In situ photoproduction of dichlorodibenzo-p-dioxin from non-ionic triclosan isolated in solid argon

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Abstract

The infrared spectrum of triclosan [or 5-chloro-2-(2,4-dichlorophenoxy)phenol] isolated in a low temperature (~15 K) argon matrix has been recorded and assigned with help of DFT calculations undertaken with the B3LYP functional and the 6-311+G(d,p) basis set. The obtained spectrum doubtlesly exhibits the characteristic vibrational signature of the neutral (phenol) form of the compound, which exists in two different conformations (forms I and II) in the matrix, in a I : II population ratio of ca. 0.75. Upon broadband UV irradiation of the matrix-isolated triclosan with unfiltered light provided by a xenon arc lamp, formation of 2,8-dichlorodibenzo-p-dioxin (2,8-DCDD) was observed, together with HCl. The reaction seems to occur through initial photoproduction of the triclosan phenol radical derivative, and involve in the initial step participation of dissociative (ππ∗) excited states along the OH stretching coordinate, as observed previously for other phenol derivatives. The photochemically detached hydrogen atom derived from triclosan may then react with the closest located chlorine atom in the triclosan molecule to yield HCl and a biradical species, which can subsequently undergo a ring-closure reaction by intramolecular recombination, leading to the observed 2,8-DCDD.

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1. Introduction

Triclosan [5-chloro-2-(2,4-dichlorophenoxy)phenol; Scheme 1] is a broad-spectrum antibacterial and antifungal agent found in a wide variety of consumer goods like detergents, dish-washing liquids, soaps, deodorants, cosmetics, lotions, anti-microbial creams and toothpastes [1–5]. It is also used as additive in various plastics and textiles [6]. Triclosan is also registered by the U.S. Environmental Protection Agency (EPA) for use as a pesticide [7]. Because of its widespread use, triclosan has been found in waste- and surface waters and streams [8–17], sediments [17–20], fish [21–23], and even in human milk [24,25].

It has been reported that triclosan can be photochemically converted to toxic 2,8-dichlorodibenzo-p-dioxin (2,8-DCDD; Scheme 2) in the environment [26–38], and although the potential health effects of triclosan on the general population are not well understood, there is a growing concern about the generalized use of this compound [39–43].

The first studies on the photochemistry of triclosan, performed for the compound in water solution or as a solid film, concluded that it can be photochemically converted into a series of photoproducts [27–32]. The formation of at least five types of photoproducts has been postulated: monochloro- and dichlorohydroxydiphenyl ethers (of formula C12H8ClO and C12H8Cl2O2, respectively) formed on reductive dechlorination involving replacement of chlorine atoms by hydrogen atoms; isomeric monochloro- and dichlorophenols, including a particularly toxic one (2,4-dichlorophenol), which can be generated by the photoinduced hydrolysis of either triclosan or the previously formed chlorohydroxydiphenyl ethers by loss of one of the aromatic rings; and 2,8-DCDD, which results from reductive photoinduced cyclization of triclosan. Also dichlorohydroxy dibenzofuran was tentatively suggested as a possible photoproduct of triclosan. At high concentrations, triclosan was found to polymerize under acidic pH seemed to be slower). Indeed, these authors observed the formation of 2,8-DCDD during photodegradation of triclosan using the photo solid phase micro extraction method (photo-SPME), where the analytes were irradiated after being extracted...
from water and retained in the polydimethylsiloxane coating of the SPME fibers. Under those conditions, the compound could be expected to be present in its molecular form. The same authors were also able to observe photoproduction of 2,8-DCDD in aqueous photodegradation experiments at pH 3 [34]. These results have been subsequently confirmed by other authors [36–38,44].

In the present study we investigated the photochemistry of triclosan isolated in a low temperature solid argon matrix, in particular the possibility of photoproduction of 2,8-DCDD under these experimental conditions. The main advantage of this technique over the previously reported experiments is that once the reactant molecules were isolated in the inert rigid matrix media no diffusion is possible and, thus, only unimolecular reactions can be observed and putative products resulting from cross reactions involving recombination of species produced from different initial molecules of the reactant cannot be formed. Moreover, in a noble gas cryogenic matrix triclosan must exist in its neutral (phenol) form, whose vibrational signature can be precisely identified by infrared spectroscopy.

