Photolytic degradation of all chlorophenols with polyoxometallates and H_2O_2

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Abstract

The photolytic degradation of all chlorophenols (CPs) under UV and near VIS light, in the presence of H_2O_2 (0.1 M) or polyoxometallate (POM) photocatalyst $PW_{12}O_{40}{}^{3-}$ (7×10^{-4} M) in aqueous solutions has been studied. In both cases, the initial rates of photodegradation of all substrates are comparable, following first-order kinetics. In both cases the photodecomposition of substrates correlates with the position and the number of chlorine atoms in the ring. The slowest is the fully chlorinated pentachlorophenol (PCP). It has been found that chlorine substituents in *meta* positions accelerate the photodecomposition process. Thus, in some cases the position dominates the number of Cl atoms, for instance 3,4,5-trichlorophenol > 3,4-dichlorophenol > 3-chlorophenol. Similar results for a few CPs have been reported with TiO_2 and H_2O_2. A target compound, 2,4,6-trichlorophenol, was used in order to compare the degradation mechanisms, by both H_2O_2 and $PW_{12}O_{40}{}^{3-}$. The intermediates detected were 3,5-dichlorocatechol, 2,6-dichlorobenzoquinone, dihydroxytrichloroben-zene, trihydroxydichlorobenzene and dichlorohydroquinone. The same intermediates have been reported with TiO_2. The similarity in the photodecomposition process of all CPs by three different methods, i.e. $PW_{12}O_{40}{}^{3-}$, TiO_2 or H_2O_2 further supports the notion that all three act, mainly, through the generation of OH radicals. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Chlorophenols (CPs) are common organic contaminants found in the environment of most industrialized countries. Nineteen congeners are possible, ranging from monochlorophenols (MCPs) to the fully chlorinated pentachlorophenol (PCP). CPs are toxic for a wide range of organisms, a property that accounts for many of their uses. Large quantities of higher CPs have been used in pressure treatment in the wood preservation industry. Although the last decade their use has been restricted, some of these are still produced in large quantities. Lower CPs serve as intermediates in the production of pesticides, such as those named commercially 2,4-D and 2,4,5-T [1,2].

CPs are present in drinking water as a result of chlorination of phenols, as by-products of the reaction of hypochlorite with phenolic acids, as biocides, or as degradation products of phenoxy herbicides. Those most likely to occur in drinking water as by-products of chlorination are 2-CP, 2,4-DCP and 2,4,6-TCP [3]. CPs as potential pollutants, widely distributed in the environment, have been used as model compounds in water decontamination studies.

Advanced oxidation processes (AOPs) are water remediation techniques that cause mineralization of organic pollutants through the generation of highly oxidizing reagents. Among those that use electromagnetic radiation are H_2O_2/UV, near VIS–UV light in the presence of TiO_2 and recently in the presence of polyoxometallates (POMs) [4–6]. All three methods have been quite effective in the mineralization of a great variety of organic pollutants. Various reports deal with the photodecomposition of several CPs by these three methods.

Some conflicting results exist with respect to the parameters that influence the photodecomposition process. For instance, the number and position of chlorine atoms.

In this report we have studied the photodegradation of all CPs, i.e. MCPs, dichlorophenols (DCPs), trichlorophenols (T_3CPs), tetrachlorophenols (T_4CPs) and PCP by H_2O_2/UV and near VIS–UV light in the presence of $PW_{12}O_{40}{}^{3-}$ and compare it with literature data on the decomposition of these substrates by near VIS–UV light in the presence of TiO_2. We

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report on the influence of the number and position of chlorine atoms, in the photodecomposition rate by these three methods.

We provide further support on the existence and the role of OH radicals (the sole powerful oxidant with H_2O_2 and reported to be the main oxidant with the others two methods) using OH radical trapping techniques.

Using a target compound, 2,4,6-TCP, the photodecomposition mode has been monitored through the formation and decay of several intermediates and compared with those reported in the literature.

