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Short communication

Photochemical conversion of triclosan to 2,8-dichlorodibenzo-*p*-dioxin in aqueous solution

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Abstract

The direct photolysis of triclosan (5-chloro-2-(2,4-dichlorophenoxy)phenol), an antimicrobial additive commonly detected in surface waters, is studied. It is found that 2,8-dichlorodibenzo-*p*-dioxin (2,8-DCDD) is produced in both buffered and natural (Mississippi River) water with yields ranging from 1 to 12% under a variety of conditions. This result indicates that triclosan is likely converted to 2,8-DCDD in sunlight-irradiated surface waters.

Keywords: Triclosan; 2,8-Dichlorodibenzo-*p*-dioxin; Direct photolysis; Photochemical cyclization; Natural water

1. Introduction

Triclosan (5-chloro-2-(2,4-dichlorophenoxy)phenol) is a widely employed antimicrobial that has been found as a contaminant of rivers and lakes [1–10]. In a recent reconnaissance for a suite of 95 pharmaceuticals, hormones and other organic wastewater contaminants, triclosan was one of the most frequently detected pollutants, being found in 57.6% of the 139 tested US streams and rivers [5]. An early set of studies in the Pawtuxet and Providence Rivers detected triclosan along with structurally related compounds, including 2,8-dichlorodibenzo-*p*-dioxin (2,8-DCDD), which were hypothesized to be derived from the synthesis of triclosan [9–11]. Because of general concern about dioxins in the environment, we have become interested in the possibility that triclosan is a dioxin precursor and can be converted to 2,8-DCDD by an intramolecular photochemical substitution reaction. This hypothesis is supported by numerous examples of photochemical nucleophilic aromatic substitution [12–15]. Our interest in this photoreaction is further piqued by the studies of Mueller and coworkers who concluded that photochemical transformation of triclosan accounts for up to 80% of its loss from the epilimnion in Lake Greifensee during the summer months [1,2].

The thermal cyclization of triclosan and other polychlorophenoxyphenols to polychlorodibenzo-*p*-dioxins is established and occurs readily for triclosan above 300 °C [15–18]. Previous work on the photochemical cyclization has led to conflicting results. It has been reported that triclosan is relatively unique among the polychlorophenoxyphenols in that it does not undergo cyclization to its corresponding dioxin in methanol solution [15,19]. More recent studies have shown that when irradiated by UV light in the solid state [16] or in aqueous solution [20], triclosan does convert to 2,8-DCDD. Due to the potentially important environmental and human health implications of this reaction, we have clarified the photochemical behavior of triclosan in aqueous solutions. This study has investigated the role of pH and irradiation wavelength on this reaction, and experiments in Mississippi River water have been performed to test if the reaction will occur in natural waters.

2. Experimental

2.1. Chemicals

Triclosan and *p*-nitroacetophenone were purchased from Aldrich. Isoprene and *m*-methoxyacetophenone were obtained from Acros Organics, and 2,8-dichlorodibenzo-*p*-dioxin (2,8-DCDD) was purchased from NeoSyn Laboratories. Isoprene was purified by vacuum distillation to

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separate it from radical inhibitors, all other chemicals and solvents were used as received.

2.2. Instrumentation

Chromatograms were obtained with an 1100 Series Hewlett-Packard HPLC with an UV-absorbance detector or an Agilent 6890 Series GC System equipped with a 5973 Mass Selective Detector. Each system was controlled by Chemstation software. HPLC conditions: Supelco, Discovery RP-Amide C_{16} column (150 mm × 4.6 mm, 5 μm particle size), 80:20 ACN:pH 5 acetate buffer, 1 ml/min, 35 μl injection volume, detector wavelength 280 nm for 6 min, 230 nm thereafter. Triclosan eluted at 5.1 min, while 2,8-DCDD eluted at 7.0 min. GC conditions: HP-5MS column (30 m × 0.25 mm × 0.25 μm film thickness), 40 °C for 4 min, 20 °C/min, 200 °C. 2,8-DCDD eluted at 14.0 min.

