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Photochemical behaviour of triclosan in aqueous solutions: Kinetic and analytical studies

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Abstract

The mechanism of the direct photolysis of the anti-microbial triclosan in aqueous solutions was investigated by using steady state and laser flash photolysis. Quantum yields were determined for the disappearance of triclosan and formation of chloride anions in steady state irradiations in the absence and in the presence of oxygen as well as a function of pH. The photoreactivity was found to be efficient with the anionic form and in the absence of oxygen. Following laser flash photolysis (226 nm), three transients were found (triclosan triplet state, solvated electron and phenoxyl radical). Several primary and secondary stable photoproducts were elucidated by means of LC/MS/MS data. They were found to arise from four main photochemical processes: isomerisation, cyclization (leading to the formation of dioxin derivatives), dimerisation of the phenolic moiety and hydrolysis. The ionic chromatography showed that the loss of chloride anion in triclosan phototransformation represents an important degradation pathway. The formation of oligomeric products was also observed for prolonged irradiation time. A detailed mechanism for the formation of the primary products is proposed and discussed. The very important photocyclization reaction is more likely involving the triplet state pathway and the homolytic dissociation of the ether bridge occurs from the singlet excited state pathway.

Keywords: Triclosan; Irgasan DP300; Photolysis; Dioxin; Photocyclization

1. Introduction

Contamination of the environment by various pollutants originating from different fields such as agriculture, industry, medicine and personal care represents a serious environmental problem. These pollutants reach the aquatic environment through several processes such as leaching, equipment washing, careless disposal of containers and can be found in significant concentration in surface and ground waters where they have to be efficiently removed. This contamination has been well documented worldwide and constitutes a major issue that gives rise to concerns at large scales. The principal degradation pathways for these pollutants involve photolysis, hydrolysis, oxidation and dehalogenation when halogenated products are concerned [1,2]. Many of these organic chemicals which are present in aqueous solutions can undergo photochemical transformations with sunlight via direct or indirect photoreactions [1–4]. Such photochemical degradation can be one of the major transformation processes and one of the factors that control the fate of the organic pollutants in the environment. It is therefore of great interest to know to what extent they are degraded via such processes and to elucidate the generated byproducts since they can present a toxicity higher than that of the parent substrate.

Among the organic compounds of disinfectant concern, triclosan (5-chloro-2-(2,4-dichlorophenoxy)phenol) with the commercial name Irgasan DP300 has been used in a variety of consumer products [5,6]. It is an anti-microbial and preservative agent used in personal care products (toothpaste, detergent, soap, shampoos, skin care creams and lotions) with a typical concentration in the range of 0.1–0.3%. Its presence in waters and waste waters in US and Europe has been reported by several studies [7–11].

In aqueous solutions, degradation of triclosan may take place by the effect of ultraviolet irradiation [12–17]. Its

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photochemistry has been the subject of intensive studies in the last few years. In many instances, the central question was its ability to produce several types of polychlorinated dibenzo-*p*-dioxins under UV irradiation via a cyclization process. In the case of triclosan such process was shown to occur thermally as with other polychlorophenoxyphenols to polychlorodibenzo-*p*-dioxins at high temperature [16,17], namely above 300 °C. The photocyclization process was also shown to proceed under exposure to sunlight in the solid state [18] as well as in aqueous solutions [12–15]. In solid state, Kanetoshi et al. [12] have shown that the irradiation of triclosan produced dichlorodibenzo-*p*-dioxins, trace amount of trichlorodibenzo-*p*-doxin together with three chlorinated derivatives of triclosan. Under sunlight irradiation, the later byproducts lead in their turn to the formation to various polychlorinated dibenzo-*p*-dioxins. The photocyclization process was studied in detail by Mezcua et al. in aqueous solutions and wastewater samples [15]. It was clearly demonstrated that triclosan was mainly photodegraded at higher pH value, namely with its deprotonated form, into 2,7/2,8-dibenzodichloro-*p*-dioxin which represented the major degradation products. Moreover, such dioxins were also observed in wastewater samples corresponding to environmental conditions [19–21]. The photodegradation of triclosan and its conversion to dibenzodichloro-*p*-dioxin was also demonstrated by photo-solid-phase microextraction [12]. It was shown in this study that this photocylization process does not require basic media.

In the present study, the photochemical behaviour of triclosan was investigated in order to get a better insight into the mechanism of photocyclization. We will focus on the triclosan disappearance quantum yields and the role of molecular oxygen concentration in the process under various pH values. The elucidation of the major photogenerated products was obtained by LC/MS/MS and the mechanism of their formation will be proposed.