2. Experimental

2.1. Materials

CPs were purchased from Fluka, AG (Switzerland) and Aldrich Steinheim (Germany), with purity better than 98%. H_2O_2 30% w/v and $PW_{12}O_{40}{}^{3-}$ were obtained from Panreac, Barcelona (Spain). Acetonitrile HPLC was obtained from Lab Scan, Dublin (Ireland) and gradient grade from Merck, Darmstadt (Germany) for monitoring with HPLC at $\lambda < 230$ nm. The water was purified with a Millipore Milli-Q Plus System. Extra pure argon was used for deaeration of solutions.

2.2. Analytical determination

Photolysis was performed with an Oriel 1000W Xe lamp equipped with a cool water circulating filter to absorb the near-IR radiation and a cut off filter to avoid direct photolysis of substrates. The degree of reduction of POM in photolyzed deaerated solutions was estimated spectrophotometrically by means of a HITACHI U-2000 UV–VIS spectrophotometer.

HPLC analysis was carried out using an HPLC apparatus consisted of a Waters (Milford, MA, USA) Model 600E pump associated with a Waters Model 600 gradient controller, a Rheodyne (Cotati, CA, USA) Model 7725i sample injector equipped with 20 μl sample loop, a reversed phase (RP) C_{18} analytical column by Phase Sep (25 cm × 4.6 mm i.d., 5 μm) and a Waters Model 486 tunable absorbance detector controlled by the Millenium (Waters) software. The eluent mixture was CH_3CN–H_2O (50:50 v/v), in isocratic mode, at a flow rate 1 ml/min.

Identification of intermediates was performed using an Agilent 5973N mass spectrometer. Samples were injected pulsed splitlessly into an Agilent 6890 gas chromatograph equipped with a J&W HP-5MS 5% phenyl methyl siloxane, 30 m × 0.25 mm × 0.25 μm film thickness, capillary column. Flow rate of helium 99.999% was 1 ml/min. The oven was programmed as follows: isothermal at 80 °C for 1 min, from 80 to 218 °C at 8 °C/min and held for 18 min, then from 218 to 250 °C at 10 °C/min and isothermal at 250 °C for 10 min. The electron energy was set at 70 eV, the ion source

temperature was maintained at 230 °C and the quadrupole temperature at 150 °C.

2.3. Photolysis experiment

Aqueous solutions of CPs were prepared by dissolving certain quantities of substrate and 0.1 M H_2O_2, or 7×10^{-4} M $PW_{12}O_{40}{}^{3-}$ in 0.1 M $HClO_4$. The substrate concentrations were as follows: MCPs, DCPs and T_3CPs, 10^{-3} M; T_4CPs and PCP, 10^{-5} M. The pH was 1 (0.1 M $HClO_4$) for both experiments, with H_2O_2 and $PW_{12}O_{40}{}^{3-}$, because this POM is perfectly stable at this pH value and for comparison purposes.

An amount of 4 ml of the above solution was added to an 8 ml spectrophotometric cell (1 cm path). In the case of $PW_{12}O_{40}{}^{3-}$, after 20 min of deaeration, the cell was closed with a serum cap. During photolysis the solutions were constantly stirred and the temperature kept at 20 °C. To have sufficient quantities for the identification of intermediates by GC–MS, samples of 30 ml of the 2,4,6-TCP (1×10^{-3} M) were photolyzed under the same conditions.

2.4. Analysis of the photolyzed solutions

Photolyzed solutions of CPs (4 ml) were analyzed by HPLC with UV detector. Photolyzed solution of 2,4,6-TCP (30 ml), was extracted with dichloromethane three times (30 ml each), and the organic layers were collected, dried with sodium sulfate, and evaporated to 200 μl, for the determination of the intermediates with GC–MS.

The degree of reduction of $PW_{12}O_{40}{}^{3-}$ in photolyzed deaerated solutions was calculated from the known extinction coefficient of the blue products ($e_{751\,nm} = 2 \times 10^3$ M^{-1} cm^{-1} for the one electron reduction products) [7]. The residual H_2O_2 in solution was determined by the KI titration method [8].

3. Results and discussion

3.1. Photodecomposition of CPs in the presence of H_2O_2

It is known that H_2O_2 upon illumination with approximately, $\lambda < 370$ nm, undergoes homolytic splitting into OH radicals, which cause mineralization of a great variety of pollutants [4,9]. This process is influenced by many factors such as pH, concentration of H_2O_2, wavelength and intensity of irradiation, as well as initial concentration of the substrate [10].

