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MARIANNA CZAPLICKA[1]

POLYCHLORINATED DIBENZO-*p*-DIOXINS AND DIBENZOFURANS AS PRODUCTS OF PHOTODEGRADATION OF CHLOROPHENOLS

Results of the study into photodegradation of 2,4,6-trichlorophenol and pentachlorophenol in aqueous solutions have been presented. Quantum yields and rate constants of the reactions were determined. Intermediate products were identified by GC/MS method. The experiments confirmed formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in photochemical reactions. The findings showed that formation of polychlorinated dibenzo-*p*-dioxins, and mainly octachlorodibenzo-*p*-dioxin, is privileged in the studied reactions when compared to polychlorinated dibenzofurans regardless of the number of chlorine atoms in the molecule. It was also established that increase in the number of chlorine atoms in a molecule resulted in higher chemical efficiency of the reaction.

1. INTRODUCTION

Chlorophenols (CP) are synthetic organic compounds produced on industrial scale by chlorination of phenol or hydrolysis of chlorobenzenes. These compounds are generated also in a form of by-products in the process of production of 2,3-dichlorophenoxyacetic acid [1], paper production, coking, destructive distillation of wood and disinfection of drinking water by chlorination method [2]. There are also other sources of chlorophenols such as natural processes of biodegradation of pesticides and herbicides [3, 4]. Microbiological degradation of herbicides, especially of 2,4-D and 2,4,5-T and pesticides in natural environment produces numerous chlorophenols as intermediate metabolites of their decomposition.

In certain conditions, chloroderivatives of phenol may turn into substrates for formation of polychlorinated biphenylenes and polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs). Studies carried out by Klanova et al. [5] showed that exposure of

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[1] Institute of Non-Ferrous Metals, 44-100 Gliwice, ul. Sowińskiego 5, Poland,
e-mail: mariannac@imn.gliwice.pl

3-chlorophenol in ice to UV light may result in formation of hydroxychlorobiphenyl and phenol. Connell [6] noticed that polychlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDFs) were emitted during combustion of wood which was soaked with pentachlorophenol. Formation of PCDDs and PCDFs was also reported in natural biodegradation processes such as enzymatic conversion of chlorophenols in soil and water [7, 8]. These reactions proceed with active contribution of enzymes from the group of peroxidases and chloroperoxidases. Hong et al. [9] demonstrated that irradiation of pentachlorophenol in aqueous solutions under a high pressure Hg lamp not only produces simple chlorinated phenolic compounds but also dimeric products, including heptachlorodibenzo-*p*-dioxins (HpCDDs) and octachlorodibenzo-*p*-dioxin (OCDD) which are more toxic than pentachlorophenol. Czaplicka and Mielżyńska [10] demonstrated that pentachlorophenol solutions after exposure to UV radiation show higher toxicity than the solutions before the irradiation. Photochemical processes in the natural environment are important chemical transformations. The most important factors in the photochemical processes are: maximum light absorption of a compound, wavelength of radiation, time of exposure to radiation and reaction conditions. Photodegradation in water may result from direct photolysis of chlorophenol or from the reaction of chlorophenol with singlet oxygen and ·OH radicals created in sunlight [11, 12]. Authors of various papers suggest that coupling of chlorophenol moieties (radicals and/or anions) can lead to formation of PCDD/Fs.

The research of various authors showed that polychlorinated dibenzodioxins and dibenzofurans are forming during photodegradation of trichlorophenols (TCPs) and pentachlorophenol (PCP) in aquatic and soil environments [12–16]. Studies into mechanisms and kinetics of PCDD/Fs formation were initiated by Wong and Crosby [13]. They reported formation of OCDD in aqueous solutions of pentachlorophenol after exposure to radiation of the wavelength above 300 nm. Liu et al. [15] in the studies into photolysis of pentachlorophenol on soil surface also found that OCDD and HpCDDs are formed.

In this work, the results of the study into kinetics of formation of PCDDs and PCDFs in PCP and 2,4,6-TCP aqueous solutions subjected to radiation of 254 nm wavelength are presented. The main intermediate products of the photodegradation reactions of chlorophenols were identified by GC/MS and GC/MS/MS methods, and concentrations of PCDD/Fs in the solutions after reaction were determined. Kinetic curves of PCDD/Fs formation were also determined.

