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Photocatalytic degradation of lindane by polyoxometalates: Intermediates and mechanistic aspects

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ABSTRACT

The photocatalytic degradation of lindane (γ-1,2,3,4,5,6-hexachlorocyclohexane) has been studied in the presence of the polyoxometalate $PW_{12}O_{40}^{3-}$ in aqueous solutions. Lindane is fully decomposed to CO_2, Cl^- and H_2O, while a great variety of intermediates has been detected using GC–MS, including aromatic compounds (dichlorophenol, trichlorophenols, tetrachlorophenol, hexachlorobenzene, di- and trichloro-benzenodiol), non-aromatic cyclic compounds (penta-, tetrachlorocyclohexene, heptachlorocyclohexane), aliphatic compounds (tetrachloroethane) and condensation products (polychlorinated biphenyls). The number and nature of the intermediates implies that the mechanism of decomposition of lindane is based on both oxidative and reductive processes. Common intermediates have been reported during photolysis of lindane in the presence of titanium dioxide. A similar overall mechanism of polyoxometalates and TiO_2 photocatalysis through the formation of common reactive species is suggested.

1. Introduction

Water detoxification has become an environmental issue of ever increasing importance. In addition to conventional technologies used for purification of water, a new type of treatment process, commonly referred as advanced oxidation processes (AOPs), is emerging. AOPs are increasingly being considered as alternatives to more conventional technologies because they destroy hazardous organic compounds rather than transferring them to other media. AOPs are generally characterized by their ability to generate hydroxyl radicals, some examples being UV light in the presence of hydrogen peroxide or ozone and UV–near-visible light in the presence of TiO_2 [1–3].

Recently the photocatalytic mineralization of a great variety of chemicals has been demonstrated using polyoxometalates (POM), providing an interesting route to the destruction of toxic and hazardous pollutants even in the ppb or few ppm levels [4–8]. POM are acid condensation products, mainly of molybdenum and tungsten [9–11] that become powerful oxidizing reagents [12] upon excitation with near-visible and UV light, capable of destroying a great variety of pollutants in the aquatic environment [4–8]. POM are at least as effective as the widely publicized TiO_2, representing a similar photocatalytic performance in terms of the overall mechanism, the intermediate species involved and the final degradation products (i.e., CO_2, H_2O and inorganic anions) [13]. The above method has been applied to many organic pollutants, for example phenol, chlorophenols and chloroacetic acids [5,6,14], diversified pesticides [15], insecticides such as lindane [4] and fenitrothion [16], herbicides such as atrazine [17], bentazone, etc. [18]. In all cases final degradation products were CO_2, H_2O and inorganic anions, with the exception of atrazine, which is degraded into the less toxic cyanuric acid.

Lindane (1,2,3,4,5,6-hexachlorocyclohexane; predominately γ-isomer) is an organochlorine insecticide which has been used on a wide range of soil-dwelling and plant-eating insects [19]. It has been found in groundwater samples, as well as in the marine environment where organisms tend to concentrate this highly lipophilic compound in the fatty tissues [20]. Due to its high toxicity, it is classified as Restricted Use Pesticide purchased only to certified applicators, it is no longer manufactured in the US and most of its uses, i.e., in agriculture and in the diary industry have been canceled by EPA.

Despite its persistence, lindane biodegradation has been reported under various aerobic and anaerobic conditions [21]. Unfortunately, the process proceeds rather slowly [22]. Alternatively, lindane can be converted by decomposition via sonochemical induced destruction [23]. Removal of lindane and its isomers can also be established by dehydrochlorination either by thermal or base-assisted processes, but these can form toxic trichlorobenzenes (TCBs) [24,25].

Another possible degradation method for hexachlorocyclohexanes (HCH) is the catalytic reduction over metal catalysts. The main disadvantage in this case is the partially decomposition of lindane to the toxic benzene [26].