CPs absorb strongly from about 270 to 300 nm. Photolysis in that region, results in considerable photodecomposition of CPs [11]. To avoid direct photolysis, all experiments in the presence of H_2O_2 were carried out with $\lambda > 320$ nm. In order to have reasonable photolysis time, 0.1 M H_2O_2, was used.
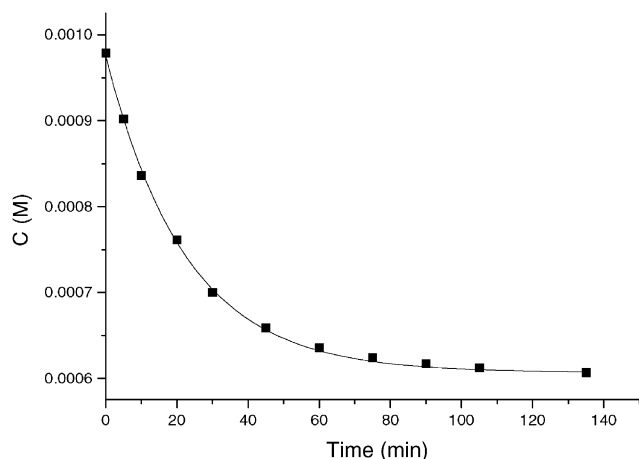
Fig. 1. Photodegradation of 2,4,6-TCP (10^{-3} M), in the presence of 10^{-1} M H_2O_2, with 320 nm cutoff filter, pH 1 ($HClO_4$) and $T \sim 20\,°C$.

Under the experimental conditions described above, effective photodegradation of all CPs takes place. Fig. 1 shows a characteristic photodecomposition of 2,4,6-TCP, upon photolysis, in the presence of H_2O_2. As with all photodecomposition processes, so far, pseudo first-order kinetics are observed with all CPs examined in this paper (Fig. 2). The rates of decomposition of CPs calculated from the first-order plots are presented in Tables 1 and 2.

3.2. Photodecomposition of CPs in the presence of $PW_{12}O_{40}^{3-}$

It has been established that $PW_{12}O_{40}^{3-}$, upon illumination with near VIS and UV light, becomes a powerful oxidant able to mineralize a great variety of organic pollutants [12].

Although the excited POM is a strong oxidant, all indication, so far, suggest that photodecomposition takes place via, mainly, OH radicals [13]. The basic photocatalytic re-
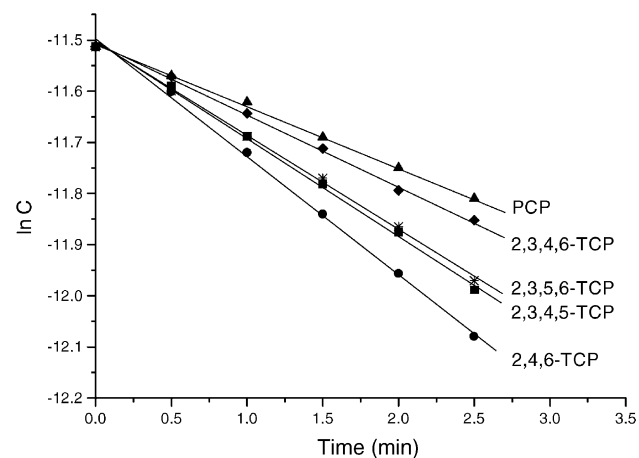
Table 1
Initial rates of degradation and reduction

Substrate[a]	Initial rate of degradation[b] $\times 10^5$ (M/min)	Initial rate of reduction[c] $\times 10^5$ (M/min)
MCPs		
3-CP	3.07	4.9
4-CP	2.23	4
2-CP	2.13	2.9
DCPs		
3,5-DCP	5.80	9
2,5-DCP	5.00	6.5
3,4-DCP	4.92	6.9
2,3-DCP	4.22	6.5
2,4-DCP	3.94	2.8
2,6-DCP	3.90	2.2
T_3CPs		
3,4,5-TCP	6.72	7.4
2,3,5-TCP	6.45	6.6
2,4,5-TCP	4.98	3.7
2,3,6-TCP	4.86	3.8
2,3,4-TCP	4.19	3.2
2,4,6-TCP	3.57	0.6