In this paper, the infrared spectrum of matrix-isolated monomeric triclosan is also reported and assigned. The harmonic vibrational frequencies and infrared intensities of the experimentally relevant conformers of the compound were evaluated at the DFT[B3LYP]/6-311+G(d,p) level of theory and used to help assignment of the experimentally observed bands. While the room temperature Raman and infrared spectra of solid triclosan have already been briefly described [45,46], no vibrational experimental data for the isolated monomeric form of triclosan have been reported hitherto.

2. Experimental and computational methods

Triclosan was obtained from Sigma–Aldrich (99.5% purity) and used without further purification. In order to prepare the low temperature Raman and infrared spectra of solid triclosan have been assigned and putative products resulting from cross reactions are predicted to be slightly more abundant than form I (II: I population ratio equal to 42.7%; 57.3%, i.e., ~−0.75).

In conformer I, the conformationally relevant C8–C9–O14–H15, C6–O7–C8–C9 and C5–C6–O7–C8 dihedral angles are predicted to be 5°, 123.8° and −22.3°, respectively, the H15–O7 distance being 218.5 pm, which is considerably shorter than the sum of the H and O van der Waals radii (~272 pm [51]). In this conformer, the inter-ring C6–O7–C8 fragment is nearly co-planar with the dichloro-substituted ring, the angle between the planes of the two rings being 72.6°. The H15–C16 and

3. Results and discussion

Triclosan has been shown before to have 4 different conformers, all of them corresponding to a pair of symmetry equivalent structures [46]. Two of these conformers exhibit an intramolecular O–H–O interaction and are considerably more stable (by more than 12 kJ mol⁻¹) than the remaining two forms. In the gas phase, at room temperature (298 K), the predicted population of the two higher energy conformers is less than 0.5%, so making these forms of no practical importance. The DFT[B3LYP]/6-311+G(d,p) optimized geometries for the two low energy conformers (Fig. 1) are provided as Supplementary Material (Table S1). According to the present calculations, conformer I is the lowest energy form. The zero-point corrected energy of conformer II is, however, only 1.42 kJ mol⁻¹ higher than that of form I, and at room temperature ΔH(I–II) = 1.65 kJ mol⁻¹, ΔS(I–II) = 7.99 J K⁻¹ mol⁻¹ and ΔG(I–II) = −0.73 kJ mol⁻¹, i.e., conformer II is predicted to be slightly more abundant than form I (I: II population ratio equal to 42.7%; 57.3%, i.e., ~−0.75).

In conformer I, the conformationally relevant C8–C9–O14–H15, C6–O7–C8–C9 and C5–C6–O7–C8 dihedral angles are predicted to be 5°, 123.8° and −22.3°, respectively, the H15–O7 distance being 218.5 pm, which is considerably shorter than the sum of the H and O van der Waals radii (~272 pm [51]). In this conformer, the inter-ring C6–O7–C8 fragment is nearly co-planar with the dichloro-substituted ring, the angle between the planes of the two rings being 72.6°. The H15–C16 and

Fig. 1. DFT[B3LYP]/6-311+G(d,p) optimized geometries of the two most stable conformers of triclosan with atom numbering.
H24–C16 distances are 420.8 pm and 469.2 pm, respectively. On the other hand, in conformer II, the C8–C9–O14–H15, C6–O7–
C8–C9 and C5–C6–O7–C8 dihedral angles and the H15–O7 and
H24–C16 distances are −2.3°, 177.7°, 90.9°: 212.8 pm and
386.1 pm, respectively, while the inter-ring C6–O7–C8 fragment
is now nearly co-planar with the phenol ring. In this conformer,
the angle between the planes of the two rings is 87.2°. The
H15–C16 distance is 417.9 pm. Conformer I was found to be
similar to the conformation adopted by triclosan in the inclusion
complexes of this molecule with native cyclomaltoheptaose
(β-cyclodextrin) and bound to enoyl reductase, as determined by
X-ray crystallography [52,53]. To the best of our knowledge, the
crystallographic structure of neat triclosan has not yet been
determined.

