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Photochemical transformation of polychlorinated phenols

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Abstract

To increase our understanding of the photocatalytic effects in the transformation of chlorinated organic compounds, the detailed mechanism of the direct photolysis of polychlorinated phenols has been established under aerobic and anaerobic conditions. The quantum yield of photolysis of 2,4,5-trichlorophenol (2,4,5-TCP) has been determined at different wavelengths and pH values.

It has been shown that direct photolysis of polychlorinated phenols is accompanied by chloride ion detachment from different positions of the benzene ring with the formation of 2,5-dichlorohydroquinone and dichlorocyclopentadiene derivatives in the case of 2,4,5-TCP, as well as polychlorinated dibenzodioxins (PCDD) and dibenzofurans (PCDF). Based on the 2,4,5-TCP direct photolysis products, it has been concluded that chlorophenol free radicals are formed as a result of C–Cl cleavage, which probably act as the origin of highly chlorinated PCDD and PCDF.

To utilize visible light in the photocatalytic destruction of organic pollutants, we investigated the kinetics of transformation of polychlorinated phenols in systems involving singlet oxygen formation (dye-sensitized reactions with Rose Bengal, Methylene Blue and Eosin). It has been shown that superoxide radical is not reactive towards 2,4,5-TCP, whereas singlet oxygen results in the destructive oxidation of polychlorinated phenols without formation of PCDD and PCDF among the reaction products.

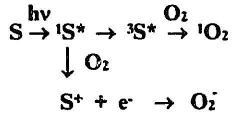
The detailed mechanism of the interaction of singlet oxygen with 2,4,5-TCP has been investigated. It has been concluded that the initial trichlorophenol is dechlorinated and singlet oxygen interaction with 2,4,5-TCP proceeds via a mechanism with the formation of hydrogen peroxide without intermediate superoxide radicals. © 1997 Elsevier Science S.A.

Keywords: Chlorophenol; Sensitized photolysis; Photodegradation; Dioxin

1. Introduction

Phenols and chlorinated phenols are widespread pollutants of waste and natural waters [1–4]. Of special note are pentachlorophenol (PCP) and the trichlorophenols (2,4,5-TCP, 2,4,6-TCP) [5–8]. Apart from their own biological activity, these pollutants can be highly toxic, as they contain micro-impurities of polychlorinated dibenzodioxins (PCDD) and dibenzofurans (PCDF) which are the most toxic of xenobiotics [9–14]. Besides, once in the environment, chlorophenols can be transformed into more toxic compounds under the action of natural factors [15–17].

In natural and waste waters, sensitized transformations proceed in parallel with direct photolysis under the action of solar light. In sensitized redox processes, the active reaction intermediate participating in the transformation of the pollutant may be simply the electronically excited sensitizer molecule [18,19], or its fragmentation or hydrolysis products, the solvated electron [20], and hydroxyl radicals (OH) [21]. Under aerobic conditions there may be additionally involved the products of interaction between the electronically excited sensitizer molecule, or the solvated electron and O_2, namely singlet oxygen ($^1O_2$) [22,23] or superoxide radical (O_2^-) [24,25], respectively (Scheme 1).



$$S \xrightarrow{h\nu} {}^1S^* \rightarrow {}^3S^* \xrightarrow{O_2} {}^1O_2$$
$$\downarrow O_2$$
$$S^+ + e^- \rightarrow O_2^-$$

Scheme 1.

In oxygenated natural waters, the main sensitizers are fulvic acids [26]. Different waste products of aquatic micro-organisms, especially microalgae, as well as organic materials of anthropogenic origin, may act as photosensitizers. To model the reactions with singlet oxygen, dyes of the thiazine and xanthene series are usually used, typical repre-

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sentatives of which are Rose Bengal (RB), Methylene Blue (MB), and Eosin (E) [18]. Each of them possesses photochemical activity, but in the presence of dissolved oxygen they effectively form $^1O_2$ with a quantum yield close to unity [27]. Much experimental material [28] has been accumulated about the reactivity of singlet oxygen in dilute aqueous solution. It is considered that $^1O_2$ interacts with organic substances forming endoperoxides and, via a mechanism of resulting one- or two-electron transfer, a superoxide radical (O_2^-) [29] or hydrogen peroxide (H_2O_2) [30], respectively. It has been also shown that reaction of $^1O_2$ with phenol derivatives proceeds mainly according to a mechanism of "physical" quenching or electron transfer [31].

