas the quantum yield for the photolysis of 4-chloro-2-methylphenol at pH 7 was 0.44 [32].

During all experiments, the concentration of $\mathrm{Cl^-}$ ions (stable product) and pH of solutions were measured simultaneously. The kinetic curves of $\mathrm{Cl^-}$ formation and pH of solution variation are presented in Fig. 3. The determined reaction rate constant of $18.08 \times 10^{-3}\,\mathrm{min}^{-1}$ of $\mathrm{Cl^-}$ formation was approximately twice larger than the rate constant of TeCP photodegradation. This indicates that $\mathrm{Cl^-}$ ions are formed not only as the result of one elementary reaction (photodegradation of one C–Cl bond), but they can also be formed as the result of parallel secondary reactions with intermediate reaction products participation or equivalent bonds C–Cl photodissociation. Please note that the natural solution was

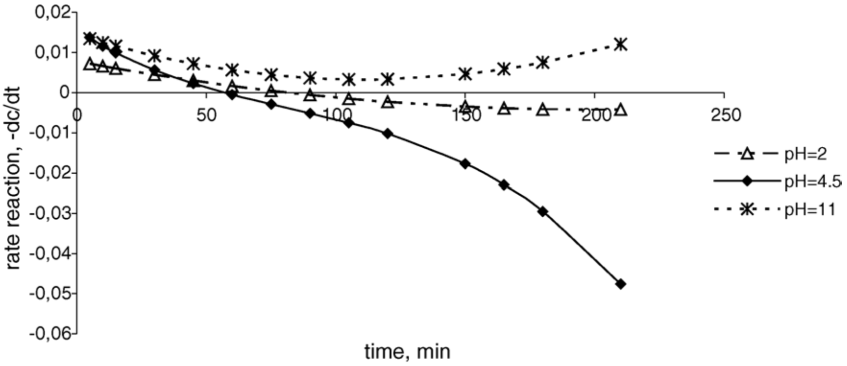

Fig. 2. The relationship rate of reaction vs. time.

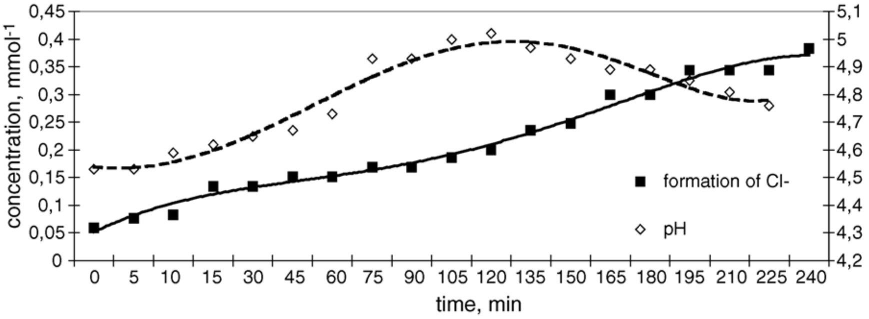

Fig. 3. The relationship formation of Cl^- ions and pH vs. time.

not buffered when its initial pH was 4.5. As can be seen in Fig. 3, the pH is also varied during the experiments. It is important to notice, that Cl^- ions concentration was increasing continuously at the same time. Simultaneous increase of Cl^- ions concentration and pH with time indicates that parallel reactions occurred. The basic and acidic compounds were formed as result of this reaction. Therefore, the kinetic data obtained during radiation experiments are only a quasi-stationary approximation.

3.2. *Influence of pH*

The effect of pH (2, 4.5 and 11) on the photodecomposition of 2,3,4,5-TeCP by UV radiation at 25 °C is presented in Fig. 1. The obtained rate constants were 6.48×10^{-3} and $18.31 \times 10^{-3}\,\mathrm{min}^{-1}$ at pH 2 and 11, respectively. The fact that the dissociated forms are more reactive than undissociated ones was observed previously [24]. The increase of the reaction rate constant with increasing pH was also observed by Benitez et al. [23] and Shen et al. [33]. The effect of pH solution on quantum yields was observed too. The relationship of reaction rate versus time at other pH values calculated using the Eq. (7) is presented in Fig. 2.