The energy barrier for conformational isomerization between I
and II was also obtained in the present study. The lowest energy
transition state structure between the two conformers was found
to have a butterfly like geometry with the inter-ring C6–O7–C8
fragment nearly perpendicular to both rings and an inter-ring
C6–O7–C8 angle of 122.6°. The C8–C9–O14–H15, C6–O7–C8–
C9 and C5–C6–O7–C8 dihedral angles and the H15–O7 distance
are −1.9°, −122.5°, 65.1° and 219.8 pm, respectively. In relation
to conformer I this transition state structure has a relative zero-
point corrected energy of 14.9 kJ mol⁻¹.

The infrared spectrum of triclosan isolated in an argon matrix
(T = 15 K) is shown in Fig. 2, together with the DFT(B3LYP)/6-
311+G(d,p) calculated spectra of the two experimentally relevant
conformers and a simulated spectrum built based on the calculated
data assuming a I: II population ratio of 0.75. The full calculated
vibrational data are provided in the Supplementary Material
(Table S2). Proposed assignments for the experimentally observed
spectrum are given in Table 1.

The theoretical simulated spectrum reproduces very well the
experimental one, suggesting the presence in the matrix of the two
conformers in a proportion similar to that predicted for the room
temperature gas phase. This is in agreement with the calculated
value for the conformational isomerization barrier reported above
(~15 kJ mol⁻¹), which is large enough to be expected to preclude
a substantial conversion between the conformers during matrix
deposition at the experimental conditions used [54,55].

The analysis of the relative intensities of the experimental fea-
tures observed at ca. 1495 and 1475 cm⁻¹ and the bands appearing
in the 880–760 cm⁻¹ region (where the two conformers are
predicted by the calculations to give rise to slightly – but discernibly
– different spectra) gives further support to the above conclusion.
In fact, the integrated intensities of the bands observed in these
spectral regions are in excellent agreement with the theoretically
predicted relative intensities assuming the I:II = 0.75 population
ratio (see Fig. S1 in Supplementary Material). In the higher fre-
quency spectral region, it is worth mentioning that the experiment-
mental band at ca. 1495 cm⁻¹ has in fact a lower integrated intensity
than that observed at ca. 1475 cm⁻¹ (0.94:1.00, matching the cal-
culated expected band intensity ratio) despite the peak intensities
follow the opposite order (see also Fig. 2).

Another spectral region where the calculated spectra of the two
conformers differ in some extent is the region below 550 cm⁻¹, in
particular for the OH vibrations (see Table 1). Unfortunately, the
analysis of this region is made difficult by the considerably low sig-
nal-to-noise ratio achievable in our setup due to the fact that in the
optical path of our instrument we have four KBr windows (note
that the transmission of KBr material is limited by ~400 cm⁻¹ in
infrared) and KBr beam splitter. Therefore the signal-to-noise ratio
in the region approaching 400 cm⁻¹ is much worse than at higher
wavenumbers). The feature ascribable to form I (predicted
at 424 cm⁻¹) is observed in the spectrum as a doublet at 432.6/ 429.6 cm⁻¹,
but the feature corresponding to form II (predicted
at 485 cm⁻¹) is not easy to observe. We can explain these findings
assuming that the experimental absorption of form II is extensively
broadened due to conformational mobility and extensive matrix
site splitting and gives rise to the broad profile observed around
540–500 cm⁻¹. Such behavior is not exceptional and has been ob-
served in other cases of loose torsional modes (e.g., the C–C torsion
in matrix-isolated dimethyl oxalate [56]).

In some cases, the proposed assignments of observed bands to
individual conformers (see Table 1) must indeed be considered as
tentative, due to the similarity between the predicted spectra of
the two conformers. Annealing of the matrix up to 35 K has been
performed in an attempt to promote any in situ conformational
interconversion (which would have made identification of bands
to each conformer clear), but without success. Such result could
in fact be anticipated taking into account the relatively large calcu-
lated isomerization barrier.