2. Experimental

2.1. Materials

Triclosan (5-chloro-2-(2,4-dichlorophenoxy)phenol) with the commercial name Irgasan DP300 was purchased from Aldrich. It was used as received. All other reactants were of the highest grade available. All solutions were prepared with deionised ultrapure water which was purified with Milli-Q device (Millipore) and its purity was controlled by its resistivity.

2.2. Steady state irradiations

For kinetic as well as analytical purposes, aqueous solutions were irradiated in a quartz cell (1 cm optical pathlength) using an arc xenon lamp (1600 W) equipped with a Schoeffel monochromator. The bandwidth was 10 nm. Solutions were deoxygenated by argon or nitrogen bubbling or oxygenated by oxygen bubbling for 20 min prior to irradiation. Then the cell was closed using a septum. The initial concentration of the solution was checked by HPLC analysis after bubbling. The irradiations at 254 nm were obtained with PHILIPS TUV 6 W lamp delivering a parallel beam. Potassium ferrioxalate was used as a chemical actinometer. The pH of the solutions was adjusted using phosphate buffers (1.0×10^{-3} mol L^{-1}, pH 5.4) and dilute solutions of $HClO_4$ or NaOH.

2.3. Laser flash photolysis

Transient absorption experiments in the 20 ns to 400 μs time scale were carried out on a nanosecond laser flash photolysis spectrometer from Applied Photophysics (LKS.60). Excitation ($\lambda = 266$ nm) was from the fourth harmonic of a Quanta Ray GCR 130-01 Nd:YAG laser (pulse width ≈ 5 ns), and was used in a right-angle geometry with respect to the monitoring light beam. A 3 cm^3 volume solution was used in a quartz cell, and was stirred after each flash irradiation. Individual cell samples were used for a maximum of five consecutive experiments. It is important to note that the signal obtained with an individual shot was too weak to permit good analysis. Therefore, the absorbance at a preselected wavelength was the result of 10–15 laser shots. Such absorbance was monitored by a detection system consisting of a pulsed xenon lamp (150 W), monochromator, and a 1P28 photomultiplier. A spectrometer control unit was used for synchronizing the pulsed light source and programmable shutters with the laser output. This also housed the high-voltage power supply for the photomultiplier. The signal from the photomultiplier was digitized by a programmable digital oscilloscope (HP54522A). A 32 bits RISC-processor kinetic spectrometer workstation was used to analyse the digitized signal.

2.4. Analyses

UV–vis spectra were recorded on a Cary 300 scan (Varian) spectrophotometer. LC/MS studies were carried out with a Waters (Alliance 2695) High performance liquid chromatography system coupled to a Quattro LC triple quadrupole mass spectrometer (Micromass, Manchester, UK) equipped with a pneumatically assisted electrospray ionisation source (ESI) and a Waters photodiode array detector. Each single experiment permitted the simultaneous recording of both UV chromatogram at a preselected wavelength and an ESI-MS full scan. Data acquisition and processing were performed by MassLynx NT 3.5 system. Chromatography was run using a Nucleodur column100-5 C8 ec (250 mm × 4.6 mm, 5 μm) and a 60/40 (v/v) mixture of acetonitrile and water with 0.2% acetic acid as mobile phase at 1 mL min^{-1}. Samples (5–10 μL) were injected either directly or after solid-phase extraction on Oasis HLB cartridges (Waters). The electrospray source parameters were: capillary voltage 3.5 kV (or 3 kV in the negative mode), cone voltage 15 V, source block temperature 120 °C, desolvatation gas temperature 400 °C. Argon was used for collisional activated dissociation (CAD) at a pressure of 1.5×10^{-3} Torr and 10–50 eV collision energy.

The consumption of triclosan and the formation of the byproducts were monitored by analytical HPLC using a Waters apparatus equipped with a 996-photodiode array detector. The experiments were performed by UV detection at 250 nm and

by using a reverse phase Merck column (Spherisorb ODS-2, 250 mm × 4.6 mm, 5 μm). The flow rate was 1.0 mL min^{-1} and the injected volume was 50 μL. The elution was accomplished with acidified water (acetic acid 0.01%) and acetonitrile (8/2 by volume). pH measurements were carried out with a JENWAY 3310 pH-meter to ±0.01 pH unit equipped with an Ag/AgCl glass combination electrode 9102 Orion.