[a] Initial concentration of substrates (1×10^{-3} M) at pH 1, 320 nm cutoff filter, in both the cases.
[b] Degradation of MCPs, DCPs and T_3CPs in the presence of H_2O_2 (0.1 M).
[c] Reduction of $PW_{12}O_{40}^{3-}$ (7×10^{-4} M).

actions involving POM [14] are given below:

$$POM \underset{}{\overset{h\nu}{\rightleftharpoons}} POM^* \quad \text{(photoexcitation)} \tag{1}$$

$$POM^* + S \rightarrow POM(e^-) + S(+) \quad \text{(redox reaction)} \tag{2}$$

$$POM^* + H_2O \rightleftharpoons POM(e^-) + OH + H^+$$
$$\text{(formation of OH radicals)} \tag{3}$$

$$OH + S \rightarrow \text{hydroxylation, H abstraction,}$$
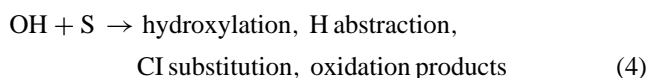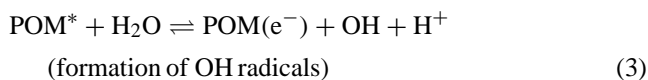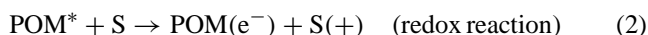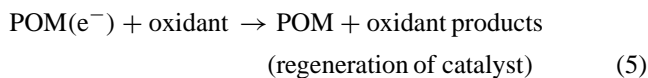$$\text{Cl substitution, oxidation products} \tag{4}$$

Table 2
Initial rates of degradation and reduction

Substrate[a]	Initial rate of degradation[b] $\times 10^5$ (M/min)	Initial rate of reduction[c] $\times 10^5$ (M/min)
2,4,6-TCP	0.23	0.8
T_4CPs		
2,3,4,5-TCP	0.19	2.1
2,3,5,6-TCP	0.18	3.6
2,3,4,6-TCP	0.14	1.5
PCP	0.12	0.33

[a] Initial concentration of substrates (1×10^{-5} M) at pH 1, 320 nm cutoff filter, in both the cases.
[b] Degradation of 2,4,6-TCP, T_4CPs and PCP in the presence of H_2O_2 (0.1 M).
[c] Reduction of $PW_{12}O_{40}^{3-}$ (7×10^{-4} M).

Fig. 2. First-order plots for the photodecomposition of PCP (10^{-5} M) and T_4CPs, in the presence of 10^{-1} M H_2O_2, pH 1 ($HClO_4$), $\lambda > 320$ nm and $T \sim 20\,°C$.

$$POM(e^-) + oxidant \rightarrow POM + oxidant\ products$$
$$(regeneration\ of\ catalyst) \qquad (5)$$

All CPs studied in this paper undergo effective photodecomposition by $PW_{12}O_{40}{}^{3-}$ in both aerated and to a certain extent, deaerated solutions.

In deaerated solutions, in which reoxidation of reduced POM does not take place, at least in the first stages of the reaction, the process is easily followed through the development of the characteristic blue color of the one-electron reduced tungstate $PW_{12}O_{40}{}^{4-}$.

It has been established elsewhere that the initial photodecomposition rate in deoxygenated solution (monitored at the development of the blue color, 750 nm, of $PW_{12}O_{40}{}^{4-}$) or in oxygenated solutions followed through the degradation of CPs are, essentially, the same [15].

Therefore, it was decided to calculate the rate of photoreactions through the easily monitored formation of the blue color of $PW_{12}O_{40}{}^{4-}$. The results together with those of H_2O_2 are tabulated in Tables 1 and 2.

3.3. The influence of the number and position of Cl atoms on the photodegradation rates of CPs by both H_2O_2 and $PW_{12}O_{40}{}^{3-}$ methods: comparison with TiO_2 literature data

It was mentioned earlier that in the photodecomposition processes, H_2O_2 acts exclusively, through the formation of OH radicals, whereas, in the case of $PW_{12}O_{40}{}^{3-}$ OH radicals have been reported to be the main oxidant.