It is also worth mentioning the extensive band splitting ob-
served in the experimental spectra (in particular for the most in-
tense vibrations), which reflects several possible different local
trapping sites and complicates the assignment of bands to individ-
ual conformers. Extensive band splitting due to multiple trapping
sites has been observed for other molecules containing bridged
six-membered rings, such as, for example, benzil [(C₆H₄CO)₂] and
α-pyridil [(C₅H₆NCO)₂] [57,58].

![Fig. 2. Bottom to top: DFT(B3LYP)/6-311+G(d,p) calculated infrared spectra of triclosan conformers II and I (wavenumbers scaled by 0.978); simulated infrared spectrum using Lorentzian profiles (FWHM = 2 cm⁻¹) built from the calculated data for the conformers I and II, with intensities scaled in the I: II ratio 42.7%: 57.3%; infrared spectrum of triclosan in an argon matrix (15 K). Note the different abscissa scales before and after the X-axis break (major ticks are separated from minor ticks by 200 and 100 cm⁻¹, in the high and low wavenumbers range, respectively).](image-url)
Fig. 3 summarizes the obtained photochemical results. Matrix-isolated triclosan was irradiated through the outer quartz window of the cryostat with unfiltered light provided by a 150 W xenon arc lamp (λ > 200 nm). The difference spectrum shown in Fig. 3 corresponds to that obtained after 185 min of irradiation from which the spectrum of the as-deposited matrix was subtracted. Bands pointing down belong to triclosan, indicating consumption of the compound. Those pointing up are due to the photoproduced species and fit well the vibrational spectrum of 2,8-DCDD. This dioxin has a very characteristic vibrational signature (Table 2; see also Table S3 in the Supplementary Material for complete set of calculated infrared data for this molecule), with three intense infrared

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Proposed assignments for the bands in the infrared spectrum of triclosan isolated in an argon matrix.*</th>
</tr>
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<tr>
<td>432.6, 429.6</td>
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*a* Wavenumbers (ν) in cm⁻¹, infrared intensities (I) in km mol⁻¹. DFT(B3LYP)/6-311++G(d,p) calculated wavenumbers were scaled by 0.978. Full theoretical data are provided in Supplementary Material (Table S2).

*b* Approximate description was determined by visual inspection of animated vibrations using the Gauss View program [50] (see Fig. 1 for the atom numbering) and only the coordinates having the largest contributions to the vibration are indicated; Ph, chloro-substituted phenol ring; PhO, dichloro-substituted phenoxy ring; Whenever the k spectrum of the as-deposited matrix was subtracted. Bands
Proposed assignments for the IR bands of photoproduced 2,8-DCDD. a Bands predicted at 1479, 1296 and 936 cm\textsuperscript{-1}. The calculated intensities of these bands are 969.2, 548.5 and 162.8 km mol\textsuperscript{-1}, respectively, and they can be assigned to B\textsubscript{2} symmetry modes approximately described as CC ring stretching (also with significant contributions from in-plane CH bendings), COC antisymmetric in-phase stretching and CCl antisymmetric stretching. These three bands are clearly observed in the experimental difference spectrum at 1485.2, 1289.6 and 936.8 cm\textsuperscript{-1}, doubtlessly confirming the photoproduction of 2,8-DCDD. The fourth most intense infrared band of 2,8-DCDD is predicted to occur at 1281 cm\textsuperscript{-1}, with an intensity of 92.0 km mol\textsuperscript{-1}, being obscured by the strong absorptions of the reagent in this region. Other less intense bands observed in the spectrum of the irradiated matrix were also tentatively assigned to 2,8-DCDD, and further support the identification of the dioxin as photoproduction of matrix-isolated non-ionized triclosan (see Fig. 3 and Table 2).