This work seeks to detail the kinetics, mechanisms and products of direct and sensitized photolysis of some polychlorinated organic compounds mainly PCP and TCP (2,4,5-TCP and 2,4,6-TCP).

2. Experimental

2.1. Reagents

Chromatographically pure pentachlorophenol, 2,4,5- and 2,4,6-trichlorophenols were used without extra purification. Aqueous solutions of the compounds investigated were prepared with doubly distilled water.

2.2. Procedures

Experiments were carried out in phosphate or borate buffered solutions. The initial pH of unbuffered solutions was varied by adding HCl or NaOH.

Experiments were conducted in sunlight (in the summer months) and also using photochemical reactors, where xenon and mercury lamps were used as light sources. In the case of the DRL-400 high-pressure Hg lamp, experiments were conducted with both unfiltered and filtered light. Both liquid and glass filters were used. The filtered light of a DRS-1000 high-pressure Hg lamp and unfiltered light of a DB-8 low-pressure Hg lamp ($\lambda = 254$ nm) were also used.

Actinometry of sunlight (at least as its component in the near-UV region) was performed using the bleaching rate of *p*-nitrosodimethylaniline (PNDMA) dye as a trap for radicals, formed in hydrogen peroxide photolysis. Actinometry of artificial light sources was measured by the standard ferrioxalate technique. Experiments were conducted in quartz, pyrex or glass test tubes. The volume of the reaction mixture ranged from 3 to 200 cm^3.

2.3. Analyses

Chlorophenol concentrations were determined by spectrophotometry and high-pressure liquid chromatography (HPLC). Electronic absorption spectra in the 200–300 nm wavelength range were obtained with UV-2100 Shimadzu and Spekord M-40 spectrophotometers.

Samples were analyzed by HPLC or using a LKB chromatograph with a UV–VIS detector at 210 nm, a Hamilton column (4.1×250 mm) with stationary radial pack reverse (RPR-1) and mobile phases, consisting of a mixture of acetonitrile and 0.1% phosphoric acid in a ratio of 3:1, or with the Lab. Pristr. (Prague) instrument at $\lambda = 290$ nm with a Silasorb column SPH 98 (3.0×250 mm) with a mobile phase consisting of a mixture of methanol, 0.1 M solution of potassium dihydrogen phosphate and acetic acid mixture in the ratio of 75:25:1. The volume of injected samples was 10 and 20 μl, respectively, and the elution rates were 1.0 and 0.5 cm^3 min^{-1}. The reproducibility in determining polychlorophenols was ±5%.

Chloride ions were determined chromatographically using a Lab. Pristr. (Prague) instrument equipped with an analytical set Dianion-1 (supplied by Elsiko, Russia). An ion exchange column (50×3.0 mm) was utilized with a mobile phase consisting of a 0.25 mM solution of potassium biphthalate. The pH of the mobile phase was adjusted to 5.5 with (0.1 M) KOH. The elution time of the chloride ion chromatographic peak output was 2.2 min. The calibration plot was linear in the range 0.1–4.0 mg Cl$^-$ dm^{-3}. The measurement precision was ±2%.

The pH of the aqueous medium was controlled with an Ecotest 01 analyser (ELIS, Russia), as well as by a pH-340 device.

Experiments were carried out both under aerobic and anaerobic conditions. In experiments under anaerobic conditions, the solution components were placed in a hermetically sealed optical cuvette supplied with a membrane, and the air was vacuum pumped from the dead space for 2–3 min with vigorous shaking of the cuvette. Then the dead space was filled with argon. Absorption spectra and chlorophenol concentrations were measured before and after solution irradiation by filtered or unfiltered light from a DRL-400 lamp at different time intervals.