3.3. *Intermediate products*

It is well known that the dechlorination occurs during direct photolysis. The previously reported studies showed that chlorine position in chlorophenol isomers influences significantly on the kinetics of photodegradation of chlorophenols [32–37]. These results showed that *para*- and *ortho*-positions are favourable in direct photolysis. The obtained results showed that trichlorophenols (2,3,5-TCP; 2,4,5-TCP; 2,3,4-TCP and 2,3,6-TCP) were the main intermediate products in the initial reaction step. The kinetic curves of their formation are shown in Fig. 4. The 2,3,5-TCP was dominant among all of the TCP formed in this reaction. The mass ratios of particular chlorophenols were varied during reaction. The mass ratios of 2,3,5-TCP; 2,4,5-TCP; 2,3,4-TCP and 3,4,5-TCP were 2:1:1:0 and 40:1:6:4 after 5 and 45 min of radiation, respectively. The obtained results indicate that C–Cl bonds in *para*-position were broken first in photodissociation process. The preference of C–Cl cleavage of bond in the *para*-position is due to inductive and mezomeric effects of functional groups. Both OH and Cl groups activated *para*- and *ortho*-positions during direct reaction of photolysis. Moreover, in the case of 2,3,4,5-TeCP, *para*-position is more privileged than *ortho*-position, which is probably a result of a steric effect and/or formation of an intermolecular hydrogen bond between the *ortho*-positioned Cl atom and hydrogen of hydroxyl group [38–40]. In aqueous solution, the distribution of free and bonded hydroxyl groups is expected to be different due to the interactions of chlorine atoms and hydroxyl groups of chloropenols with hydroxyl groups of water, which certainly affect the photoreaction pathway.

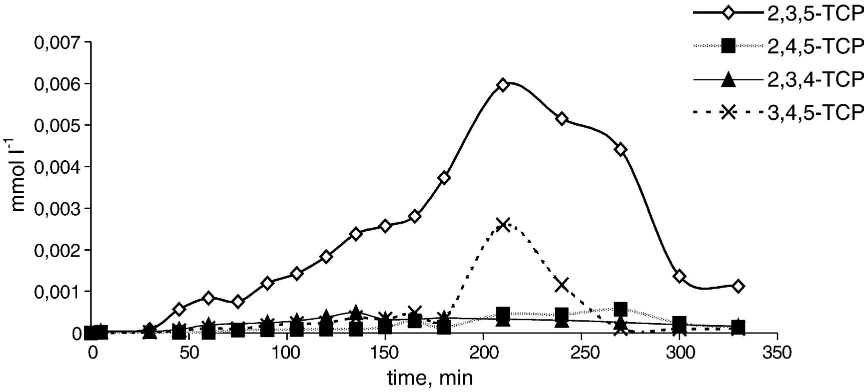

Fig. 4. Kinetic curves of formation of TCP during photodegradation of 2,3,4,5-TeCP.

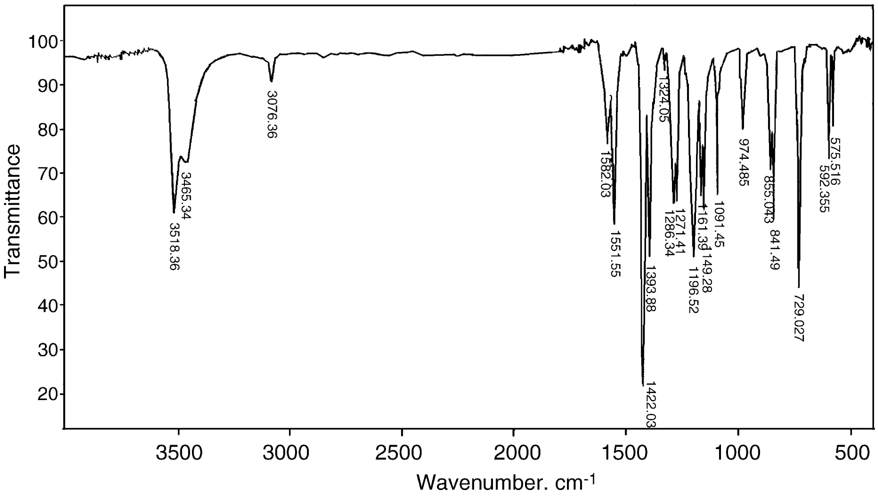

Fig. 5. Infrared spectrum of initial solution.