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In this paper, we report a detailed examination of the intermediates formed during the photocatalytic degradation of lindane in the presence of POM, of which the complete mineralization to CO_2 and Cl^- has already been reported [4]. Lindane was selected as a target compound in this study, not only due to its high environmental impact but also due to its well-studied photodegradation in the presence of TiO_2, which indicated the formation of a plethora of intermediates through both oxidative and reductive pathways. The aim of this work was focused on (i) the careful control of all transformation steps of the process, (ii) the definition of the photodegradation mechanism in the presence of POM, comprising both oxidative and reductive pathways and (iii) comparison with TiO_2 literature data, in order to define possible similarities of POM and TiO_2 on the degradation mechanism.

2. Experimental

2.1. Materials

$H_3PW_{12}O_{40}$, dichloromethane 99.8% and sodium sulfate were obtained from Panreac (Barcelona, Spain). Lindane 99.5% was purchased from Dr. Ehrenstorfer (Augsburg, Germany) and hexachlorobenzene 99.5% from Riedel de Haën (Seeize, Germany). Analytical reagent grade perchloric acid ($HClO_4$ 70%) was product of Riedel de Haën (Seeize, Germany). Aqueous solution containing lindane at 2.4×10^{-5} M were prepared by stirring the solid in water for 10 h followed by filtration to remove any undissolved substrate. Water was purified with a Millipore Milli-Q Plus System and extra pure dioxygen was used for oxygenation of solutions.

2.2. Instrumentation

GC–MS analysis was performed using an Agilent 6890 Series gas chromatograph interfaced to an Agilent 5973 mass selective detector (Wilmington, DE, USA). Data acquisition, processing and instrument control were performed by the Agilent MSD ChemStation software. The analytical column was a HP-5MS (5% diphenyl and 95% dimethylsiloxan) capillary column, 30 m × 0.25 mm i.d., 0.25 mm film thickness. A split-splitless injector was used in pulsed splitless mode. The injector temperature was 210 °C and the injection volume 2.0 μl. When concentrated extracts were analyzed for intermediates identification, the mass spectrometer detector was set to be off at the time of lindane elution, to avoid filament damage. Non-concentrated extracts were also analyzed for monitoring lindane. In that case the mass spectrometer detector was set to be on during sample analysis. Flow rate of helium was 1 ml/min. The oven was programmed as follows: isothermal at 50 °C for 4 min, from 50 to 150 °C at 5 °C/min, then from 150 to 230 °C at 10 °C/min and held for 15 min. The electron energy was set at 70 eV, the ion source temperature was maintained at 230 °C and the quadrapole temperature at 150 °C.

2.3. Photolysis experiments

Photolysis experiments were performed with Oriel 1000 W Xe arc lamp (Stratford, CT, USA), equipped with a cool water circulating filter to absorb the near IR radiation. This lamp gives a flat response from ca. 320 to 750 nm corresponding to irradiance at 0.5 m, ca. 200 mW m^{-2} nm^{-1} according to the supplier. The incident radiation was reduced to about 40% with a slit diaphragm in order to obtain reasonable photolysis times. A 320 nm cut off filter was used to avoid direct photolysis of substrate.

Aqueous solution of lindane (2.4×10^{-5} M) in the presence of $PW_{12}O_{40}{}^{3-}$ (7×10^{-4} M) was adjusted to pH 1 using perchloric acid, because this POM is perfectly stable at this pH value. An amount of 4 ml of the above solution was added to an 8 ml spectrophotometric cell (1 cm path). After 20 min of oxygenation, the cell was closed with a serum cap. For identification of intermediates products 60 ml of the above solution were added to a cell and after 30 min of oxygenation was closed with an airtight cap. Photolysis was performed at 20 °C under constant stirring.

2.4. Analysis of the photolyzed solutions

When the GC–MS was used for the identification of the intermediate products of lindane, the photolyzed solution of lindane was extracted with dichloromethane three times (60 ml each), and the organic layers were combined, dried over sodium sulfate, concentrated in a rotary evaporator to ~1 ml and evaporated under a gentle stream of nitrogen to dryness. The residue was redissolved in 200 μl of dichloromethane for GC–MS analysis. For the construction of the lindane disappearance curve, photolyzed solutions of lindane (4 ml) after being extracted and dried as above, were concentrated and adjusted to a final volume of 4 ml dichloromethane and injected to the GC–MS.