In replicate experiments the chlorophenol solution at a given pH was bubbled with argon in a quartz cell for 3–5 min, and then it was hermetically sealed.

In some cases during experiments under anaerobic conditions, the analyzed solutions were subjected only to vacuum pumping with subsequent hermetic sealing (without subsequent filling by argon). The results obtained were similar irrespective of the method used.

The transformation products of the chlorophenol were analyzed by GCMS using an ITD-800 Finnigan MAT-instrument. Photolysis products and residual amounts of chlorophenols were extracted from the aqueous phase by methylene chloride after acidification of the medium to pH 3. Test components were separated in the 30 m×0.32 mm quartz capillary column with a DV-5 stationary phase. The thermostated column temperature was programmed from 40 to 250 °C at 10 °C min^{-1}. Argon was used as the mobile gas phase. Mixture components were identified by a computer mass-spectrum comparison with electron impact ionization using the NIST database (USA). Some low-molecular compounds were interpreted according to fragmentation patterns of organic compounds under electron impact [32].

The concentration of hydrogen peroxide in aqueous solutions was determined spectrophotometrically using a peroxidase oxidation method of triphenylmethane leuco-dyes [33–35].

To avoid the interfering effect of direct photolysis on the chlorophenols, the experiments were conducted in the presence of sensitizers, usually with filtered light at λ > 400 nm. A 1 cm layer of 1.0 M potassium dichromate solution was used as the filter.

The concentrations of transition metals (Cu, Fe, Mn, Co) were determined by atomic absorption analysis with a sample atomization in a graphite cell using a Perkin-Elmer spectrometer.

All experiments in the photochemical transformation of polychlorinated phenols were conducted at ambient temperature (23–25 °C).

3. Results and discussion

3.1. Direct photolysis

The effective rate constant of direct photolysis (k_d) of substance P at low optical densities is determined from:

$$k_d = 2.3\varphi_{d,\lambda} \int \varepsilon_\lambda(\lambda) I_{o,\lambda}\, d\lambda$$

where $\varphi_{d,\lambda}$ is the quantum yield of the reaction, $I_{o,\lambda}$ is the light intensity, $\varepsilon(\lambda)$ is the molar extinction coefficient of the substance P at wavelength λ, $\int \varepsilon_\lambda(\lambda) I_{o,\lambda}\, d\lambda$ is the overlap integral of the radiation source and the absorption of substance P (the action spectrum) [36].

The absorption spectra of 2,4,5-trichlorophenol and pentachlorophenol in distilled water depend on the pH. For the anionic form, the action spectrum increases in amplitude and shifts to longer wavelength.

Kinetic investigations have shown that direct photolysis of polychlorinated phenols in neutral aqueous solution under unbuffered conditions is accompanied by a significant decrease of the pH and retardation of the process. This is caused by formation of acidic products of the initial transformation of the phenol and involvement of its ionized form in photochemical processes. Considering this fact and that natural and waste waters are buffer systems, all subsequent investigations were conducted under buffered conditions. The control series of experiments has shown that the photochemical transformation rate of 2,4,5-TCP does not depend on buffer concentration.

The pH dependence of the photochemical transformation rate of 2,4,5-TCP under sunlight (Fig. 1) shows that the ionized form of chlorophenols is the principal source of photochemical activity. The pK_a value of (6.7 ± 0.2) found from these kinetic data practically coincides with that calculated from spectrophotometric data.