2. EXPERIMENTAL

Materials and reagents. 2,4,6-trichlorophenol (2,4,6-TCP) and pentachlorophenol (PCP) of purity as required for gas chromatography without purification and methanol of spectral purity were purchased from Merck. Redistilled water was used in the experiments. Potassium ferrioxalate, produced by reaction of potassium oxalate with ferric chloride, was crystallized three times and kept in the darkness.

The standard solutions consisted of 1.035×10^{-3} mol·dm^{-3} of 2,4,6-trichlorophenol and 0.755×10^{-3} mol·dm^{-3} of pentachlorophenol. To avoid potential precipitation of the examined compounds (clouding of the solution under irradiation), the solutions were modified with addition of methanol. Blank tests of 2,4,6-TCP and PCP solution before radiation were performed. The characteristics of standard solutions are presented in Table 1.

Table 1

Characteristics of irradiated solutions

Compound	Compound concentration $c\times10^3$ [mol·dm^{-3}]	Water/methanol ratio in solution, v/v	O_2 concentration [mg·dm^{-3}]	pH
2,4,6-trichlorophenol	1.035	100:3	8.55	5.0
Pentachlorophenol	0.755	100:10	7.40	4.8

Irradiation experiments. The solutions were introduced into quartz tubes and exposed to the radiation of 254 nm wavelength emitted by a low-pressure 16 W mercury lamp. The solutions were maintained in the constant temperature of 25 °C during the whole experiments. The irradiation time of PCP was 270 min, and 210 min of 2,4,6-TCP. Chlorophenols and products of their photodegradation were sampled for analysis every 15 min. Quantum yields of reactions were determined using potassium ferrioxalate [17]. Each experiments was repeated fivefold, the presented results being the arithmetic average.

Analytical procedures. The concentration of PCP, 2,4,6-TCP and products of their photodegradation in the solutions after irradiation were determined with a Perkin Elmer Clarus 500 gas chromatograph equipped with a mass detector and DB-5 capillary column (30 m × 0.25 mm, 0.25 μm film thickness, J & W). Identification of the compounds was based on two or three typical of each compound ions analyzed by selected ion monitoring mode (SIM). The procedure of sample preparation has been described in details elsewhere [18].

The concentrations of PCDDs and PCDFs were determined by the following method. After irradiation the samples were spiked with a mixture of ^{13}C-labeled PCDDs/PCDFs solution and extracted with toluene of the pesticide grade in a Soxhlet apparatus for 48 h. EPA-1613LCS mixture of 16 congeners of ^{13}C-PCDDs in acetone was used as an internal standard. The extracts were purified by a 3-stage open column chromatographic procedure with application of a multilayer silica, florisil and basic alumina column, respectively. The analyte was eluted with dichloromethane/hexane mixture and concentrated to 0.001 dm^3 using a rotary evaporator. Finally, the analyte was concentrated in a stream of nitrogen to incipient dryness prior to addition of the recovery standard (EPA-1613CSS $^{37}Cl_4$-2,3,7,8-TCDD). Samples were analysed with GCQplus Finnigan system GC-MS/MS equipped with DB-5MS (60 m×0.25 mm 0.25 μm film thickness, J & W). Column temperature programs were as follows: 100 °C for 1 min, 20 °C/min to 200 °C, 2 °C/min to 280 °C and annealing for 15 min. The transfer line temperature was adjusted to 270 °C. Because of different structures of cores of PCDDs and PCDFs molecules, there is also difference in the optimum of collision energies with helium atoms in a MS/MS system. Details of the analytical methods are given in [19]. The standard ISO 9297. *Determination of chloride in water* was used in defining the chloride level in water.

3. RESULTS

Direct photolysis of CP can lead to several reactions, e.g. hydrolysis and/or homolytic cleavage of C–Cl bonds to form chlorine and carbon-centred phenoxy radicals. The quantum yields of photodegradation in the experiment conditions amounted to 0.076 for PCP and 0.128 for 2,4,6-TCP, respectively. The constant rates of reaction of chlorophenol degradation were 9.23×10^{-3} min^{-1} for 2,4,6-TCP and 0.036 min^{-1} for PCP, respectively, when making the assumption that it is a pseudo-first order reaction. Kinetic curves of photodegradation of PCP and 2,4,6-TCP are presented in Fig. 1.