The results of this paper support this notion and looking through the literature data for TiO_2, support the notion that the latter also acts via, mainly, the formation of OH radicals, as it will be explained below.

It should be noticed that an argument exists in the literature that hydroxylation products detected in the photodecomposition of various organic compounds might not be the result of OH radical attack, rather the hydroxylated products may originate from the hydrolysis of the cation radical produced from the direct hole (h$^+$) trapping by the substrate [16]. The results of this paper are in support of OH radical being the main oxidant for photodecompositions taking place by TiO_2, $PW_{12}O_{40}{}^{3-}$ and of course H_2O_2.

As is known, the OH group, in the phenolic ring, is *ortho* and *para* directing with activation, whereas, Cl substituents is *ortho* and *para* directing with deactivation. Thus, it is expected, the OH radical, an electrophilic reagent, in attacking CPs, to be directed to the electron rich positions and cause faster oxidation of these substrates. This seems to be the case. For instance, in MCPs when the Cl atom is *meta* to OH group, two *ortho* and *para* positions are susceptible to OH attack and 3-CP reacts faster than 2-CP and 4-CP (Table 1).

When two chlorine substituents exist in the *meta* positions of the phenolic ring, the photodegradation rate increases significantly, for both H_2O_2 and POM processes, as shown
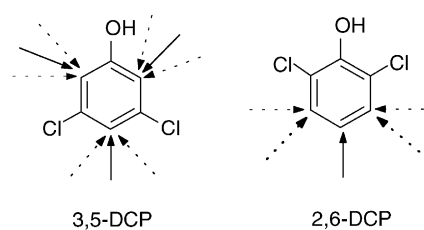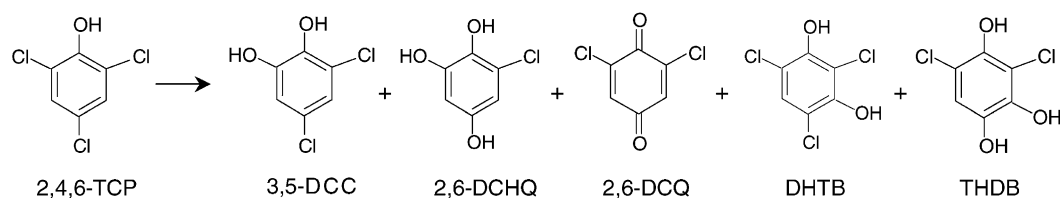

Scheme 1.

in Table 1. This can be attributed to the stronger activation of the free positions compared to MCPs. In Scheme 1, solid arrows represent the enhanced electron density imposed by the hydroxyl group, whereas the *ortho* and *para* directing effect with deactivation of chlorine atom is represented with dashed arrows. On the other hand, in 2,6-DCP the activation of the free positions is weaker compared to that of 3,5-DCP, resulting in lower photodegradation rates by both methods (Table 1). This *ortho* chlorosubstituents retardation could also be attributed to stereochemical inhibition to OH radical attack, due to the close proximity of OH and Cl groups on the aromatic ring [17] and/or to the formation of intramolecular hydrogen bonding between the OH and Cl groups in the aromatic ring [18].

Also, in the case of T_3CPs, the experimental results for both H_2O_2 and POM processes, were very similar (Table 1). The T_3CPs, 3,4,5-TCP and 2,3,5-TCP with two *meta* positions occupied by Cl atoms, have a faster rate of decomposition compared to the others with only one *meta* position occupied. For 2,4,6-TCP with two *ortho* and *para* positions occupied by Cl atoms, the lowest rate of decomposition is observed.

Table 2 shows the degradation rates of T_4CPs and PCP with H_2O_2 and the initial rates of formation of $PW_{12}O_{40}{}^{4-}$. It is reminded that in photodegradation processes of CPs in the presence of $PW_{12}O_{40}{}^{3-}$, the initial rate of formation of reduced POM is similar to the rate of decomposition of CPs. Due to the low solubility in aqueous solution of these compounds, the experiments were performed in lower concentrations level (10^{-5} M). In this case, 2,4,6-TCP was also used at the same concentration for comparison reasons. It can be seen that 2,3,4,6-TCP with two *ortho* and *para* positions occupied by Cl atoms, has the lowest rate of decomposition among T_4CPs, whereas PCP, with five Cl substituents in the phenolic ring is the slowest one.