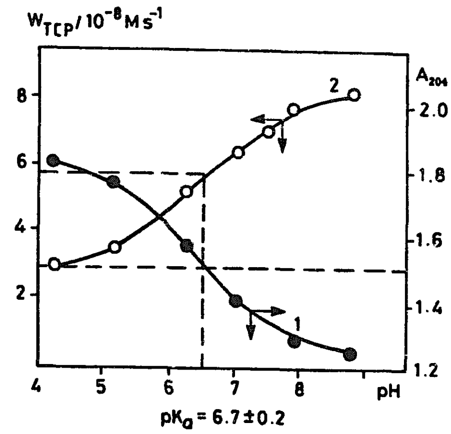


Fig. 1. pH dependence of absorption at 204 nm (1) and the rate of direct photolysis of 2,4,5-TCP. $C_{o,TCP} = 5 \times 10^{-5}$ M; xenon lamp; 150 W.

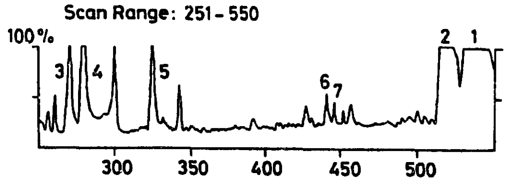


Fig. 2. GCMS of products of direct solar photolysis of 2,4,5-TCP. $C_{o,TCP} = 5 \times 10^{-5}$ M; pH 7.0; exposure time, 4 h. Curve 1, 2,4,5-TCP; curve 2, 2,5-dichlorohydroquinone; curve 3, 2,4-dichlorocyclopentadiene [a]; curve 4, 2,5-dichlorocyclopentadiene [a]; curve 5, 5-chlorocyclohexene-1-one; curve 6, 2,4-dichlorophenol; curve 7, 2,5-dichlorophenol. [a] Dichlorocyclopentadienes can be formed from corresponding carboxylic acids.

The rate of direct photolysis of polychlorinated phenols is proportional to the irradiation intensity. The quantum yield of direct photolysis of 2,4,5-TCP is $(5.9 \pm 0.5) \times 10^{-2}$ and is virtually independent of pH and irradiation wavelength. Control experiments have shown that, under normal conditions, the contribution of dark processes is insignificant.

GCMS and HPLC data show that the principal organic products, formed in the early stages of photolysis of 2,4,5-TCP are: organic acids (probably dichlorocyclopentadiene carboxylic acids [37–39]) 2,5-dichlorohydroquinone and 3,4-dichlorocyclopentadiene with trace quantities of 2,4- and 2,5-dichlorophenols (Fig. 2).

Solar irradiation of pentachlorophenol yielded the following low-molecular products: tetrachloro-, 2,3,5-trichloro- and 2,4-dichlorohydroquinones and traces of 4,5-dichloro-4-cyclohexene-1-one, 5-chloro-4-cyclohexene-1-one, 2,4,5- and 2,3,6-trichlorophenols and 2,5-dichlorophenol (Fig. 3).

The structures of these products are indicative of dechlorination of the polychlorophenol as a result of the primary stages of chemical transformation. For example, the loss of 2,4,5-TCP is accompanied by accumulation of stoichiometric amounts of chloride ion in the medium. Thus, the dissociation of one of three chlorine atoms in the form of chloride ion proceeds faster than the other two (Fig. 4).

Kinetic curves of the transformation of 2,4,5-TCP, and the growth of 2,4-dichlorocyclopentadiene and 2,5-dichlorohy-

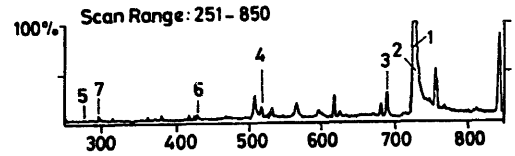


Fig. 3. GCMS of products of direct solar photolysis of pentachlorophenol. $C_{0,\mathrm{PCP}}=5\times10^{-5}$ M; pH 7.0; exposure time, 4 h. Curve 1, pentachlorophenol; curve 2, 2,3,5,6-tetrachlorohydroquinone; curve 3, 2,3,5-trichlorohydroquinone; curve 4, 2,4-dichlorohydroquinone; curve 5, 2,3-dichloro-2-cyclopropene-1-one; curve 6, 4,5-dichloro-4-cyclohexen-1-one-4,5-dichloro; curve 7, 5-dichloro-4-cyclohexen-1-one.