The evolution of chloride ions concentration as a function of irradiation time was obtained by ionic chromatography using a Gilson 305 pump equipped with a Waters 431 conductivity detector and an IC-PAK anion HC column from waters (4.6 mm × 150 mm). The elution was accomplished according to Waters 431 conductivity manual specifications. First solution A is prepared as follows: 851.5 mL deionised ultrapure water + 23.5 mL gluconic acid solution (50%, w/w) + 8.6 g lithium hydroxide + 34.0 g boric acid + 250 mL glycerin. The final elution mixture is prepared by adding 20 mL of solution A to 500 mL of deionised ultrapure water under stirring. Then addition of 20 mL *n*-butanol and 120 mL acetonitrile, and finally addition of remaining water (340 mL). The flow was adjusted to 1.0 mL min^{-1}.

3. Results and discussions

3.1. Spectral features

The UV absorption spectra of triclosan at a concentration of 2.5×10^{-5} mol L^{-1} in aqueous solution at two pH values, 5.5 and 11.8, are given in Fig. 1. In acidic as well as in neutral conditions, the absorption spectrum exhibits a band with a maximum at 280 nm and a shoulder at 232 nm. The molar absorption coefficient was evaluated to 4200 mol^{-1} L cm^{-1} at 280 and to 13,300 mol^{-1} L cm^{-1} at the shoulder. In alkaline conditions, the first absorption band shifted to 291 nm. Under these conditions, the molar absorption coefficient was evaluated to 8300 mol^{-1} L cm^{-1}. By studying the changes of the absorbance at 291 nm, namely the maximum absorption of the anionic form, as a function of pH, we could estimate that the value of pK_a was 8.0 in agreement with the value reported in the literature (7.9) [22]. Triclosan shows a low solubility in water (10 mg L^{-1} corresponding to 3.5×10^{-5} mol L^{-1} at room temperature). The experiments were then performed within the concentration range of 1.0×10^{-5} to 3.5×10^{-5} mol L^{-1}. It has to be pointed out that the absorption spectrum of the protonated form of triclosan shows a very weak overlap with that of the solar emission. By contrast, the absorption spectrum of the anionic form presents a much more important overlap leading to its possible photochemical transformation under sunlight exposure.

3.2. Steady-state irradiation

As shown in Fig. 2, the photolysis at 254 nm of aerated aqueous solutions of triclosan (2.7×10^{-5} mol L^{-1}) at pH 5.5 led to a continuous increase of the absorbance over the whole UV–vis absorption spectrum (up to 600 nm) without a clear evidence for the emergence of new absorption bands. The spectrum obtained after the complete disappearance of triclosan corresponds to the sum of the various photoproducts spectra. Similar evolutions were observed for solutions in acidic medium. The HPLC analysis clearly showed that triclosan efficiently disappeared within 30 min irradiation time under our experimental conditions (see insert Fig. 2). Similar changes on the absorption spectrum as a function of irradiation time and also similar degradation kinetic profile were observed by excitation within the wavelength region 270–305 nm using a xenon lamp setup. At pH 5.5, the excitation at 300 nm led to the complete degradation within roughly 90 min irradiation time due to the low absorbance of the protonated form at this wavelength.

Quantum yields of triclosan photolysis were measured upon irradiation within the first absorption band (254–305 nm) in aerated, deaerated and oxygen-saturated solutions. The data are gathered in Table 1. These results clearly show that whatever the pH of the solution, the disappearance of triclosan is favoured in the absence of oxygen. Although only three oxygen concentrations were studied, the disappearance quantum yield is clearly not a linear function of oxygen concentration for the three pH values studied (Fig. 3). Moreover, the dependence of the quan-

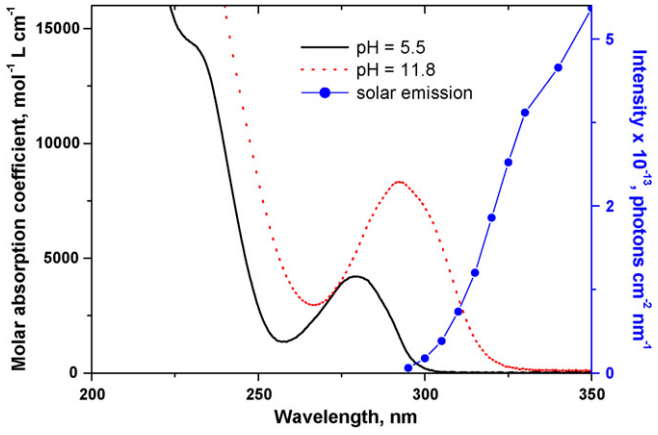


Fig. 1. Absorption spectra of an aqueous solution of triclosan at pH 5.5 and 11.8 compared to the emission spectrum of sunlight.