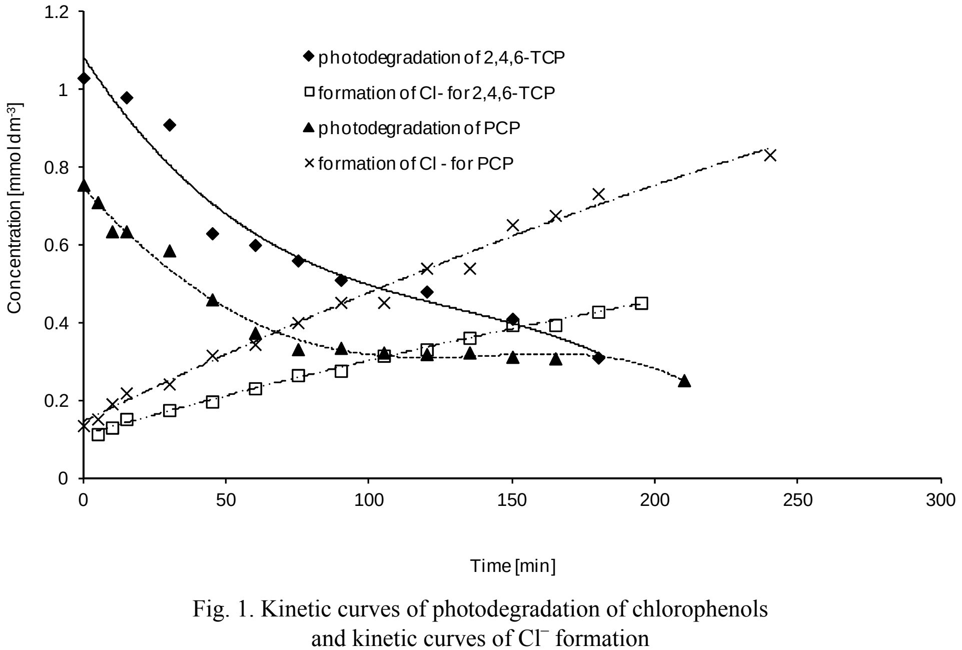

Fig. 1. Kinetic curves of photodegradation of chlorophenols and kinetic curves of Cl^- formation

GC/MS data show that products of dechlorination are the principal organic products formed in this process. Products of oxidation, e.g. dichlorobenzodiols and chlorobenzodiols were identified in the solution after irradiation as the products of CP reaction with oxygen dissolved in water and/or with hydroxyl radicals. The identified intermediate products of 2,4,6-TCP photodegradation were: 2,4-dichlorophenol, 4-chlorophenol, 2,6-dichlorophenol, 3,4-dichlorobenzo-1,2-diol and 4-chlorobenzo-1,2-diol. The following compounds were identified in the PCP solutions after reaction: 2,3,4,6-tetrachlorophenol, 2,3,4,5- tetrachlorophenol, 2,4,5,6- tetrachlorophenol, 2,3,5-TCP, 3,5-dichlorophenol, tetrachlorobenzodiols, trichlorobenzodiols and chlorobenzodiols. After 200 min of reaction, 2,4-phenyl-4,H-1,3-benzodioxin in the solutions was found by GC/MS method. The mechanism of formation of the products of reduction has already been explained [20].

The analysis by GC/MS/MS method showed that PCDD/Fs also occur in the solutions generated after reaction. Concentrations of the determined PCDD/Fs in those solutions depended on the nature of chlorophenol and on the irradiation time. In both examined chlorophenols, toxic equivalent (pg TEQ·dm^{-3}) of tested solutions, which was determined by the quantitative analysis, increased upon increasing irradiation time (Fig. 2). The pg-TEQ·dm^{-3} for 2,4,6-TCP in the solution after 210 min of irradiation was 11.15, while for PCP it reached the value of 448 after 270 min of irradiation.