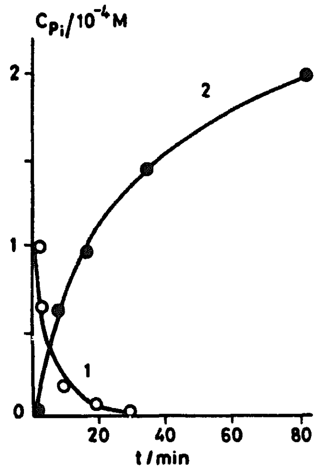


Fig. 4. Kinetic curves of photolysis of 2,4,5-TCP (1) and chloride ion accumulation (2). $C_{0,\mathrm{TCP}}=10^{-4}$ M; pH 8.2; DRL-440 lamp.

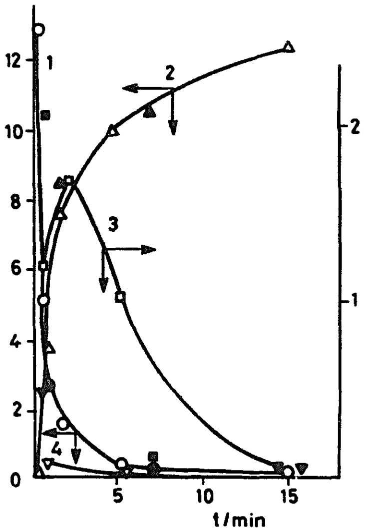


Fig. 5. Kinetic curves (relative units) of photochemical transformation of 2,4,5-TCP (1) and formation of some reaction products (2–4) under aerobic (light symbols) and anaerobic (dark symbols) conditions. $C_{0,\mathrm{TCP}}=10^{-4}$ M; pH 8.2; DRL-440 lamp. Curve 1, 2,4,5-TCP ($\times10^3$); curve 2, 2,4-dichlorocyclopentadiene (carboxylic acids); curve 3, 2,5-dichloro-1,4-hydroquinone; curve 4, 2,5-dichlorophenol.

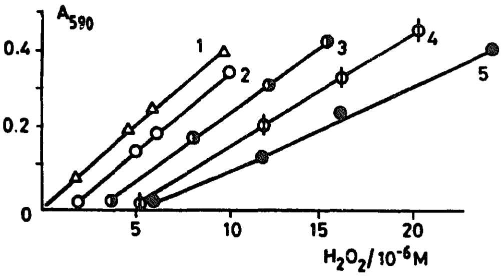


Fig. 6. Curves of 2,4,5-TCP titration by hydrogen peroxide following irradiation at λ = 313 nm. Irradiation time: curve 1, 0 min; curve 2, 1 min; curve 3, 2 min; curves 4, 5, 5 min (5, anaerobic conditions). A_{590}, optical density at λ = 590 nm (of the crystal violet absorption).

droquinone are presented in Fig. 5. Clearly dichlorohydroquinone is a direct product of the initial transformation of the chlorophenol: its concentration reaches a maximum at the point of disappearance of 2,4,5-TCP and then it falls rather quickly due to the following photochemical transformations (under dark conditions this product is rather stable).