3. Results

3.1. Photocatalytic degradation of lindane in the presence of polyoxometalates

Photocatalytic degradation of aqueous, dioxygen saturated solutions of lindane (2.4×10^{-5} M) took place effectively in the presence of $PW_{12}O_{40}{}^{3-}$ (7×10^{-4} M). Irradiation was performed at $\lambda > 320$ nm to avoid direct photolysis of substrate. The disappearance of lindane (Fig. 1) was monitored by GC-MS analysis of extracted solutions at various photolysis intervals. Lindane shows a chromatographic peak at $t_R = 29.31$ min (Table 1) which, under the experimental conditions used, disappeared after about 3 h of photolysis, whereas complete mineralization to CO_2 and Cl^- required a much longer time (ca. 10 h) [6]. When the same experiment was performed in the absence of catalyst, lindane showed high stability for more than 5 h of illumination.

3.2. Identification of Intermediates

A detailed study of the photodegradation of lindane (I) (Scheme 1) with POM reveals the formation of numerous

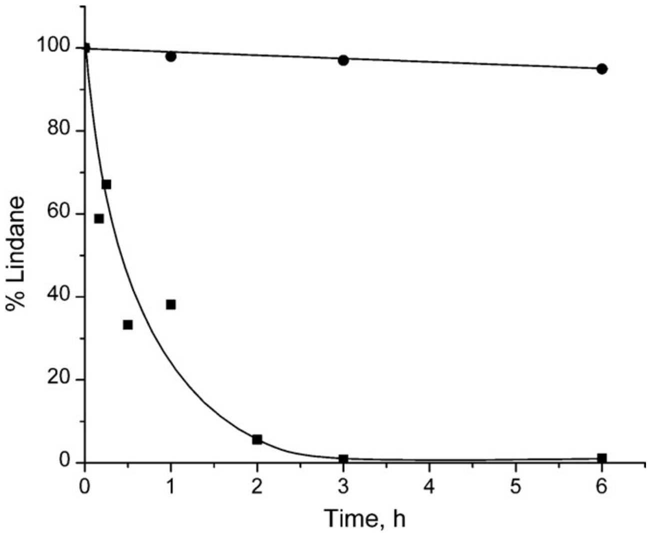


Fig. 1. Photodegradation of oxygenated aqueous solution of lindane (2.4×10^{-5} M) in the absence (●) and presence (■) of $H_3PW_{12}O_{40}$ (7×10^{-4} M), at pH 1 ($HClO_4$ 0.1 M).

Table 1
Intermediates with their retention time and spectral characteristics.

Intermediates	t_R (min)	M^+	*m*/*z*
Lindane (I) (target compound)	29.31	290	219, 183, 111
1,1,2,2-Tetrachloroethane (XVII)	7.52	166	131, 95, 83, 61
2,4-Dichlorophenol (VII)	16.75	162	135, 126, 98, 63
4,5-Dichloro-1,2-benzenodiol (XIII)	20.69	178	132, 115, 97, 51
2,4,5-Trichlorophenol (X)	21.22	196	160, 132, 97, 62
4,6-Dichloro-1,3-benzenodiol (XII)	21.32	178	149, 115, 86, 51
2,3,6-Trichlorophenol (VIII)	21.76	196	160, 132, 97, 62
2,3,5-Trichlorophenol (IX)	23.31	196	160, 132, 97, 62
2,3,4,5,-Tetrachlorocyclohexene (IV)	23.63	218	183, 147, 122, 111
2,3,4,5,6-Pentachlorocyclohexene (III)	23.68	252	219, 181, 146, 111
2,3,4,6-Tetrachlorophenol (XI)	25.80	230	194, 168, 131, 96
3,4,6-Trichloro-1,2-benzenediol (XIV)	25.89	212	178, 148, 113, 85
Hexachlorobenzene (V)	28.37	282	249, 214, 177, 142
1,1,2,3,4,5,6-Heptachlorocyclohexane (II)	30.36	322	289, 253, 217, 180
Tetrachloro-biphenyl (XV)	30.82	290	220, 185, 150, 110
Tetrachloro-biphenyl (XV)	31.39	290	255, 220, 184, 150
Hexachloro-biphenyl (XVI)	35.68	358	290, 218, 181, 145