UV-Vis spectra of triclosan, the triclosate anion, 2,8-DCDD, and Mississippi River water were collected with a Jasco V-530 spectrophotometer. An Accumet portable AP62 pH meter from Fisher Scientific was used with a Corning combination electrode to measure pH. Varian Inova 300, 500, and 600 MHz instruments were used to obtain NMR spectra.

Mississippi River water was analyzed for total organic carbon (TOC) by a Tekmar Dohrmann, Phoenix 8000 instrument that was calibrated with standard solutions of potassium hydrogen phthalate. The water was then passed through cellulose 0.45 μm filters. Following filtration, the Mississippi River water was analyzed for anions with a Dionex ion chromatography system with an AS14 column and carbonate buffered eluent. The anions were quantified relative to calibration curves prepared from NIST standards. Cations were quantified in comparison to NIST standards by a ThermoElemental PQ ExCell inductively coupled plasma mass spectrometer.

2.3. Photolysis experiments

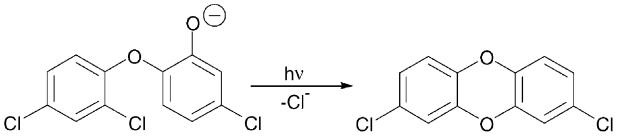
Aqueous solutions (25 or 50 ml) of triclosan (3.5–76 μM) exposed to air in quartz bottles were irradiated in a merry-go-round reactor with filtered light (>280, >290 (Pyrex) or >320 nm) from a medium-pressure Hg-vapor lamp (450 W, Ace Glass). The lamp was placed inside of borosilicate or quartz cooling wells (Ace Glass). In kinetic analyses, small aliquots of sample were withdrawn at predetermined intervals and substrate decay and product growth were determined by HPLC analysis.

The triclosan disappearance and dioxin appearance occurring in the first 5 min of irradiation were simultaneously fit to a first-order kinetic model using Scientist for Windows (v. 2.01). After 5 min, the kinetics deviated from first-order due to increased light screening from light absorbing reaction products. Rate constants were determined from a least-squares fit of the data to numerically integrated solutions of the system of differential equations. The triclosan rate constant was apportioned into two pathways, namely triclosan → 2,8-DCDD and triclosan → other products. Quantum yields were calculated by comparing the rate constant for the disappearance of the reactant triclosan or dioxin or the appearance of the product dioxin to the rate constant for the disappearance of the *p*-nitroacetophenone actinometer which has a known quantum yield [21]. The method used is the phase two test method [21]. Specific absorbance values for the triclosan and 2,8-DCDD were determined from UV-Vis spectra of the compounds, and light intensities for the emission wavelengths of the Hg-vapor lamp were obtained from [22]. Quantum yields were corrected for light screening of triclosan, triclosan anion, and Mississippi River water [23]. An average path length of 3.4 cm through the quartz bottles was used as the mixing depth.

The presence of dioxin in the irradiated samples was confirmed by GC–MS, HPLC (UV absorbance), and NMR spectroscopy through comparison with the authentic standard. There have been previous reports of false detection of dioxins by GC due to thermal cyclization reactions in the heated inlet [24] and of contamination of commercial triclosan with 2,8-DCDD [25]. These potential complications were controlled by combining GC with other analysis methods and analyzing the triclosan starting material for 2,8-DCDD (none was detected).

3. Results and discussion

The results of the photolysis experiments are summarized in Table 1. Ring closure to 2,8-DCDD was observed in aqueous solutions buffered at pH 8 or above (Eq. (1)).



(1)

Kinetic measurements were performed to assess the quantum yield for triclosan degradation (Φ_T) and 2,8-DCDD formation (Φ_D) under a variety of conditions (entries 1–13, Table 1). Quantum yields were determined by comparison with the pyridine/*p*-nitroacetophenone actinometer [21]. Both Φ_T and Φ_D are sensitive to pH, inflecting at the pK_a of triclosan (7.9), suggesting that the phenolate form is the photoreactive species. This is in agreement with the observations of others [2,3] that the phenolate form of triclosan is photoreactive, while triclosan and its methyl ether are photostable. This finding that triclosan cyclizes only in solutions where the phenolate form is present also reconciles the discrepancies on dioxin formation reported in the literature, namely, why 2,8-DCDD is not formed in methanol solution [15,19]. Conversion yields (Φ_D/Φ_T) vary with pH and irradiation wavelength, but are in the range of 1–12% (at pH 8 or above). This indicates that conversion to 2,8-DCDD is a