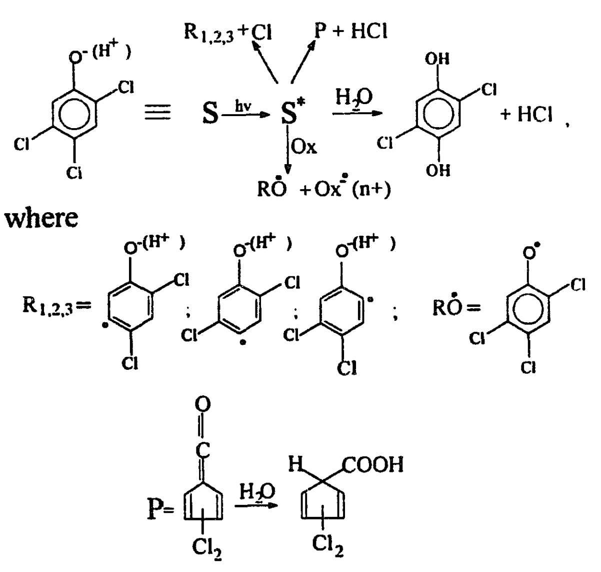
It is interesting to note that neither the initial rate of photochemical transformation of 2,4,5-TCP nor the formation rates of dichlorohydroquinone or cyclopentadienes depend on the presence of oxygen in the solution. At the same time, under anaerobic conditions more than a 10-fold increase in 2,5- and 2,4-dichlorophenols is observed. Moreover, perceptible amounts of 2,6-dichlorophenols are detected (it should be noted that in the initial 2,4,5-TCP chlorine is absent from position 6).

Comparison of experimental data obtained under aerobic and anaerobic conditions allows us to conclude: (i) oxygen or its activation products are not involved in direct photolysis of polychlorophenols; (ii) under the action of near UV radiation there is not only heterolytic (with Cl^- ion detachment), but also homolytic cleavage of the C–Cl bond with the formation of a chlorine atom and free alkylphenoxy radicals.

The absence of hydrogen peroxide under aerobic conditions also indicates no role for oxygen in the mechanism of photochemical transformation of 2,4,5-TCP. Instead of H_2O_2, we have observed reducing substances in the medium, which can be titrated by hydrogen peroxide in the presence of peroxidase (Fig. 6). The amount of these substances does not depend on the oxygen content in the solution and correlates with the formation of 2,5-dichlorohydroquinone.

The primary intermediate product of direct photolysis of 2,4,5-TCP displays marked electron-donor properties. For example, photolysis at 313 nm of 2,4,5-TCP is accompanied by bleaching of dichlorophenolindophenol dye (DCIP), which is an effective electron (and superoxide radical) acceptor. The presence of oxygen in the medium has no effect on the rate of bleaching of DCIP, nor on the rate of photochemical transformation of 2,4,5-TCP. In the presence of DCIP, photolysis of 2,4,5-TCP is not accompanied by chloride ion formation in the medium; the detection of Cl^- is observed only after an induction period, during which the dye is completely bleached.

Based on the body of data described, a mechanism of direct photolysis may be suggested, which includes an electronically excited state of 2,4,5-TCP with marked electron-donor properties. This state can lead to several reaction channels: (i) hydrolysis with Cl^- ion detachment from different positions and (ii) homolytic cleavage of C–Cl bonds to form chlorine and carbon-centred phenoxy radicals (Scheme 2).



Scheme 2.

As to the possible role of free radicals in transformation of 2,4,5-TCP and PCP, this is strongly suggested by the observation of polychlorinated dibenzodioxins (PCDD) and dibenzofurans (PCDF) among the products of direct photolysis.

The formation of these dimeric products in dilute aqueous solutions at ambient temperature is possible only as a result of recombination of chlorophenol free radicals.

3.2. Sensitized photolysis of polychlorophenols

As expected, in the absence of sensitizers, chlorophenols undergo no change under the action of visible light ($\lambda > 400$ nm), either in weakly acidic or weakly alkaline media; such transformation is observed only under aerobic conditions in the presence of a sensitizer (Fig. 7).

The rate of sensitized transformation of 2,4,5-TCP does not depend on the type of sensitizer and is proportional, as expected, to its concentration and irradiation intensity. Inhibition of the sensitized reaction by adding the singlet oxygen quenchers sodium azide or 1,4-diazobicyclo[2,2,2]-octane (DABCO) is indicative of the participation of singlet oxygen in the process.