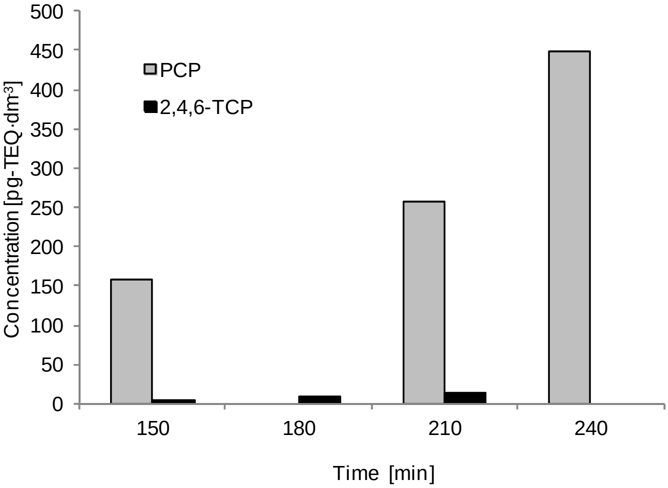

Fig. 2. Concentration pg-TEQs dm^{-3} of 2,4,6-TCP
and PCB solutions after irradiation vs. irradiation time

3.1. PHOTODEGRADATION OF 2,4,6-TCP

The results of the research show that PCDDs represented from 22.7% to 37.9% of the total determined PCDD/Fs congeners, depending on irradiation time, and prolongation of the time of exposure resulted in decrease of PCDDs fraction in the total amount of the determined PCDD/Fs congeners. Regardless of irradiation time, 1,2,3,7,8,9-hexachlorodibenzo-*p*-dioxin (1,2,3,7,8,9-HxCDD) was the main congener among the PCDDs, and it represented 15.4% of the generated PCDD/Fs in the solution irradiated for 180 minutes and 10.9% in the solution which was irradiated for 210 min (Table 2). No OCDD and 1,2,3,4,5,7,8-HpCDD were observed.

Table 2

Concentration of PCDDs and PCDFs in solution of 2,4,6-TCP after irradiation [pg·dm^{-3}]

Congener	Irradiation time, min		
	150	180	210
2,3,7,8-TCDD	nd	nd	nd
1,2,3,7,8-PeCDD	0.8	1.4	2.5
1,2,3,4,7,8-HxCDD	1.2	2.0	2.8
1,2,3,6,7,8-HxCDD	2.6	5.7	7.0
1,2,3,7,8,9-HxCDD	5.0	11.3	11.4
1,2,3,4,6,7,8-HpCDD	nd	nd	nd
OCDD	nd	nd	nd
2,3,7,8-TCDF	3.8	6.9	17.6
1,2,3,7,8-PeCDF	1.1	2.1	1.4
2,3,4,7,8-PeCDF	0.6	4.0	5.3
1,2,3,4,7,8-HxCDF	0.2	0.5	2.0
1,2,3,6,7,8-HxCDF	1.6	2.7	4.2
2,3,4,6,7,8-HxCDF	4.1	17.2	21.1
1,2,3,7,8,9-HxCDF	4.4	19.5	29.0
1,2,3,4,6,7,8-HpCDF	nd	nd	nd
1,2,3,4,7,8,9-HpCDF	nd	nd	nd
OCDF	nd	nd	nd
Total	25.3	73.3	104.3

nd – below the limit of detection.

Kinetic curves of PCDFs formation slightly differ. The total amount of these compounds in the irradiated solutions represented from 62.1% to 77.3% of the determined PCDDs and PCDFs congeners. In that group of the compounds, with the increase of the irradiation time, mainly increase of concentrations of 1,2,3,7,8,9-hexachlorodibenzofuran (1,2,3,7,8,9-HxCDF), 2,3,4,6,7,8-HxCDF and 2,3,7,8-tetrachlordibenzofuran (2,3,7,8-TCDF) was observed. The majority of the determined PCDFs in the solutions which were irradiated for 150 min was at the similar concentration level, around 0.2–4.4 pg·dm^{-3}. Significant concentration increase of 1,2,3,7,8,9-HxCDF, 2,3,4,6,7,8-HxCDF and 2,3,7,8-TCDF was recorded in the solutions irradiated for more than 180 min. The concentration ratio of 2,3,7,8-TCDF, 2,3,4,6,7,8-HxCDF, 1,2,3,6,7,8-HxCDF was 1:2.5:2.8 after 180 min of irradiation and 1:1.2:1.6 after 210 min. Kinetic curves of PCDFs formation are presented in Fig. 3.