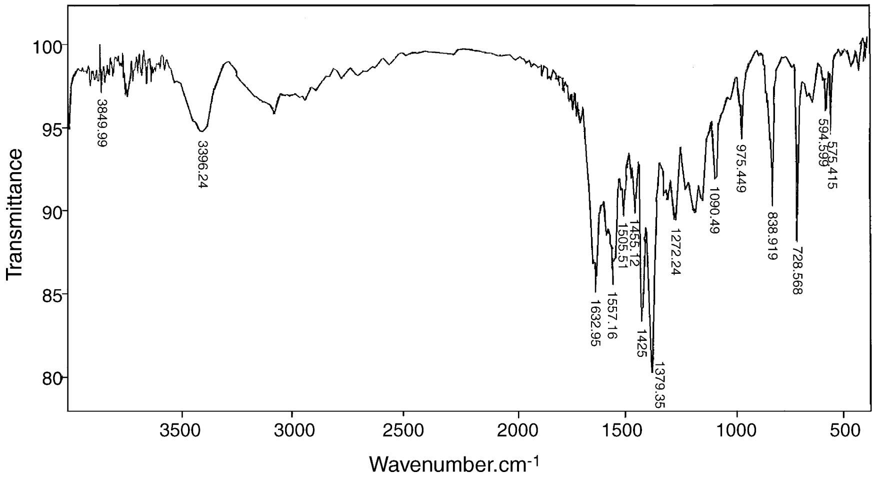

Fig. 6. Infrared spectrum of irradiated solution.

The 2,3,4,5-TeCP molecule with two conformers, *anti*- and *syn*-, may form intramolecular hydrogen bond between the hydroxyl group hydrogen and the chlorine atom substituted in *ortho*-position with the hydrogen bond energy of 3.12 kcal mol^{-1} [41]. 2,3,4,5-Tetrachlorophenol shows relatively high area band at 3465 cm^{-1} which is attributed to OH–Cl interactions. Two bands ascribed to vibrations of free hydroxyl groups at 3521 and 3511 cm^{-1} are notably smaller than in the case of bonded ones (Fig. 5). However, FT-IR analysis of a solution irradiated longer than 2 h showed

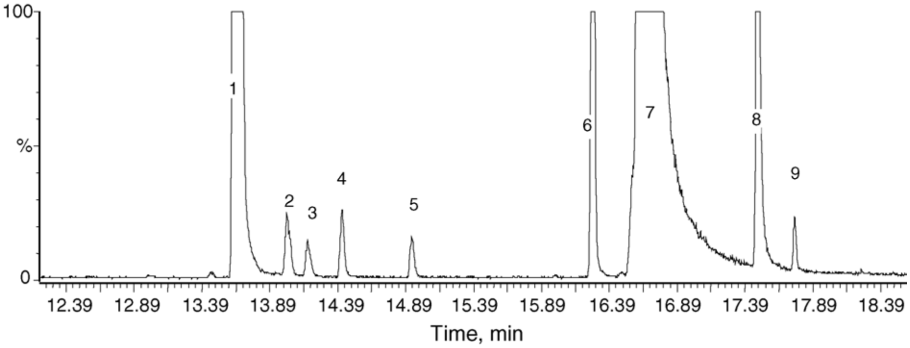

Fig. 7. Total ion chromatogram of 2,3,4,5-TeCP after 240 min irradiation: (1) 2,3,5-TCP, (2) 2,4,5-TCP, (3) 2,3,4-TCP, (4) 3,5-DCP, (5) dichlorodihydroxybenzene, (6) 3,4,5-trichlorocatechol, (7) 2,3,4,5-TeCP, (8) 3,4,5-TCP and (9) 3,4,6-trichloro-2-methoxyphenol.

significant difference in the spectrum before and after irradiation (Fig. 6). Spectrum of the water-soluble photoreaction product of the 2,3,4,5-tetrachorophenol shows a weak band with a maximum at 3396 cm^{-1} instead of two characteristic bands with maximum at 3518 and 3465 cm^{-1} to be attributed to the stretching vibrations of hydroxyl group. Simultaneously, the band appearing in pure 2,3,4,5-tetrachorophenol at 1286 and 1275 cm^{-1} ascribed to deformation of vibrations of hydroxyl group has disappeared. This shows that some O–H bonds were broken during the reaction.