species. Several chromatographic peaks not present in the non-irradiated solution appeared in the photolyzed one. The identification of the species detected was performed on the basis of comparison with mass spectra libraries HP Pest and Wiley 275, authentic standards when they were available, literature data and EI fragmentation patterns. For all library matched species the degree of match was mostly more than 95%. The intermediates together with their retention times and spectral characteristics are given in Table 1. They are compiled in the following categories: aromatic compounds (chlorophenols, chlorodiols and hexachlorobenzene), non-aromatic cyclic compounds (chlorocyclohexenes, heptachlorocyclohexane), aliphatic compounds (tetrachloroethane) and condensation products (polychlorinated biphenyls). The formation of all intermediates is followed by their decay, during the photocatalytic process, coming finally to total photodecomposition to CO_2 and HCl [6].

In more details, among the aromatic intermediates identified were chlorophenols, specifically 2,4-dichlorophenol (VII), three isomers of trichlorophenol (2,3,6-trichlorophenol (VIII), 2,4,5-trichlorophenol (X), 2,3,5-trichlorophenol (IX)) and 2,3,4,6-tetrachlorophenol (XI). Their formation and decay with photolysis time is depicted in Fig. 2A. There were also identified two benzenediols-dichloro (1,3-benzenediol 4,6-dichloro (XII), 1,2-benzenediol 4,5-dichloro (XIII)) and 1,2-benzenediol 3,4,6-trichloro (XIV), see Fig. 2B. Hexachlorobenzene (V) was also formed and decayed, Fig. 2C. It can be seen that the highest concentration of the aromatic intermediates is formed after 0.5–2 h of photolysis.

The non-aromatic cyclic intermediates identified were 2,3,4,5,6-pentachlorocyclohexene (III), 2,3,4,5-tetrachlorocyclohexene (IV) and 1,1,2,3,4,5,6-heptachlorocyclohexane (II). The formation and decay of II and III are shown in Fig. 2C, with a higher concentration formed after 2 h and 15 min of photolysis, respectively. The IV was only identified at the 1-h photolyzed solution.

The only linear compound that could be identified was 1,1,2,2-tetrachloroethane (XVII), after 2 h of photolysis. The formation and decay of this compound is also shown in Fig. 2C.

Furthermore, condensation products are being formed, i.e., two polychlorinated biphenyls with two (XV) and three chlorine atoms (XVI) to each ring. These products were detected from the beginning of photolysis. These by-products can be easily recognized as they are eluted at long retention times and they are well separated from the other degradation intermediates. From comparison of the spectra with Wiley database, it is possible to extract data on the molecular structure of the condensation products, e.g., the number of Cl atoms. However, without comparison with standards, the mass spectra of XV and XVI do not give further information about the position of Cl atoms in the two aromatic rings. The formation and decay of these intermediates, at various photolysis intervals, is shown in Fig. 2D.

4. Discussion

Absorption of light by POM ($\varepsilon \sim 10^4\,M^{-1}\,cm^{-1}$) at the oxygen to metal charge-transfer (O → M CT) band below 400 nm, enhances their oxidizing ability (~3 eV), and makes them powerful oxidizing reagent able to oxidize a great variety of pollutants in the aquatic environment through a hole–electron mechanism similar to semiconductor photocatalysis. Thus continuous photolysis in the presence of POM results in complete mineralization of substrates with final products CO_2, H_2O and inorganic ions [13].