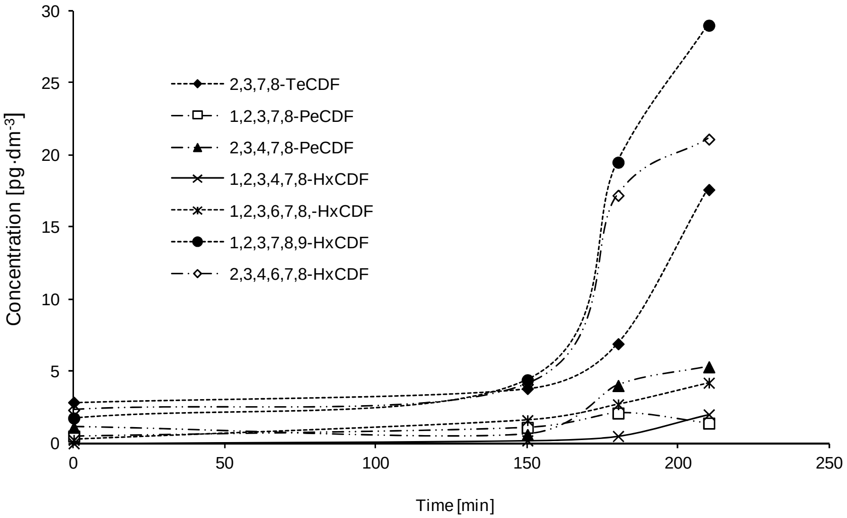

Fig. 3. Kinetic curves of formation of PCDFs during photodegradation of 2,4,6-TCP

The obtained results, especially the dominant role of hexachlorodibenzodioxins and furans in the total amount of the determined congeners, indicate that radical dimerization is the main reaction which leads to formation of those compounds in the process of photodegradation of 2,4,6-TCP. The generated 1,2,3,7,8-pentachlorodibenzo-*p*-dioxin (1,2,3,7,8-PeCDD) most probably results from photoinduced dechlorination of hexachlorodibenzo-*p*-dioxins and/or from reaction with trichlorophenoxy radical and with dichlorophenoxy radical generated in secondary reactions. In that process, 1,2,3,7,8,9-HxCDD is the main hexachlorodibenzodioxin generated. Concentration of the other congener of that compound in the solutions – 1,2,3,6,7,8-HxCDD – is two times lower, while concentration of the 1,2,3,4,7,8-HxCDD is from four to five times lower compared to the concentration of 1,2,3,7,8,9-HxCDD depending on irradiation time. Similar efficiencies of formation of two hexachlorodibenzofuran congeners, i.e. 1,2,3,7,8,9-HxCDF, 2,3,4,6,7,8-HxCDF, were observed with PCDFs. Concentration of the third of the congeners 1,2,3,6,7,8-HxCDF in the solutions after reaction was about 7 times lower than in 1,2,3,7,8,9-HxCDF.

3.2. PHOTODEGRADATION OF PCP

The GC/MS/MS examination of solutions of pentachlorophenol which were exposed to UV (254 nm) radiation showed that PCP, like 2,4,6-TCP, undergoes photochemical reactions leading to formation of PCDDs and PCDFs. The results indicate that prolongation of irradiation time leads to increase of concentration of PCDD/Fs in the solutions (Table 3).

Table 3

Concentration of PCDDs and PCDFs
in PCP solution after irradiation [pg dm^{-3}]

Congener	Irradiation time [min]		
	180	240	270
2,3,7,8-TCDD	0.9	2.9	1.2
1,2,3,7,8-PeCDD	12.0	28.4	39.2
1,2,3,4,7,8-HxCDD	157.7	312.9	503.7
1,2,3,6,7,8-HxCDD	195.5	200.5	265.5
1,2,3,7,8,9-HxCDD	72.8	180.8	345.8
1,2,3,4,6,7,8-HpCDD	2772.5	4469.6	7898.7
OCDD	46 653.4	84 689.1	119 906.9
2,3,7,8-TCDF	3.6	6.9	14.1
1,2,3,7,8-PeCDF	1.8	6.1	16.1
2,3,4,7,8-PeCDF	20.5	48.3	106.6
1,2,3,4,7,8-HxCDF	50.5	110.6	237.7
1,2,3,6,7,8-HxCDF	64.4	165.0	192.5
2,3,4,6,7,8-HxCDF	243.6	624.7	622.7
1,2,3,7,8,9-HxCDF	7.1	12.2	19.8
1,2,3,4,6,7,8-HpCDF	2319.1	2608.4	4144.9
1,2,3,4,7,8,9-HpCDF	4.2	27.8	89.2
OCDF	518.6	409.0	960.5
Total	53 098.0	93 903.5	135 365.1