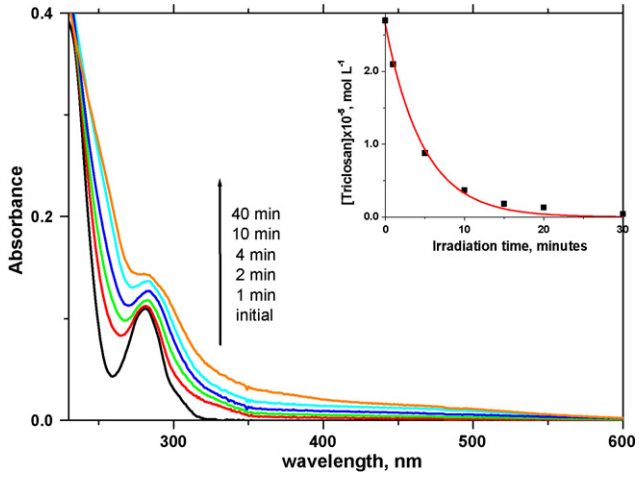


Fig. 2. Evolution of the absorption spectrum of an aerated aqueous solution of triclosan (2.7×10^{-5} mol^{-1} L s^{-1}) upon irradiation at 254 nm (pH 6.4).

Table 1
Quantum yields of triclosan photolysis in aerated, deaerated and oxygen-saturated solutions as a function of pH and excitation wavelength

Oxygen concentration [23] (mol L^{-1})	$\lambda_{excitation}$ = 254 nm			$\lambda_{excitation}$ = 300 nm		
	pH 2.6	pH 6.4	pH 11.6	pH 2.6	pH 6.4	pH 11.6
$<5 \times 10^{-6}$	0.46	0.56	0.81	0.44	0.58	0.79
2.6×10^{-4}	0.30	0.38	0.70	0.31	0.40	0.68
1.2×10^{-3}	0.20	0.28	0.57	0.18	0.25	0.55

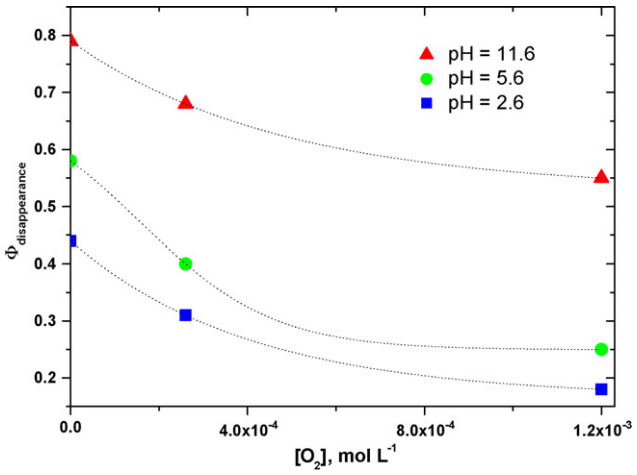


Fig. 3. Effect of the oxygen concentration on the quantum yield of triclosan disappearance at various pH conditions and at the excitation wavelength of 300 nm.

tum yield on the pH showed that the phototransformation process was more efficient with the deprotonated form as reported in the literature [13]. It is worth noting that no significant effect of the phosphate buffer or excitation wavelength was observed under our experimental conditions. Since three chlorine atoms are present in triclosan molecular structure, we quantified the release of chloride ions by ionic chromatography in neutral and basic conditions. In aerated conditions at pH 5.5 and 11.8, the quantum yield for chloride ions formation by excitation at 300 nm was evaluated to 0.16 and 0.29, respectively. Similarly to the results obtained for triclosan disappearance, the quantum yield for chloride ions formation depended on oxygen concentration and pH. It increased under irradiation in oxygen-free solutions ($\Phi_{deaerated}$ = 0.43 at pH 11.8). These results demonstrate that the loss of chloride anion in triclosan phototransformation represents an important degradation pathway.