Another relevant piece of information giving further support to the identification of 2,8-DCDD resulted from the analysis of the 2900–2700 cm\textsuperscript{-1} spectral region. In the spectrum of the irradiated matrix, a group of bands with maxima at 2810.7, 2777.2, 2768.0 and 2757.1 cm\textsuperscript{-1} was observed. These bands can be ascribed to HCl, which is produced together with 2,8-DCDD. Monomeric HCl isolated in an argon matrix absorbs at 2888 cm\textsuperscript{-1} [59], while formation of complexes of this molecule with other species were found to shift the position of this band to lower wavenumbers. The reported shifts were found to spread a wide range of values, depending on the acceptor molecule (e.g., 35 cm\textsuperscript{-1} with CO\textsubscript{2}, 124 cm\textsuperscript{-1} with C\textsubscript{2}H\textsubscript{4}, 228 cm\textsuperscript{-1} with H\textsubscript{2}O [59,60]). The observed band shifts for the HCl resulting from photolysis of triclosan range from ca. 77 to 138 cm\textsuperscript{-1}, clearly reflecting the interaction of HCl with the dioxin molecule formed in the same matrix cage upon photolysis. Observation of multiple bands are in agreement with the expected formation of different HCl/2,8-DCDD complexes, since the 2,8-DCDD molecule has several possible interacting sites (O and Cl atoms, and ring \pi electronic systems).

Contrarily to what happens for the photochemical conversion of ionized (phenolate) form of triclosan into 2,8-DCDD in aqueous solution, whose mechanism has been the subject of several studies [30,36], the mechanism for conversion of neutral (phenol) form of triclosan into the dioxin has never been addressed before.

The UV absorption spectrum of triclosan in aqueous solution at low pH (where triclosan phenol form predominates) is known [36]. This spectrum can be expected to be similar to that of isolated neutral triclosan. It exhibits two bands with maxima at 280 and 232 nm and a shoulder at 232 nm, with molar absorption coefficients of 4200 mol\textsuperscript{-1} L cm\textsuperscript{-1} and 13300 mol\textsuperscript{-1} L cm\textsuperscript{-1}, respectively [36]. The light used in the present study to irradiate triclosan

![Fig. 3. Bottom to top: Simulated infrared spectrum of triclosan using Lorentzian profiles (FWHM \(= 2\) cm\textsuperscript{-1}) built from the DFT(B3LYP)/6-311++G(d,p) calculated data for the conformers I and II, with intensities scaled in the I: II ratio 42.7%: 57.3% and Lorentzian profiles (FWHM = 2 cm\textsuperscript{-1}) minus lamp wavenumbers scaled by 0.978; difference spectrum: irradiated matrix by Xe arc lamp minus as-deposited matrix; simulated infrared spectrum of 2,8-DCDD using Lorentzian profiles (FWHM = 2 cm\textsuperscript{-1}) built from DFT(B3LYP)/6-311++G(d,p) calculated infrared spectrum of 2,8-DCDD (wavenumbers scaled by 0.978). Note the ~1.5 cm\textsuperscript{-1} break in the difference spectrum.

Table 2

<table>
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<tr>
<th>Observed (Ar matrix)</th>
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<th>Approximate description\textsuperscript{b}</th>
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<td>(B\textsubscript{2})</td>
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</tbody>
</table>

\(\textsuperscript{a}\) Wavenumbers (\(\nu\)) in cm\textsuperscript{-1}, infrared intensities (\(I^\text{\tiny in}\)) in km mol\textsuperscript{-1}.