The results, so far, suggest that the chlorine content of CPs influences the initial rate of degradation in the following way. Increase of Cl atoms in the ring blocks some favorable positions susceptible to hydroxyl attack. As a result, the rate of degradation will decrease. In addition, the electron density on the ring decreases, due to the electron withdrawing properties of Cl atoms, making the ring less favorable to electrophilic (OH) attack. As a general rule, we may say, that increase in the Cl content in PCs lowers the degradation rates. The rates depicted in Table 2 confirm the previous statement.

Scheme 2.

However, for 3-CP, 3,4-DCP and 3,4,5-TCP, the inverse is noticed: 3,4,5-TCP > 3,4-DCP > 3-CP, i.e. the position of chlorine atoms in the phenolic ring dominates the effect of the number of chlorine substituents. The latter observation tends to suggest that in the case of MCPs, DCPs and T$_3$CPs, the position rather than the number of Cl atoms dominates the order of initial rates of degradation.

Similar results have been noticed among several MCPs, DCPs and T$_3$CPs photodecomposed by TiO$_2$ [19]. In this case, in agreement with the results of this report, di-*meta*-substituted CPs degraded faster, while 2,4,6-TCP was more resistant to photocatalytic degradation.

Experiments curried out with Fenton's reagent showed that the order of degradation among MCPs was 3-CP > 4-CP > 2-CP indicating that *meta*-substituted CPs degrade faster than *ortho* and *para* [17,20], in agreement, overall, with our results.

Photolysis by plain UV and UV in the presence of H$_2$O$_2$, of 2-CP, 2,4-DCP and 2,4,6-TCP, showed that the addition of H$_2$O$_2$ hardly affected the rate of degradation of 2,4,6-TCP, indicating, again, the resistance of the ring to OH radical attack when all *ortho* and *para* positions are occupied by Cl atoms [21]. Another study, performed in pH close to 1 with H$_2$O$_2$/UV, with 2-CP, 2,4-DCP and 2,4,6-TCP showed the latter to be the slowest [22].

It should be mentioned that two factors affect significantly the rate of photodegradation of CPs, wavelength and pH. In some reports direct photolysis of CPs goes along with photolysis through added catalysts, or H$_2$O$_2$ and the results are confusing. Keeping pH 1 ensures the existence of CPs in molecular form. In higher pH, some CPs are ionized and their photodegradation rates are significantly affected [22–24].

3.4. Intermediates detected by H$_2$O$_2$ and PW$_{12}$O$_{40}{}^{3-}$ methods: comparison with TiO$_2$ literature data

A detailed study of the photodegradation of 2,4,6-TCP by H$_2$O$_2$ reveals the formation and decay of several intermediates shown in Scheme 2. The intermediates identified were 2,6-dichlorohydroquinone (2,6-DCHQ), 2,6-dichlorobenzoquinone (2,6-DCQ), 3,5-dichlorocatechol (3,5-DCC), a dihydroxytrichlorobenzene (DHTB) and a trihydroxydichlorobenzene (THDB). Identification was performed with GC–MS by comparison using Willey database. A high quality factor (over 90%) was obtained for all intermediates except trihydroxydichlorobenzene which identified by interpretation of its mass spectrum according to its fragmentation pattern. The formation and decay of intermediates involved in the process, are shown Fig. 3. The same intermediates were identified in the photodecomposition of 2,4,6-TCP in the presence of PW$_{12}$O$_{40}{}^{3-}$ [15].