3.3. Laser flash photolysis studies

In order to establish the mechanism and kinetic details of triclosan degradation under UV light excitation, we employed a nanosecond laser flash photolysis technique. The excitation wavelength was set at 266 nm since no effect of excitation wavelength was observed in steady state studies leading us to the conclusion that similar photochemical reactions are involved. Owing to the weak signal, the recorded trace was the result of several individual shots (see Section 2). When triclosan (2.7×10^{-5} mol L^{-1}) in argon saturated aqueous solution at pH 5.5 is flash photolysed at 266 nm, several transient species were formed (Fig. 4). The spectral features of solvated electrons (λ_{max} = 720 nm) were observed. Its amount, as monitored by its absorbance at the end of the laser pulse, was linearly dependent upon the initial light intensity within 1–10 mJ laser energy range. This clearly shows that we are dealing only with a monophotonic process. Another transient absorption band is observed at shorter wavelength during the 8 μs following the pulse end. It presented a maximum at 320 nm. Similar results were obtained when the experiments were performed at pH 11.8.

When triclosan was flash photolysed in oxygen saturated solution, the decay rate of the solvated electron and that of the 320 nm transient species were significantly enhanced. Both species showed pseudo-first order decays. The second order rate constants were evaluated to 1.1×10^{10} and 4.7×10^{9} mol^{-1} L s^{-1}, respectively. On the basis of the effect of oxygen concentration, the 320 nm absorption band may be assigned to the triplet–triplet absorption. Moreover, it is worth noting that under oxygen saturated conditions, the absorbance around 420 nm appeared to decrease less rapidly than that at 320 nm. This suggested to us the presence of a third species. Its spectrum may be obtained after the complete disappearance of both initial, namely the triplet transient and the solvated electron species (insert Fig. 4). It presents a spectrum with a vibrationnal structure: a shoulder at 335 nm and two absorption maxima at 375 and 421 nm. Such absorption spectrum features may be easily compared to those reported in the literature for phenoxyl radical derivatives [24–27]. These radical species may be formed

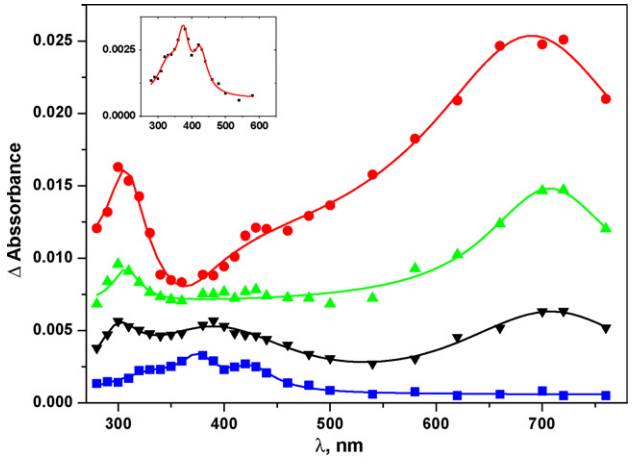
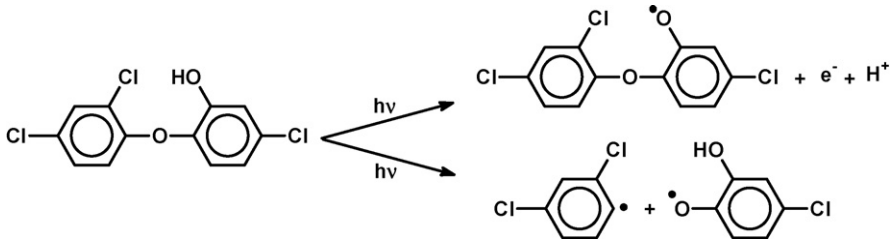


Fig. 4. Transient absorption spectra from deoxygenated aqueous solution of triclosan under excitation at 266 nm (2.7×10^{-5} mol^{-1} L s^{-1}, pH 5.5). (●) Absorbance at the pulse end; (▲) absorbance at 1 μs; (▼) at 3 μs and (■) 6 μs after the pulse end.



Scheme 1.

either by an ionisation process or a homolytic scission of the ether bridge of triclosan (Scheme 1).

3.4. Analytical studies

The characterization of the byproducts was achieved by HPLC/ESI/MS/MS technique. As described in the experimental section, the mass spectrometry experiments were performed in both positive and negative ion modes. However, under our experimental conditions, the negative mode was found to be more sensitive and suitable for the parent compound and also for the majority of photogenerated products. This is more likely owing to the presence of the hydroxyl group which can be more easily deprotonated. It is of interest to note that the mass spectrum of unknown products was very informative about the number of chlorine atoms present in the molecular structure. This was obtained from the intensities of the peaks arising from the various possibilities of the two isotopes combinations (^{35}Cl 24.23% and ^{37}Cl 75.77%). The identities of some of these byproducts were already given in the literature by means of GC–MS, liquid chromatograpghy/time-of-flight mass spectrometric, LC/MS experiments [14,17,28].