\(\textsuperscript{b}\) Approximate description was determined by visual inspection of animated vibrations using the GaussView program [50] and only the coordinates having the largest contributions to the vibration are indicated; \(\nu\), stretching; \(\epsilon\), bending; \(\gamma\), out-of-plane rocking; \(\alpha\), antisymmetric; \(\iota\), symmetric.
(λ > 200 nm) overlap considerably the most intense UV absorption band of the compound observed at lower wavelengths. Since the wavelength 275 nm corresponds to the origin of the S1-S0 (π⁺ → π⁻) transition in parent phenol, as reported in several works [61–64], it can be expected that excitations to singlet state(s) higher than S1 are being promoted in the present case. According to previous studies [61–63], H– atom detachment upon UV photolysis of phenol derivatives involves predominantly the ground and first two excited singlet electronic states, S0(ππ*), S1(ππ*) and S2(ππ*). The profiles of the potential energy curves of these states result in two conical intersections due to the dissociative shape of the potential energy curve of S2(ππ*) along the OH stretching coordinate [65]. Hence, it can be postulated that after the initial excitation, the observed photo-reaction of λ > 200 nm irradiated matrix-isolated triclosan should evolve towards formation of the corresponding phenoxyl radical (bridged with the dichloro substituted six-membered ring). Meanwhile, the detached hydrogen atom, which can be expected to be produced with appreciable kinetic energy [62,65], may recombine back to form the reactant or further react with the closely located chlorine atom (Cl16 in Fig. 1), to yield HCl and a biradical species that can subsequently undergo a ring-closure reaction by intramolecular recombination, leading to the observed 2,8-DCDD. It is also worth mentioning that the change of intensity with time of irradiation of the bands ascribable to the two conformers of triclosan was found to be identical. This points to the irrelevance of the conformation in relation to the observed conversion of triclosan into 2,8-DCDD. Indeed, this is in accord with the fact that the distances between H15 and Cl16 in the two conformers are c. 2170 pm in I and 417.9 pm in II as well as their O–H bond lengths (96.72 pm in I vs. 96.65 pm in II).

Besides the above described photochemical studies, we have also performed additional investigations of the photochemistry of triclosan subjected to excitation using different light sources, including narrow band laser light sources. Very interestingly, those experiments led to the additional observation of other reaction channels, which will be reported in details separately. In the photochemical experiments considered in the present paper there is also evidence of occurrence of at least one reaction path alternative to that leading to formation of 2,8-DCDD. This path led to production of a ketene species, and is noticeable by the observation in the spectra of the photolyzed matrix of the intense infrared absorbance around 2130 cm⁻¹ characteristic of the C=CC=O antisymmetric stretching vibration.

The conversion of triclosan into a ketene had never been observed previously and, by its complexity (different types of ketenes can be a priori formed; besides, the putative ketene species can exist in a large number of conformers and configurational isomers), it will be the matter of a separate publication. With the present article we essentially wanted to solve (expectably in a final form) the already long-term discussion about the ability of non-ionic triclosan to be converted into the extremely toxic 2,8-DCDD dioxin. On the other hand, the triclosan-to-ketene conversion does not constitute a matter of toxicological interest, since any ketene, if formed, would quickly react under normal conditions.

4. Conclusion

Triclosan has been isolated in a cryogenic argon matrix and the possibility of photochemical formation of 2,8-DCDD from its neutral (phenol) form investigated. The infrared spectrum of the as-deposited matrix of triclosan was found to doubtlessly exhibit the characteristic vibrational signature of the neutral form of the compound. According to the performed DFT(B3LYP)/6-311++G(d,p) calculations, this form exists in two different conformations (forms I and II) in the matrix, in a II: I population ratio of ca. 0.75, which was predicted as the equilibrium gas phase population of the two conformers at room temperature. Upon broadband UV irradiation of the matrix-isolated triclosan with unfiltered light provided by a xenon arc lamp, formation of 2,8-dichlorodibenzo-p-dioxin (2,8-DCDD) was observed, together with HCl. This experiment appears as the ultimate proof for the possibility of conversion of the phenolic form of triclosan into 2,8-DCDD. Indication of a never described before competitive reaction pathway leading to formation of a ketene species could also be found in the spectra of the irradiated matrix. The UV-induced triclosan → 2,8-DCDD reaction seems to occur through initial photoproduction of the corresponding phenoxyl radical, and involve in the initial step participation of dissociative (ππ*) excited states along the OH stretching coordinate, as observed previously for other phenol derivatives. The photochemically detached hydrogen atom derived from triclosan may then react with the closest located chlorine atom in the triclosan molecule to yield HCl and a biradical species, which can subsequently undergo a ring-closure reaction by intramolecular recombination, leading to the observed 2,8-DCDD.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2011.10.023.

References