It should be emphasized, however, that for the majority of the determined congeners the concentrations of PCDDs in photodegradation of PCP are at the level of several hundred of pg·dm^{-3}, and with OCDD the concentration reaches the level of several dozen of ng·dm^{-3}.

Total amount of the determined polychlorinated dibenzo-*p*-dioxins reaches 93–95% of the generated PCDDs and PCDFs congeners. OCCD is a dominant compound among the determined PCDDs congeners. That compound represented around 87–91% of the total amount of the determined PCDD/Fs. Hong et al. [9] obtained similar results and suggested that polychlorinated dibenzo-*p*-dioxins as minor products were also generated by dimerization during photolysis of pentachlorophenol.

The other PCDDs generated in significant amounts in photochemical reaction of PCP decomposition are: 1,2,3,4,6,7,8-HpCDD, 1,2,3,6,7,8-HxCDD and 1,2,3,4,7,8-HxCDD. There was also formation of 2,3,7,8-TCDD observed, which has not been identified after irradiation of 2,4,6-TCP solution.

Formation of HpCDDs and HxCDDs during irradiation of PCP solution most probably results from photoinduced dechlorination of *peri* position of OCDD. The OCDD photodegradation in aqueous solutions takes place at the constant rate of 1.6×10^{-3} min^{-1}, while only 2% of the products come from dechlorination reaction [21]. Therefore efficiency of the reaction of HpCDDs and HxCDDs formation during dechlorination of OCDD is low. It is impossible, however, to exclude generation of hepta-, hexa-, and pentachlorodibenzodioxins in parallel reactions with radicals of the compounds produced in the result of earlier dechlorination of PCP such as: tetra- and trichlorophenols.

Taking under consideration that the rates of photodegradation of PCDDs and PCDFs increase upon decreasing number of chlorine atoms in a molecule [22] and assuming that the less chlorinated PCDDs and PCDFs are generated in the dechlorination reaction, not only presence of pentachlorodibenzodioxins can be expected but also of tetrachlorodibenzodioxins (TCDDs). The results confirmed the presence of 2,3,7,8-TCDD in that process (Table 3).

PCDFs congeners represented from 5 to 7% of all PCDD/Fs. The dominant polychlorinated dibenzofuran generated in the PCP photodegradation was 1,2,3,4,6,7,8-HpCDF. Concentration of that compound varied from 2319 $\text{pg}\cdot\text{dm}^{-3}$ for irradiation time of 180 min to 4145 $\text{pg}\cdot\text{dm}^{-3}$ in irradiation for 270 min.

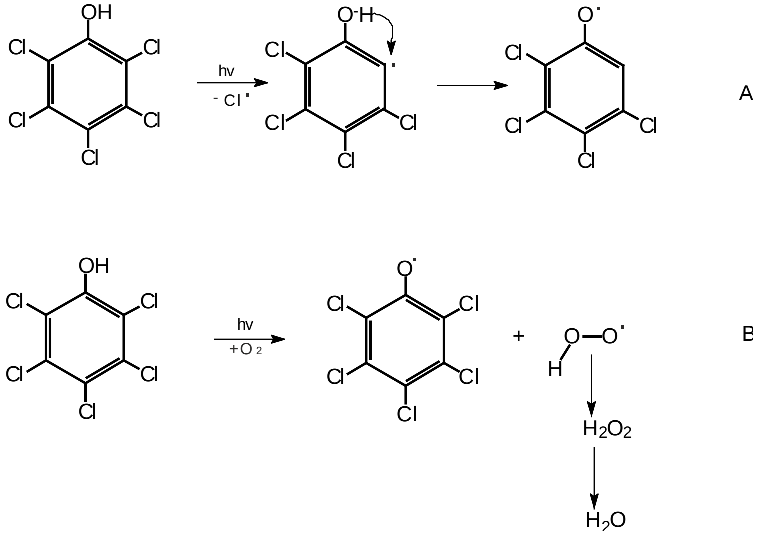

Fig. 4. Formation of phenoxy radical by dechlorination without (A) and in the presence of oxygen (B)

In most cases, radical mechanism of generation of PCDD/Fs in the processes of pyrolysis and photolysis of chlorophenols is postulated [9, 21–25]. In the described systems, generation of chlorophenoxy radicals takes place in the first stage of the process in the result of cleavage of C–Cl bond in a chlorophenol molecule. Similarly to pyrolytic reactions, chlorophenoxy radicals can also be generated in reactions with oxygen in the singlet state (Fig. 4).