Fig. 5 depicts the UV chromatogram recorded at 240 nm which was quite similar to the ESI-MS full-scan in negative mode. This was obtained for an irradiated solution ($t_{irradiation}$ = 20 min) of triclosan at pH of 5.5. It clearly shows the presence of several photoproducts. Most of them are eluted before triclosan (t_{ret} = 20.00 min) indicating that we are dealing with smaller and/or more polar products when compared to the parent compound. However, some compounds containing several aromatic rings and five chlorine atoms are eluted after triclosan and showed very high masses ([$M - H^+$] = 539). They probably resulted from radical oligomerisation reactions via the formation of phenoxyl radical derivatives as demonstrated by laser flash photolysis results. Such products did not appear significantly when the irradiation was stopped at the early stages of the irradiation. These high mass products formed from triclosan are probably similar to that reported by Latch et al. [17]. Their molecular structures cannot be easily determined since various possibilities can be proposed. In contrast, those of the primary as well as the most significant byproducts were tentatively elucidated by studying their MS and ES/MS/MS spectra in negative mode. Table 2 gathers the molecular ions and the most important fragment ions along with the proposed structures.

The identified byproducts can be classified as arising from four different primary photoprocesses: isomerisation, photocyclization, dimerisation of the phenolic moiety and photohydrolysis.

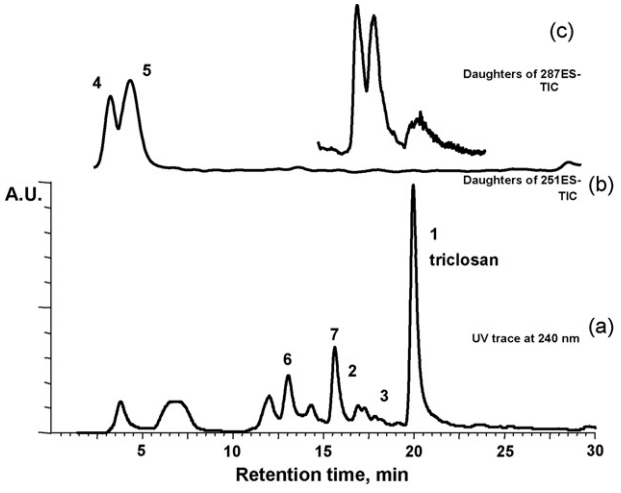


Fig. 5. UV and abundance of ions chromatograms in negative mode for the irradiated solution ($t_{irradiation}$ = 20 min) of triclosan at 300 nm. (a) UV chromatogram at 240 nm for an irradiated solution at pH 5.5. (b) Abundance of ions for the formation of dioxin derivatives under irradiation in alkaline medium, pH 11.8. (c) Abundance of ions formation of triclosan isomers. The peak numbers correspond to the products numbers in Table 2.

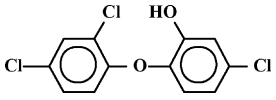
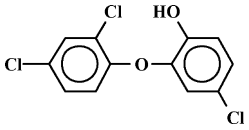
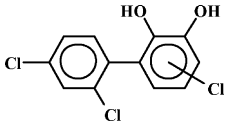
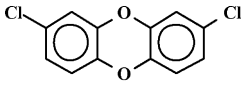
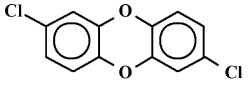
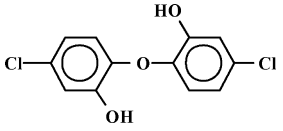
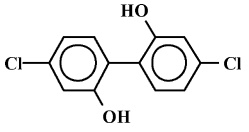
3.4.1. Isomerisation process

In addition to triclosan, $[M - H^+]^- = 287$, with the retention time of 20 min two products, 2 and 3, showing the same molecular ion were detected during the analysis of an irradiated solution of triclosan at pH 5.5. Product 2 showed a retention time of 17.0 min but a UV spectrum similar to that of triclosan. Moreover, the similarity in the type of fragmentation within the MS/MS spectrum permitted us to conclude that the whole molecular structure is more likely conserved. It can be identified as 4-chloro-2-(2,4-dichlorophenoxy)phenol.

Product 3 ([$M - H^+$]$^-$ = 287; t_{ret} = 17.9 min): the UV spectrum of this product is different from that of triclosan. The presence in the MS/MS spectrum of the fragment ion at m/z = 269 more likely indicates the elimination of water molecule which permitted us to suggest the vicinity of two hydroxyl groups in the molecular structure. According to the structure of triclosan, various catechol derivatives may be proposed as possible products.