As mentioned earlier, the high oxidizing ability, leading to the decomposition of various pollutants, is exclusively

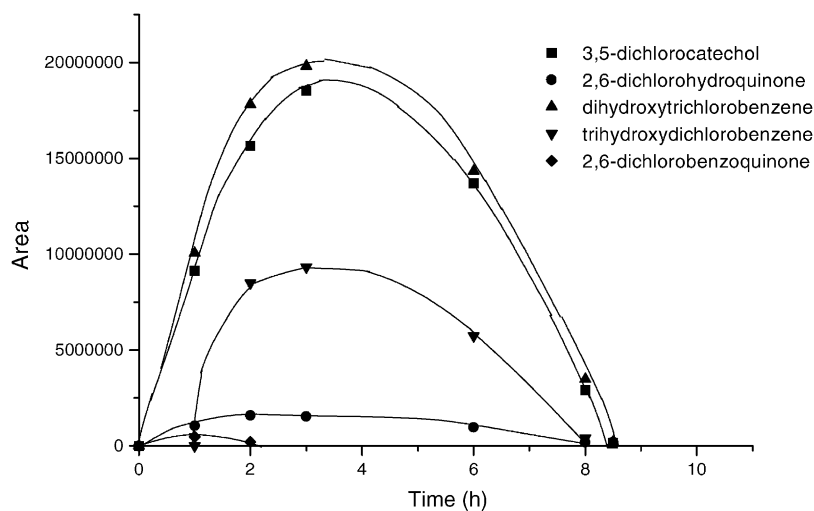
Fig. 3. Formation and decay of intermediates identified upon photolysis of aqueous solution of 2,4,6-TCP (10^{-3} M), in the presence of 0.1 M H$_2$O$_2$, pH 1 (HClO$_4$), $\lambda > 320$ nm and $T \sim 20\,^\circ$C.

due to OH radicals formed during H_2O_2/UV photolysis. In addition, photodecomposition of pollutants in the presence of POM has been attributed, mainly, to the formation of OH radicals. It is therefore expected that these two methods will give similar overall results, concerning the degradation mode of target compound, as is indeed the case.

The same intermediate products have been reported with TiO_2 [19]. This provides further evidence that TiO_2 acts, also, mainly, through OH radicals. Key reactions involved in the photodecomposition of 2,4,6-TCP by these three methods (i.e. H_2O_2, $PW_{12}O_{40}^{3-}$ and TiO_2) are: (a) hydroxylation of the aromatic ring, (b) substitution of chlorine by OH and (c) oxidation of chlorinated hydroquinone to the corresponding quinone.

3.5. The effect of OH radicals trapping reagents on photodegradation rates of CPs in the presence of $PW_{12}O_{40}^{3-}$

Even though there are still arguments on OH radical versus direct reaction with the substrate, in POM/UV–near VIS process, there is enough evidence in favor of the former. The experimental data, so far, suggesting the OH radical formation, are given below:

(a) OH radicals have been detected upon photolysis of POM by ESR trapping techniques [25,26].
(b) Hydroxylation intermediates have been identified in photolysis of CPs and other aromatic compounds [27,28]. The same mode of reaction is followed by both H_2O_2/UV and TiO_2 processes known to react through OH radicals [29,30].
(c) The photodecomposition of trichloroacetic acid, which lacks α-hydrogen atoms, is much slower than that of chloroacetic acid, in the presence of POM [31]. As is well established OH radicals attack, preferentially, α-hydrogen atoms.

In the framework of this study, two series of experiments have been performed, with OH radicals trapping reagent, in the presence of both POM or H_2O_2. The 2,3,5-TCP has been selected as model substrate, due to its high rate of photodecomposition. Isopropanol, with α-hydrogen atoms, served as OH radicals trapping reagent [13]. The results are presented in Table 3. It can be seen that the percentage of photodecomposition of 2,3,5-TCP is reduced in the

presence of isopropanol, to 13 and 4%, for POM and H_2O_2 processes, respectively. This further supports the argument that photodecomposition of organic compounds in the presence of POM ($PW_{12}O_{40}^{3-}$) is mainly, due to OH radicals. The slightly higher values obtained in the presence of POM relative to H_2O_2 (Table 3) can be attributed to the direct reaction of the excited POM with substrate.

Acknowledgements

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Table 3
Degradation of 2,3,5-TCP in the presence or absence of OH radicals trapping reagent in 20 min 2,3,5-TCP

2,3,5-TCP (5×10^{-4} M)	+	+	+	+	+	+	+
$PW_{12}O_{40}^{3-}$ (7×10^{-4} M)				+	+		
H_2O_2 (10^{-1} M)						+	+
Isopropanol (10^{-2} M)		+		+			
Isopropanol (1 M)			+			+	
Degradation (%)	1.5	1.5	1.5	13	86	4	62

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