Then the radicals undergo direct recombination to form OCDD (Fig. 5) or undergo disproportionation, or they transfer a hydrogen atom to another radical. Since there is no knowledge on any reaction of attaching of phenoxyl radicals to benzene ring in aqueous phase, the reaction between phenoxyl radicals and molecules of chlorophenols is impossible.

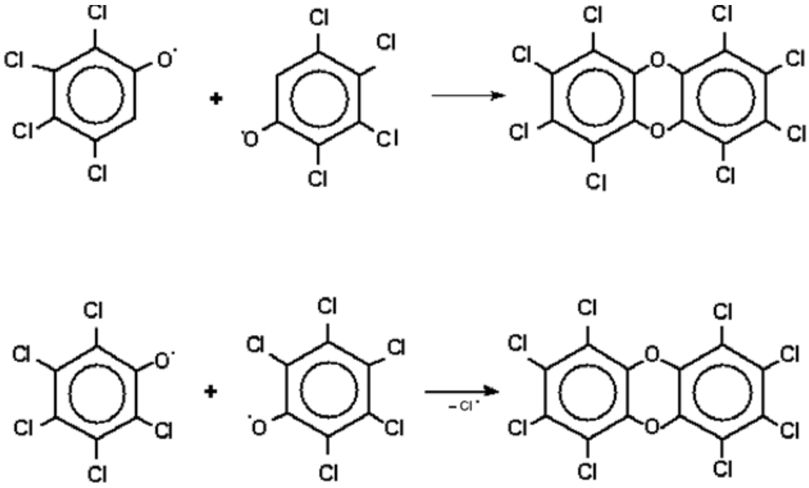

Fig. 5. Formation of OCDD during radical/radical reactions

The presented mechanisms of reactions suggest that photochemical reactions lead mainly to formation of OCDD with PCP, which is confirmed by the presented results. The lower chlorinated PCDDs are formed as a result of photoinduced dechlorination, mainly in *peri* positions of OCDD, and in radical reactions with products of primary reactions. The results of author's studies show also significant content of PCDDs congeners in the determined PCDD/Fs during PCP photodegradation. Such a relation can be explained by the Gibbs energy, which favors formation of PCDDs when compared to PCDFs. On the other hand, substitution of the chlorine atom in the particle influences reactivity of chlorophenol. In their studies into mechanisms of PCDD/Fs formation in chlorophenol pyrolysis, Weber and Hagenmaier [25] proved that the reaction of chlorophenol with chlorine atoms in *orto* position leads to formation of PCDFs. An indirect confirmation of that thesis can be seen in the higher amount of PCDFs congeners in comparison to PCDDs in the case of 2,4,6-TCP photodegradation. Therefore, the efficiency of PCDFs and PCDDs formation is determined by the value of the Gibbs energy on one hand and by the reactivity of chlorophenol in photochemical reaction on the other.

4. CONCLUSION

- Formation of PCDDs and PCDFs results from photochemical reactions of 2,4,6-TCP and PCP, which were initiated by absorption of radiation of the wavelength of 254 nm.
- The dominant congener of PCDD/Fs generated in photodegradation of 2,4,6-TCP is 1,2,3,7,8,9-HxCDF, and in the case of PCP it is OCDD. A certain regularity was observed, i.e. prolongation of irradiation time results in the increase of concentration of PCDD/Fs in the solutions after reaction.
- The increase of the number of chlorine atoms in a molecule results in the increase of efficiency of PCDD/Fs formation.
- The number of chlorine atoms and their position in relation to the hydroxyl group in molecules of 2,4,6-TCP and PCP influence the efficiency of formation of individual PCDD/Fs congeners.

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