The formation of these isomers appeared to be independent of oxygen concentration and of the pH showing the possible involvement of the singlet excited state. Their structures as well

Table 2
LC/MS/MS data in ES negative mode for the photogenerated products and their proposed structures

Product[a]	t_{ret}[b] (min)	UV[c] data (nm)	$[M-H^+]^-$; main fragment ions	Cl[d]	Structure
1	20.0	232, 280	287; 251 (weak), 215, 159	3	
2	17.0	230, 282	287; 251, 215, 159	3	
3	17.9	238, 270	287; 269, 251, 215	3	
4	3.7	250, 288	251; 207, 189, 179, 165, 143	2	 mainly observed in basic medium
5	4.5	245, 288	251; 223,179,144	2	 mainly observed in basic medium
6	13.6	242, 285	269; 251, 233, 205,177	2	
7	15.6	246, 280	253; 235, 217, 189	2	

[a] The numbers refer to the peaks in LC/MS/MS chromatogram given in Fig. 5.
[b] Retention time.
[c] UV data obtained by using a photodiode array detector.
[d] Number of chlorine atoms obtained from the intensities of the peaks for the molecular ion ($[M-H^+]^-$) arising from the various possibilities of the chlorine isotope combinations.

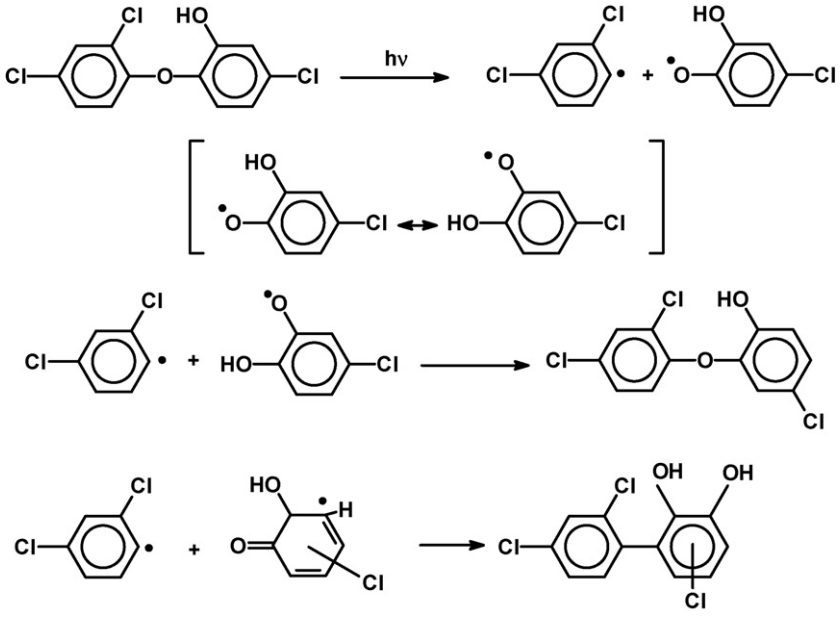
as the formation of high masses photoproducts ($[M-H^+]=539$) suggest that a homolytic dissociation of the C–O bond of the ether bridge from dichlorobenzene side. This process leads to the formation of phenoxyl radical as shown by laser flash photolysis studies. The recombination of the benzene radical with various forms of the phenoxyl radical leads to the formation of the desired products (Scheme 2).

3.4.2. Photocyclization process

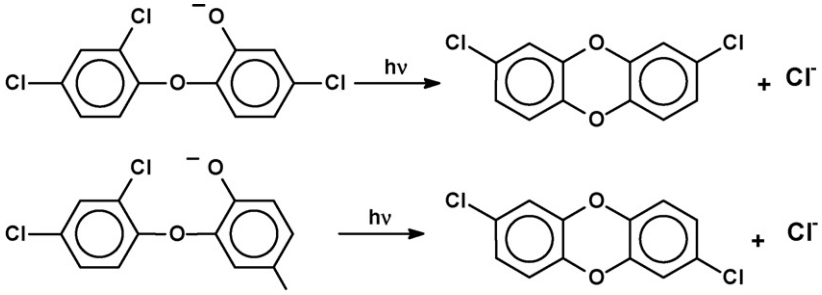
Two compounds, product 4 ($t_{ret}=3.7$ min) and product 5, with the same molecular ion ($[M-H^+]^-=251$) were mainly detected by the analysis of a solution irradiated at pH 11.8 (Fig. 5b). They are reported in the literature [15] as resulting from the elimination of chloride anion via the formation of dioxin structures. Their structures are given in Table 2. It should be pointed out that if product 4 is clearly generated from the direct photocyclization process of triclosan [12–15], product 5 is without any doubt a secondary product formed through the cyclization of product 2. This is an evidence for the occurrence of the isomerisation process as stated above. It is worth noting that these products are mainly observed when the irradiation is undertaken in alkaline solution, pH 11.8, namely with the anionic forms of their precursors. Moreover, their formation was inhibited by molecular oxygen showing that it likely involves the triplet excited state which formation was demonstrated by laser flash photolysis studies (Scheme 3).