In most of the proposed mechanisms concerning the photocatalytic degradation of organic pollutants (S), in the presence of POM, the oxidation is supposed to be performed by highly oxidizing $^{\bullet}OH$ radicals produced indirectly [27], through the reaction of excited POM (POM*) with water. The overall reactions that take place in the photocatalytic circle in the presence of oxygen are:

$$\mathrm{POM} \xrightarrow{h\nu} \mathrm{POM}^* \quad \text{i.e.,} \quad \mathrm{POM}\ (h^+ + e^-) \tag{1}$$

$$\mathrm{POM}(h^+ + e^-) + H_2O \rightarrow \mathrm{POM}(e^-) + {}^{\bullet}OH + H^+ \tag{2}$$

$$\begin{aligned} &{}^{\bullet}OH + S \rightarrow \text{oxidation products} \\ &\quad \rightarrow\rightarrow\rightarrow CO_2, H_2O \text{ and inorganic ions} \end{aligned} \tag{3}$$

$$\begin{aligned} &\mathrm{POM}(h^+ + e^-) + S \rightarrow \mathrm{POM}(e^-) + S^+ \\ &\quad \rightarrow\rightarrow\rightarrow CO_2, H_2O \text{ and inorganic ions} \end{aligned} \tag{4}$$

Dioxygen is a very effective oxidant for reduced POM [28–30], thus its main action is the regeneration of the catalyst.

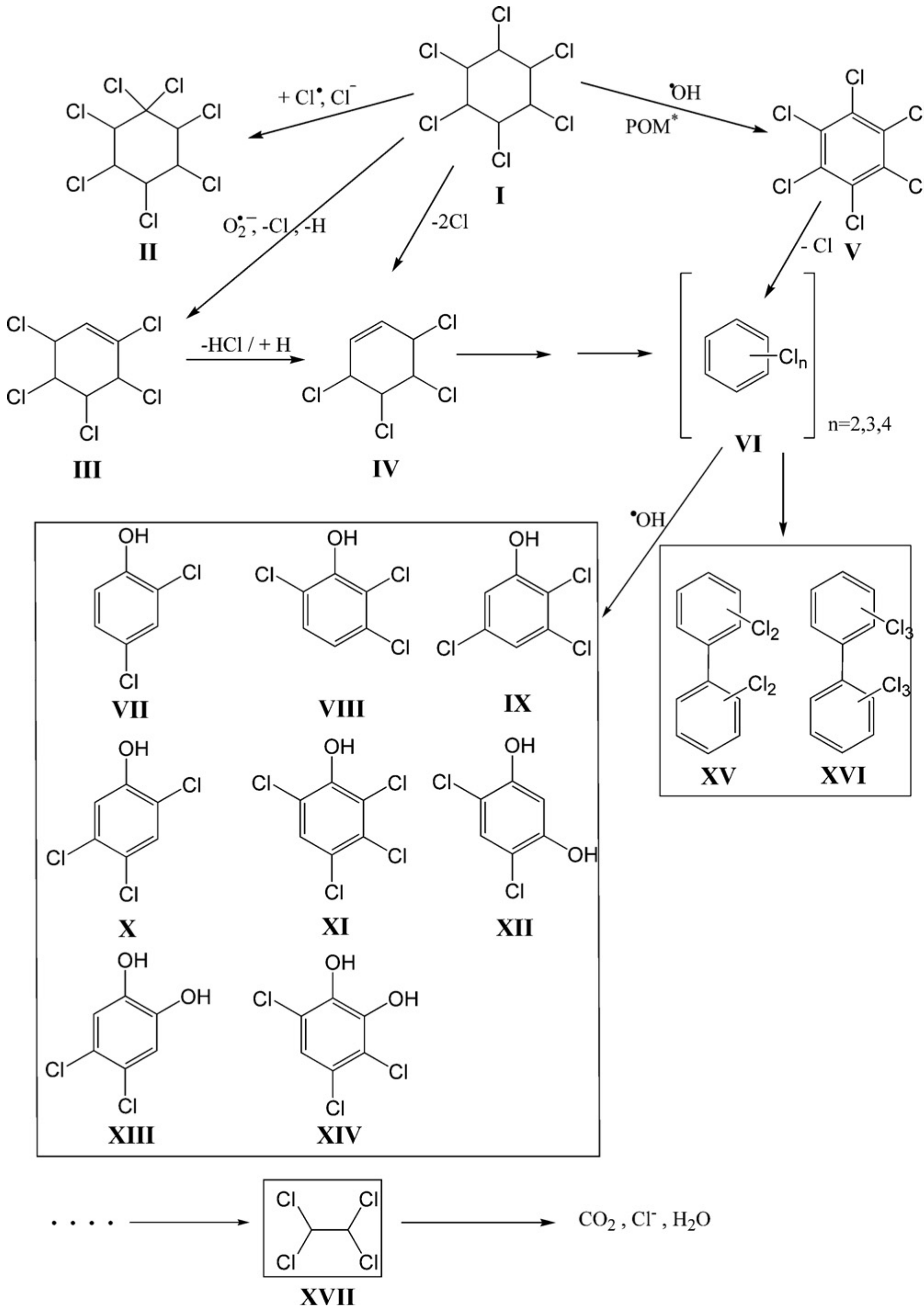
$$\mathrm{POM}(e^-) + O_2 \rightarrow \mathrm{POM} + O_2^{\bullet -} \tag{5}$$