Table 1
Reaction conditions, quantum yields, and conversion yields for triclosan decay (Φ_T) and 2,8-dichlorodibenzo-*p*-dioxin (2,8-DCDD) formation (Φ_D) and decay (Φ_{-D})

Triclosan

Entries	$[Triclosan]_i$ (μM)	pH	Conditions	Φ_T[a]	Φ_D[a]	Yield (%; Φ_D/Φ_T)
1	21.0	11.5	Pyrex[b]	0.32	3.9×10^{-2}	12
2	76.0	8.0	Pyrex	0.84	3.9×10^{-2}	4.6
3	32.5	8.0	Pyrex	0.84	2.7×10^{-2}	3.2
4	18.4	8.0	Pyrex	0.74	3.0×10^{-2}	4.1
5	3.4	8.0	Pyrex	0.73	3.0×10^{-2}	4.1
6	13.5	7.2	Pyrex	0.36	ND[c]	ND
7	15.3	6.3	Pyrex	0.04	ND	ND
8	16.1	3.9	Pyrex	0.02	ND	ND
9	19.9	11.5	280 nm[d]	0.54	9.3×10^{-3}	1.7
10	19.9	11.5	280 nm[e]	0.56	8.4×10^{-3}	1.5
11	15.6	8.0	280 nm	0.85	1.5×10^{-2}	1.8
12	16.3	11.6	320 nm	0.47	1.0×10^{-2}	2.2
13	16.5	8.2	320 nm[f]	0.70	3.0×10^{-2}	4.2
14	16.2	9.1	Pyrex, MR[g]	0.54	2.0×10^{-2}	3.7
15	15.1	7.8	280 nm, MR	0.93	1.3×10^{-2}	1.4
16	14.7	8.0	320 nm, MR	0.34	4.0×10^{-3}	1.2

2,8-Dichlorodibenzo-*p*-dioxin (2,8-DCDD)

Entries	$[2,8\text{-DCDD}]_i$ (μM)	pH	Conditions	Φ_{-D}[a]
17	1.3	11	280 nm	4.4×10^{-3}
18	0.73	8	280 nm	5.9×10^{-3}
19	1.3	8	320 nm	1.4×10^{-3}

[a] Quantum yields are corrected for internal screening of the triclosan, triclosan anion, and Mississippi River water as appropriate.
[b] Performed with a Pyrex borosilicate glass well which blocks wavelengths <290 nm.
[c] No 2,8-DCDD detected.
[d] Quartz well with a <280 nm filter.
[e] Experiment performed in deoxygenated water (samples sparged with N_2 prior to photolysis).
[f] Quartz well with a <320 nm filter.
[g] Experiment performed in filtered Mississippi River water.

significant loss process, but not the dominant one. Polymers derived from triclosan are likely to be the main reaction products, as other researchers have shown that polymerization occurs when phenols are irradiated [26,27] or when triclosan is subjected to oxidative conditions [28].

Reverse-phase HPLC chromatograms of the photolyzed samples show a well separated peak for the hydrophobic 2,8-DCDD at longer retention times than triclosan and the other photolysis products. A sample for NMR analysis was prepared by extraction of a photolyzed sample with hexanes. Both one-dimensional ^1H (Fig. 1) and two-dimensional $^1H/^{13}C$ HMQC analyses demonstrated that the extract was primarily comprised of triclosan and 2,8-DCDD.