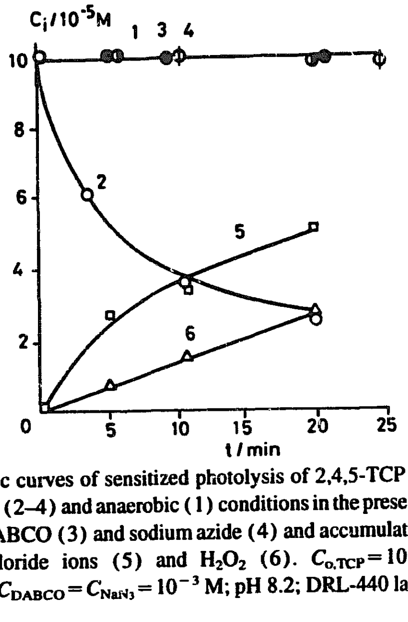


Fig. 7. Kinetic curves of sensitized photolysis of 2,4,5-TCP ($\lambda \leq 400$ nm) under aerobic (2–4) and anaerobic (1) conditions in the presence of quenching agents DABCO (3) and sodium azide (4) and accumulation of reaction products: chloride ions (5) and H_2O_2 (6). $C_{0,TCP} = 10^{-4}$ M; $C_{MB} = 5 \times 10^{-5}$ M; $C_{DABCO} = C_{NaN_3} = 10^{-3}$ M; pH 8.2; DRL-440 lamp.

The pH dependence of the sensitized photolysis rate demonstrates an insignificant contribution of the unionized form of trichlorophenols in the process (Fig. 8). The reaction is accompanied by chloride ion detachment and, unlike the direct photolysis, produces hydrogen peroxide (Figs. 7 and 8). Fig. 8 shows the ratio between the initial rates of formation of Cl^- ion and H_2O_2 and the initial rate of decomposition of 2,4,5-TCP.

To address the question of whether O_2^- radicals precede H_2O_2, an experiment was performed with the O_2^- scavenger, dichlorophenolindophenol (DCIP) [40,41]. No effect of addition of DCIP on the rate of H_2O_2 accumulation was observed, which confirms that the formation of hydrogen peroxide does not occur as a result of disproportionation of superoxide radicals. Experiments were conducted to produce O_2^- radicals via photolysis ($\lambda = 350$ nm) of sulfonated anthroquinone in the presence of ethanol as a hydrogen donor [42]. In these experiments, the concentrations of 2,4,5-TCP and hydrogen peroxide were determined. Dichlorophenolindophenol (DCIP) was used as a scavenger of O_2^- radicals. It was found that the presence of 2,4,5-trichlorophenol does not influence the rate of H_2O_2 formation in this system, and thus chlorophenol does not undergo any notable transformations. In contrast, addition of DCIP results in the inhibition of H_2O_2 formation, and the period of induction is removed by addition of superoxide dismutase, which confirms the formation of O_2^- radicals as precursors of H_2O_2 and their nonparticipation in any interaction with 2,4,5-TCP. In other words $^1O_2$ interacts with 2,4,5-TCP without intermediate free radical formation. This is confirmed also by the absence of PCDD and PCDF among the products of sensitized transformation of 2,4,5-TCP (Table 1). The oxygen-bridged compounds, 4,4′-dihydroxy-2,2,5,5-tetrachlorodiphenyl ether in particular (see Table 1), are found by GCMS among the

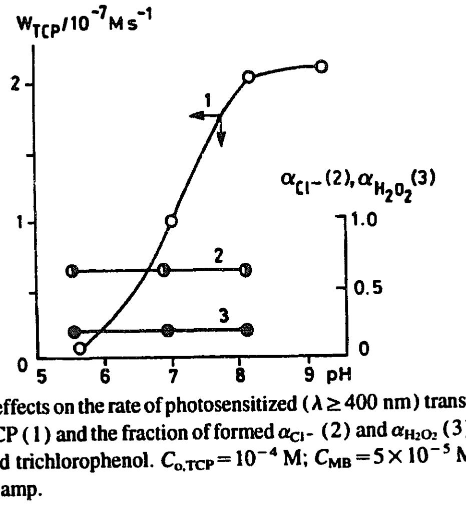


Fig. 8. pH effects on the rate of photosensitized ($\lambda \geq 400$ nm) transformation of 2,4,5-TCP (1) and the fraction of formed α_{Cl^-} (2) and $\alpha_{H_2O_2}$ (3) products of degraded trichlorophenol. $C_{0,TCP} = 10^{-4}$ M; $C_{MB} = 5 \times 10^{-5}$ M; pH 8.2; DRL-440 lamp.