Additionally, relatively strong bands at 1633 and 1379 cm^{-1} corresponding to the vibrations of a carbonyl or C=C groups appear. The other bands were slightly moved and their intensities were slightly changed in relation to the pure 2,3,4,5-tetrachorophenol spectrum. The first band can be interpreted as the stretching vibration of a carbonyl group and the other one as a result of a change in aromatic ring substitution.

It is important to note that in solutions radiated for over 150 min, the presence of 3,4,5-trichlorocatechol and tetrachloromethoxybenzene was pronounced. In solutions irradiated for 280 min dichlorodihydroxybenzene was identified which is probably the result of dechlorination of 3,4,5-trichlorocatechol. The total ion chromatogram is presented in Fig. 7. The tetrachloromethoxybenzene and 3,4,6-trichloro-2-methoxyphenol are the products of the reaction between TeCP and methanol added to the solution before irradiation. The existence of tetrachloromethoxybenzene indicates that the C–OH bond in chlorophenol molecule was cleaved and that the dehydroxylation reaction occurred. As described in the previous case, the *ortho*-positioned Cl atom was substituted by a CH_3O– group. In the solutions

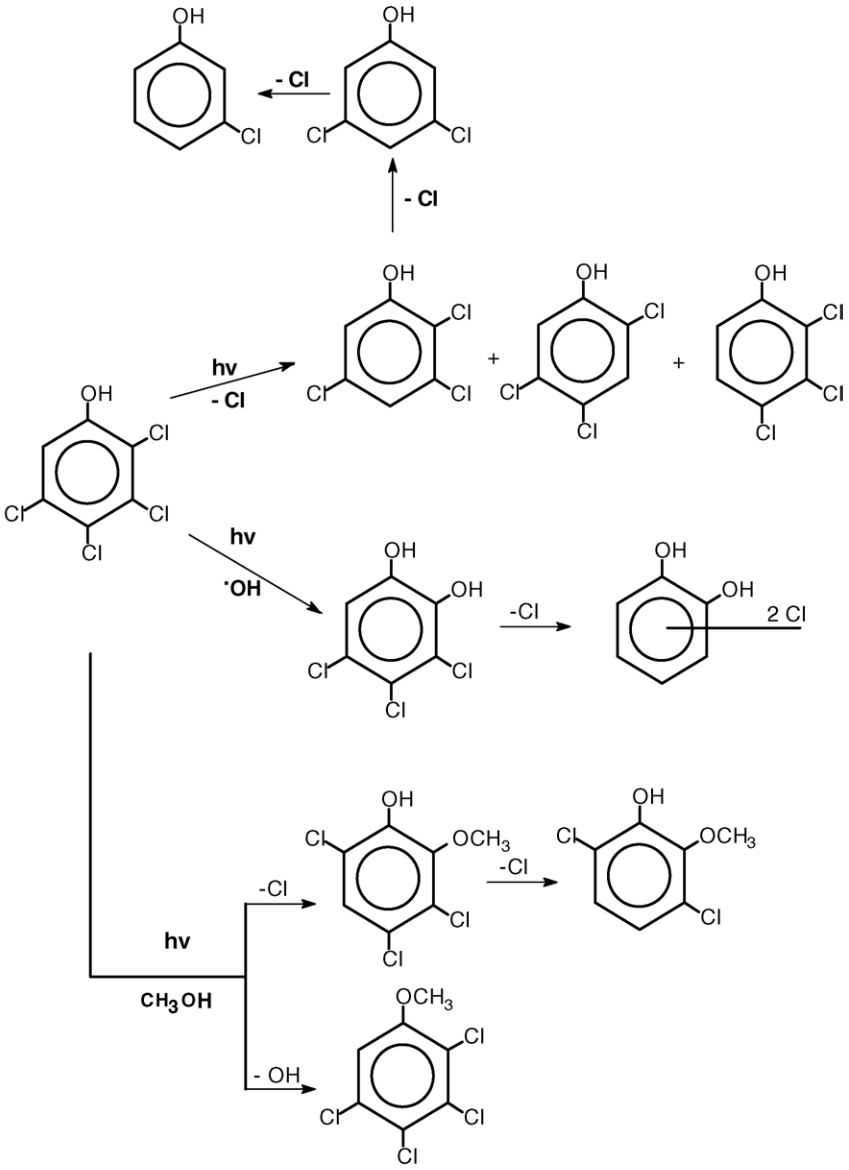

Fig. 8. Pathway of photodegradation of 2,3,4,5-TeCP.