3.4.3. Dimerisation of the phenolic moiety

At least one biphenyl compound, containing two chlorine atoms, with the molecular ion at $m/z=253$, was present in the irradiated solution (product 7, $t_{ret}=15.6$ min). It corresponds more likely to the dimerisation of the phenolic group of tri-



Scheme 2.



Scheme 3.

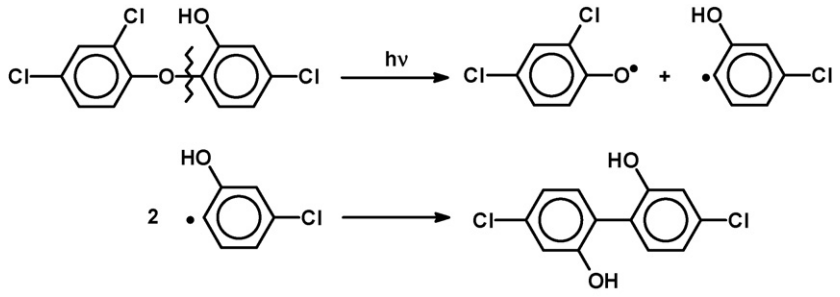
closan leading to the formation of 2,2′-dihydroxy-4,4′-dichloro biphenyl. The MS/MS spectrum clearly showed the presence of the fragment ion at $m/z = 235$ as the result of the elimination of a water molecule due to the adjacency of the two hydroxyl groups.

The formation of such biphenyl product may involve the homolytic dissociation of the ether bridge within the phenolic moiety and the recombination of the obtained radicals (Scheme 4). No effect of triclosan concentration was observed within the concentration range 1.0×10^{-5} to 3.5×10^{-5} mol L^{-1}.

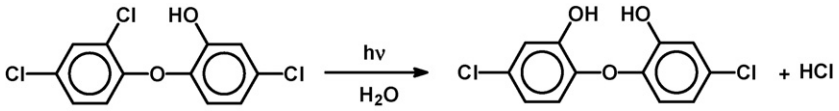
The formation of such 2,2′ bis-phenol compound may also involve the photochemical dissociation of a dioxin derivative such as product 4 as described in the literature [29].

3.4.4. Photohydrolysis

The presence of the fragment ion with two chlorine atoms at $[M - H^+]^- = 269$ shows the substitution in the triclosan structure of one chlorine atom by an hydroxyl group (product 6, $t_{ret} = 13.6$ min). Unfortunately, the MS data did not provide more detailed structural information to determine the position of the added hydroxyl group on the benzene ring, so that several iso-



Scheme 4.



Scheme 5.

mers can be hypothesized for this compound. The presence in the MS/MS spectrum of the fragment ion at 251 which corresponds to the elimination of a water molecule is again in favour for the vicinity of the hydroxyl functions. The mechanism of its formation may involve a photohydrolysis process as largely reported for chlorinated phenols (Scheme 5) [30,31].

In addition to all the above photoproducts, trace concentrations of compounds at $[M - H^+]^- = 303$ with two chlorine atoms were also detected. They are the result of an hydroxylation process of triclosan involving more likely the photoionisation process.

Several other secondary products were also detected in the MS experiments in the irradiated solution even though the conversion percentage was stopped at about 5–10%. They correspond to chlorine substitution and hydroxylation processes of the various elucidated products.

4. Conclusion

The photochemical degradation of triclosan within the wavelength range $254 < \lambda < 305$ nm was dependent on oxygen concentration and on pH. Several photoproducts arising from various processes were formed. The isomerisation process as well as dimerisation reaction were shown to proceed through the homolytic dissociation of the oxygen bridge. The photocyclization pathway leads to the formation of dioxin derivatives via the intermediate formation of the triplet excited state. Such reaction was shown to mainly occur in the absence of oxygen and with the anionic form of triclosan. The formation of oligomeric products was also observed for prolonged irradiation time.

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