This superoxide radical anion $O_2^{\bullet -}$ ($H^+ + O_2^{\bullet -} \leftrightarrow HO_2^{\bullet}$ $pK_a = 4.8$) [31] may participate further in oxidative processes [5].

$$O_2^{\bullet -}/HO_2^{\bullet} + S \rightarrow \text{oxidation products} \tag{6}$$

as well as reductive processes [32].

Thus, upon photolysis of an aqueous solution of POM both oxidative and reductive species are formed. The oxidative species are $^{\bullet}OH$ radicals, the excited POM and the superoxide radical anions, while the reductive species are reduced POM, POM (e^-), and the superoxide radical anions. It should be noticed that POM, for example $H_3PW_{12}O_{40}$, being at their highest oxidation state (all tungsten are W^{6+}) participate in the photoredox process, at the beginning, exclusively as oxidant.



Scheme 1. Proposed pathways for the photocatalytic degradation of lindane by $H_3PW_{12}O_{40}$.

The detailed study of the photocatalytic degradation of lindane in the presence of POM reveals the formation of a great variety of intermediates prior to mineralization, suggesting a complex mechanism of degradation (Scheme 1).

Fig. 2(A–C) shows that too many diversified intermediates appear, with the exception of 1,1,2,2-tetrachloroethane (XVII), right from the beginning of photolysis. However, their peak appearance in the formation and decay curves varies considerably.

For instance, most of the intermediates start to form from the first minute of photolysis, as mentioned, and last for about 1 h. However, for what is worth, 2,3,6-triclorophenol (VIII) and 2,3,5-trichlorophenol (IX) appear to be resilient to photocatalytic decomposition being present in the photolyzed solution for about 3 h. Heptachlorocyclohexane (II) is also present in the photolyzed solution and lasts about 3 h. This, however, is reasonable since the species that originates from, i.e., lindane (I) seem to disappear at about that time. Polychlorinated biphenyls also start to form from the beginning of photolysis. They last, though, to about 6 h, whereas one of them (hexachloro-biphenyl, XVI), persists up to 12 h of photolysis, i.e., long after all intermediates have disappeared. As shown earlier [4] CO_2 and Cl^- build up during the photocatalytic process and present the final disintegrating products of lindane (I).

It appears, then, that too many processes, i.e., chlorination, dechlorination, hydrogenation, dehydrogenation, dimerization, etc. take place at about the same time, right from the beginning of photocatalytic process.

We will attempt, below, to provide reasonable mechanistic aspects that lead to the formation of the intermediates identified in