irradiated for 280 min, 3,5-dichlorophenol, 3-chlorophenol, 3,6-dichloro-2-methoxyphenol and 2,5-dichloro-1,1′-biphenyl were also identified. The 3,5-DCP and 3-CP were probably formed as the result of secondary reaction of TCPs. The kinetic curves of TCP formation with the characteristic maximum confirm this hypothesis. After this maximum the TCPs concentration decreases with time. This correlation indicates that TCPs are the substrates in secondary reactions. However, the 2,5-dichloro-1,1′-biphenyl is probably a result of a radical reaction with the participation of phenyl radicals formed in the secondary reactions.

The described results suggest that in the first stage of TeCP photodegradation, the heterolytic scission of the C–Cl bond in the *para*-position occurred. Thus, Cl^- ions are formed. In the next step, the less-chlorinated chlorophenols were formed. Chlorodihydroxybenzenes, such as 3,4,5-trichlorocatechol, were probably a product of the reaction between TeCP and hydroxyl radicals formed in parallel and secondary reactions. Reaction conditions preclude direct water photolysis, so it is important to determine in which reactions the hydroxyl radicals are generated if it is assumed that chlorodihydroxybenzenes are formed in radical reaction with OH participation [42].

Okamoto et al. [43] and Mattews [44] showed that hydroxyl radicals can be generated by phenol and benzoic acid exposure processes in an aqueous environment. Eberhardt and Fuentes-Aponte [45] proved that hydroxyl radicals can be formed in reactions with ion radical 4-CP in an aqueous environment without the presence of oxygen. The hydroxyl radicals can be also formed according to the Buxter mechanism for the parallel reaction of Cl^- ions and $Cl^\bullet$ radicals (Eqs. (6)–(9)) [46,47].

$$Cl^\bullet + Cl^- \rightarrow Cl^{\bullet -}_2 \quad (6)$$

$$Cl^{\bullet -}_2 + HOH \rightarrow HOClH^\bullet + Cl^- \quad (7)$$

$$HOClH^\bullet \leftrightarrow H^+ + HOCl^{\bullet -} \quad (8)$$

$$HOCl^{\bullet -} \leftrightarrow Cl^- + {}^\bullet OH \quad (9)$$

The experimental results do not clearly show which presented mechanism of ${}^\bullet OH$ formation occurs in the discussed systems. Chlorodihydroxybenzenes in aqueous solutions can also be formed as the result of chlorophenol photohydrolysis with hydroxyl ion participations [9,24,48]. Nevertheless, this mechanism proceeds with the participation of chlorine atom in the *meta*-position in most cases.

The second hydroxyl group substitution to *ortho*-position in 3,4,5-trichlorocatechol molecule suggests that in hydroxyl radical reactions the *ortho*-position is favoured. This is in agreement with investigation reported by Hirvonen et al. [37], where photooxidation reaction between chlorophenols and OH radicals upon irradiation at 254 nm lead to chlorodihydroxybenzene formation. In dechlorination reactions, *para* was the favored position. However in reactions with ${}^\bullet OH$ radicals, the favored position was *ortho*-position.

The proposed pathway of 2,3,4,5-TeCP photodegradation is presented in Fig. 8.

4. Conclusions

The rate of reaction strongly depends on the pH. In basic solutions the rate of reaction is higher than in an acidic one. Photodegradation of 2,3,4,5-TeCP in water/methanol mixture yields TCPs as the main products. The mechanism of this reaction is based on the heterocylic scission of C–Cl bond in the *para*-position. Parallel oxidation reactions are also occurred, mainly in the *ortho*-position resulting in formation of chlorodihydroxybenzenes. Formation of intermolecular hydrogen bonding in the radiated solution was also observed.

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