Freeman and Srinivasa have noted that the photochemical cyclization of 3,4,5,6-tetrachloro-2-(pentachlorophenoxy)-phenol, the perchlorinated analogue of triclosan, to octachlorodibenzo-*p*-dioxin is facilitated by triplet sensitizers [29–31]. In the case of triclosan, the opposite behavior is observed. Performing the photochemical reaction in 10% acetone or in the presence of *m*-methoxyacetophenone (0.35 mM), resulted in slower conversion due to light screening by the sensitizers (data not shown). The presence of the triplet quenchers oxygen (entries 9 and 10, Table 1)

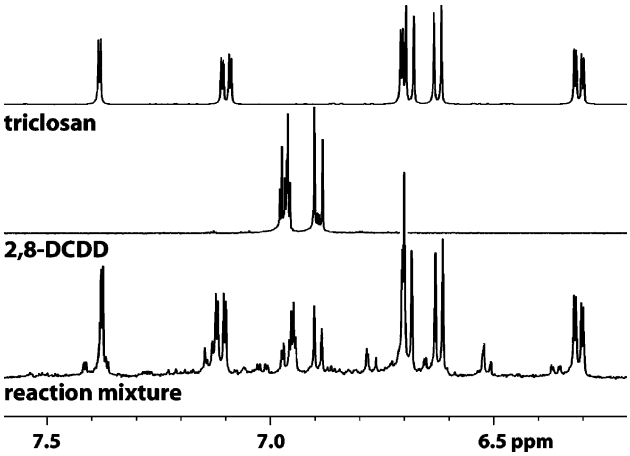


Fig. 1. Downfield region of the ^1H NMR spectra (500 MHz) of triclosan (top, CD_3OD/NaOD), 2,8-DCDD (middle, CD_3OD), and a mixture resulting from the photolysis of triclosan in water (bottom, CD_3OD/NaOD). The sample corresponding to the bottom spectrum was obtained by hexanes extraction of the aqueous photolysate. Small differences in the chemical shifts are due to their pH sensitivity.

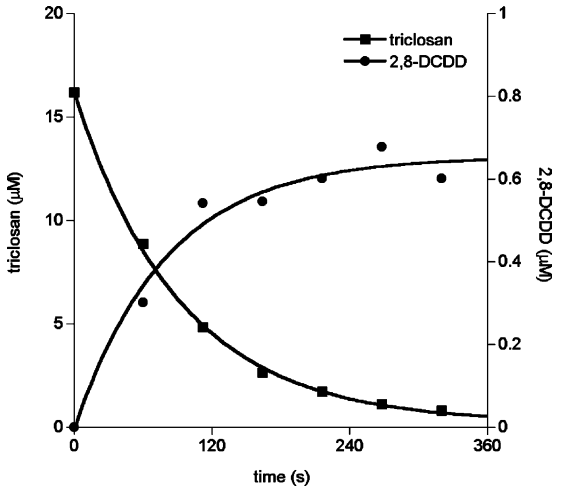


Fig. 2. Photochemical conversion of triclosan to 2,8-DCDD in Mississippi River water. These data correspond to entry 14 in Table 1. The solid lines are non-linear least-squares fits to exponential growth ($r^2 = 0.9746$) and decay ($r^2 = 0.9991$), and were used to calculate the quantum yields given in Table 1.

or isoprene had no effect on the conversion rate or yield. The results of these experiments suggest that cyclization is not occurring through an excited triplet state.

Kinetic traces of the dioxin product, 2,8-DCDD, displayed growth and decay profiles characteristic of an intermediate species. Experiments with pure 2,8-DCDD confirmed that it is also photoreactive, with degradation quantum yields (Φ_{-D}) between 2 and 20 times lower than the appearance quantum yields, Φ_D (entries 17–19, Table 1). Dioxins are known to undergo photochemical degradation [18,32–39], and the values for Φ_{-D} in this study are comparable to that found for 2,7-DCDD in 60% acetonitrile/water under similar conditions [33]. The decomposition products of 2,8-DCDD have not been identified, but may include dechlorinated congeners or rearranged products [18].

As a test of the environmental significance of these results, Mississippi River water was spiked with triclosan and irradiated with three different cutoff filters (Pyrex, >280, and >320). In each sample, triclosan was photodegraded and 2,8-DCDD was formed (entries 14–16, Table 1 and Fig. 2). After correction for internal screening due to naturally occurring chromophores in the river water, the quantum efficiencies for triclosan degradation and 2,8-DCDD formation in Mississippi River water were comparable to those found under similar conditions in buffer solutions prepared with reverse osmosis-purified laboratory water. These results suggest that triclosan is likely converted to 2,8-DCDD in sunlight-irradiated surface waters.

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