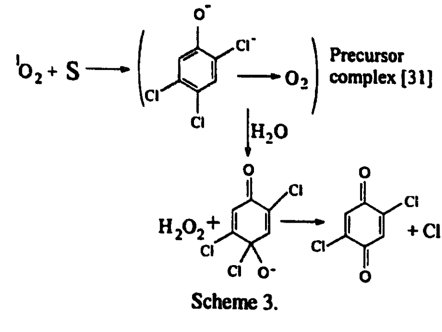
Table 1
Products of sensitized conversion of polychlorinated phenols under aerobic conditions

Compound	Sunlight pH 7, $\Delta\tau = 150$ min 2,4,5-TCP = 10 mg dm^{-3}	Lamp DRL-400($\lambda \geq 400$ nm) pH 8, 2,4,5-TCP$_0$ = 20 mg dm^{-3}	
		$\Delta\tau = 3$ min	$\Delta\tau = 60$ min
2,4,5-trichlorophenol/mg dm^{-3}	0.2	5.3	0.45
2,5-dichlorophenol	−	+	−
2,5-dichlorohydroquinone	+	−	−
2,5-dichloro-1,4-hydroquinone	−	+	+
2,5-dichloro-1,4-benzoquinone	−	+	+
2-chloro-1,4-benzoquinone	−	−	+
2,4-, 2,5-dichlorocyclopentadienes	+	−	−
5-chloro-4-cyclohexene-1-one	+	−	−
2-chlorophenol	+	−	−
4,4-dihydroxy-2,2,5,5-tetrachlorodiphenyl ether	+	+	+

dimeric products of transformation of 2,4,5-TCP. Unidentified dimeric products were also recorded by HPLC. Among the products of sensitized oxidation of 2,4,5-TCP at $\lambda \geq 400$ nm, there are no cyclopentadiene derivatives. However, we do detect 2,5-dichlorohydroquinone and its oxidation product, 2,5-dichlorobenzoquinone (see Table 1). These products do not accumulate in the course of reaction; their stationary concentration is insignificant and cannot affect much the H_2O_2 content determined in the medium by the method [33].

Dichlorobenzoquinone as a product of transformation of 2,4,5-TCP may be formed by non-radical oxidation by singlet oxygen of initial trichlorophenol with subsequent detachment of a chloride ion from position 4. Such a reaction can proceed via a charge-transfer precursor (Scheme 3).

It has been supposed [31] that the precursor complex may react by either complete one-electron transfer to give a superoxide anion radical and a phenoxy radical or to give an endoperoxide, back-reaction resulting in quenching of $^1O_2$, or a combination of these mechanisms. In our experiments no O_2^- radical forms in this reaction. By contrast, we observed hydrogen peroxide as the product of resulting two-electron transfer. The question arises about the mechanism of dichlorohydroquinone formation among the primary products of interaction of $^1O_2$ with 2,4,5-TCP. We assume that dichlorohydroquinone can be formed as a result excited-state electron transfer in the precursor complex followed by hydrolysis of 2,4,5-TCP. In this case the formation rate of chloride ion in sensitized photolysis may exceed that of hydrogen peroxide (see Fig. 8).



Scheme 3.

The simultaneous formation of dichlorohydroquinone and dichlorobenzoquinone in solution results in the appearance of the product of their mutual reaction, i.e. quinhydrone, with subsequent transformations accompanied by dimeric products different from PCDD and PCDF.

Acknowledgements

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