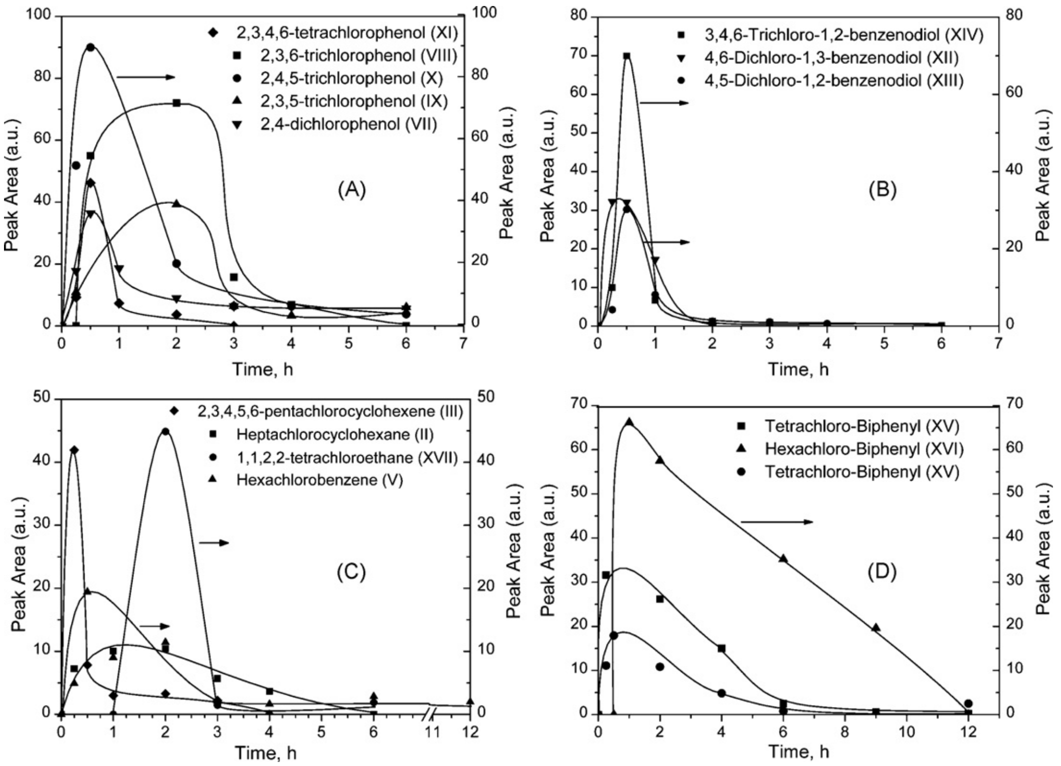


Fig. 2. Formation and decay of (A) chlorophenols, (B) di- and trichloro-benzenodiols, (C) heptachlorocyclohexane, hexachlorobenzene, pentachlorocyclohexene, tetrachloroethane and (D) polychlorinated biphenyls upon photolysis of aqueous solution of lindane (2.4×10^{-5} M) in the presence of $H_3PW_{12}O_{40}$ (7×10^{-4} M), at pH 1 ($HClO_4$ 0.1 M).

the study. Firstly, chlorine radicals must form either from homolytic scissions of lindane (I) and their chlorinated products or oxidation of chloride ions by hole trapping or through $^\bullet$OH radicals [33]. Superoxide radicals ($O_2^{\bullet-}$) are known to form in photolyzed oxygenated aqueous POM solutions (reaction (5)). The existence of H atoms can be attributed to the known reaction

$$\mathrm{POM(e^-)} + \mathrm{H^+} \leftrightarrow \mathrm{POM} + 1/2\mathrm{H_2} \qquad (7)$$

and quite reasonably through the knocking out of H atoms from “aliphatic” and aromatic rings during the photocatalytic process via attacks by excited POM* and/or Cl atoms [13].

Thus, chlorine atoms must attack lindane (I) to form heptachlorocyclohexane (II) and this process seems to last to the point where all lindane (I) has decomposed, about 3 h, as mentioned earlier.

Alternatively, heptachlorocyclohexane (II) can be produced by the addition of chloride ion to the lindane radical cation. This cation could be formed during photolysis of lindane aqueous solution with POM through oxidation directly by POM ($h^+ + e^-$) or indirectly via attack of $^\bullet$OH radical. A similar explanation has been reported by Chen et al. [34] on the formation of 2,4,6-trichlorophenol as Cl adduct upon photolysis of 2,4-dichlorophenol in the presence of POM/TiO_2 photocatalyst. Guillard et al. [35] identified the same intermediate during photolysis of aqueous solution of lindane with TiO_2. The formation of CCl_2 groups has also been observed in 1,1,2,2-tetrachloroethane (XVII), an intermediate product detected upon photolysis of POM/lindane. This appeared after 1 h of photolysis by which time breaking of cyclic intermediates has taken place.

The formation of 2,3,4,5,6-pentachlorocyclohexene (III) directly from lindane can be attributed to the dehalogenation of lindane by superoxide radical anions. The latter have been reported to dehalogenate aliphatic halocarbon substrates to the corresponding alkenes via a reductive pathway [32]. The alternative formation of pentachlorocyclohexene (III) by the known mechanism involving alkaline hydrolysis followed by rapid dehydration [36] must be excluded given our acidic conditions. Zaleska et al. [37] reported the formation of pentachlorocyclohexene (III) as by-product of lindane with TiO_2 in the form of powdered anatase, rutile and supported on glass hollow microspheres as well. The same intermediate was detected in TiO_2 photocatalysis by Guillard et al. [35] and Vidal [38]. It was also identified as intermediate product of lindane, due to temperature effect under subcritical conditions without the use of catalysts or other additive, by Kubatova et al. [39].

There are two possible pathways for the formation of 2,3,4,5-tetrachlorocyclohexene (IV), either from pentachlorocyclohexene (III) or directly from lindane through reductive dehalogenation by superoxide radical anions, according to the above. Guillard et al. [35] also found tetrachlorocyclohexene during photocatalysis of lindane with TiO_2. This intermediate makes a brief appearance after 60 min of photolysis.

Chlorobenzenes (VI) could be formed by further Cl elimination from 2,3,4,5,6-pentachlorocyclohexene (III), 2,3,3,5-tetrachlorocyclohexene (IV) [39], or hexachlorobenzene (V) through reductive dechlorination [40], resulting in less substituted chlorobenzenes. Dechlorination of hexachlorobenzene by direct electron transfer and/or hydrogen atom addition is proposed as the likely mechanism of hexachlorobenzene degradation on alumina nanoparticles [41]. Trichlorobenzenes are also known to be formed upon photolysis of a lindane/TiO_2 solution [37]. Although chlorobenzenes besides hexachlorobenzene were not directly detected in our case, their presence was indirectly suggested by the formation of their hydroxylation products (chlorophenols) and dimerization products (polychlorinated biphenyls). The latter procedure of dimerization was also reported in the case of chlorophenols as substrates, which were subjected to reductive dechlorination (elimination of one Cl atom) upon photolysis in the presence of TiO_2 to result in the corresponding phenyl radical which was finally converted to dimerization products of one Cl atom less in each ring compared to the parent substrate [34,42]. In an analogous way, the formation of polychlorinated biphenyls with two and three Cl atoms to each ring could be attributed to the reductive dechlorination of tri- and tetrachlorobenzenes, respectively.

Reaction of hydroxyl radicals with organic compounds is known to include both addition to the aromatic or double bond and H abstraction. Thus, the electrophilic hydroxyl radicals abstract H atoms from lindane gradually forming the aromatic hexachlorobenzene (V). Guo et al. [43] have also identified the same intermediate upon photolysis of lindane in a POM/SiO_2 microporous slurry in aqueous solutions, attributing its formation to the action of hydroxyl radicals. This intermediate is known to be further degraded and finally mineralized to CO_2, H_2O and Cl^- upon extended illumination in the presence of POM [6].

Chlorophenols are the oxidized derivatives of chlorobenzenes via attack of hydroxyl radicals on the aromatic ring, substituting Cl or H atoms. They could also be produced from attack of Cl on a less substituted chlorophenol, as reported in TiO_2 photocatalysis [34]. Chlorophenols are known to form chloro benzenediols as byproducts in POM [14] and TiO_2 photocatalysis [34] as shown in Scheme 1.

5. Conclusions

The photocatalytic degradation of lindane in the presence of POM leads to a plethora of intermediate products. Their great number serves as a useful matching tool in order to compare POM and TiO_2 photocatalysis. In both POM and TiO_2 photocatalysis, the photodegradation of lindane proceeds via processes that comprise both oxidative and reductive pathways, i.e., chlorination, dechlorination, hydroxylation, hydrogenation, dehydrogenation, etc. finally leading to breaking of carbon–carbon bonds and mineralization products, i.e., CO_2, H_2O and Cl^-.

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