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Environmental Implications of the Surfactant Effect on the Photochemistry of (Substituted) 4-Chlorophenols in Water

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The effect of surfactants (cationic, anionic, and nonionic) on the direct photochemistry of selected chlorophenol antimicrobials in aqueous solution has been investigated. The inclusion of the starting aromatics into micelles markedly directs the reaction towards a cleaner process (mainly photoreduction), contrasting with the variety of processes observed when the irradiation is carried out in neat water. This could have some implications from the environmental point of view because such paths may be significant in natural aquatic systems.

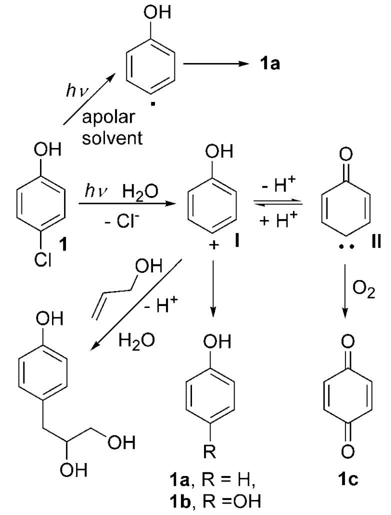
Introduction

Chlorinated aromatics are perhaps the most harmful organic contaminants present in the environment.[1] Among them, chlorophenols play an important role as broad-spectrum antimicrobial agents and disinfectants, intermediates in the synthesis of pesticides and herbicides, and as preservative agents (e.g., for leather or wood). Chlorophenols are persistent environmental pollutants with a strong bioaccumulation potential and toxicity.[2] Some of them are included in the list of priority pollutants by the US Environmental Protection Agency.[3]

The environmental impact and the toxicity are mainly determined by the number of chlorine atoms present and on their position, although medium parameters, such as pH, temperature, and the presence of various organic and inorganic compounds also have a role. Chlorophenols are widely detected especially in natural aquatic systems where their concentration can reach up to about several $\mu g\,L^{-1}$.[4]

Apart from specific removal treatments,[5,6] the disappearance of such pollutants in the environment mainly involves photochemical and biochemical paths.[7] Solar light-induced reactions[8] include C–Cl bond dissociation, substitution, oxidation and reduction with largely varying yields and rates.

The photochemistry of 4-chlorophenol (**1**) is often chosen as a model.[9] In apolar solvents such as cyclohexane, homolytic cleavage of the aryl–chlorine bond takes place, whereas in protic or nonprotic polar media, the cleavage is heterolytic and forms a triplet phenyl cation.[10,11] The latter is the primary step in water and is followed by further processes that in turn depend on the additives present,[12] as summarized in Scheme 1. The 4-hydroxyphenyl cation (**I**) is in equilibrium with 4-oxocyclohexa-2,5-dienylidene carbene (**II**). In oxygen-saturated solutions the latter intermediate adds oxygen and yields benzoquinone[12–14] along with some 2,4′-hydroxy-5-chlorobiphenyl. If a sufficient amount of a π nucleophile such as an olefin (e.g., allyl alcohol)[11] is present in solution, this traps cation **I** resulting in an overall $Ar S_N 1$ reaction (Scheme 1).[15]



Scheme 1. Photochemistry of 4-chlorophenol in apolar and aqueous media.

The above results suggest that the photoreaction of chlorophenols does not guarantee depollution of the aquatic system because photoproducts **1a–c** are as least as toxic as **1**[16] and at any rate formation of a mixture of products makes the assessment difficult. However, we recently observed that cyclodextrin (CD) complexation makes the course of the reaction independent of the presence of oxygen and phenol, the main (or exclusive, this depends on the size of the CD cavity) product.[12] This result was rationalized by the efficient hydrogen abstraction from CD by the phenyl cation (Scheme 2). The simplification of the reaction course obtained by complexing the

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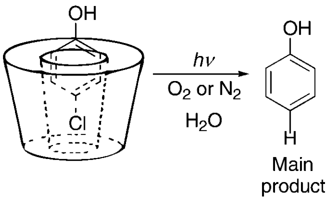


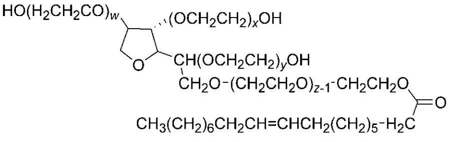
Scheme 2. Photochemical behavior of 4-chlorophenol in cyclodextrins

phenol is appealing and we reasoned that this may extend to other complexing agents, more likely to be present in polluted water. We thus investigated the photochemistry of chlorophenols in water in the presence of surfactants, which are themselves pollutants often present in river waters that can easily form micelles, with the aim of assessing whether they affected the photochemical fate of chlorophenols.[17]

Results and Discussion

The chlorinated phenols chosen for this investigation were 4-chlorophenol **1**, the most studied compound of this class, and two common antimicrobials, namely 4-chloro-3-methyl sodium phenate (**2**) and 2-benzyl-4-chlorophenol[19] (**3**). These compounds were irradiated in water in the presence of selected surfactants (see Table 1), chosen among the most often used in commercial formulations, namely, the anionic sodium dodecyl sulfate (SDS, **4**), the cationic *N*,*N*-didecyl-*N*,*N*-dimethylammonium chloride (**5**) and two nonionic surfactants of polyether structure, namely the C_{12}–C_{18} fatty alcohol polyglycol ether (**6**) and the polyethylene glycol sorbitan monooleate (Tween 80, **7**). The last additive was previously treated with active charcoal to eliminate most of the color, although a residual absorption at $\lambda < 260$ nm remained (see below). The surfactants were used in 1–2% w/w solutions (10–20 g L^{-1}), thus in a concentration above their critical micelle concentration (cmc),[18] and phenols **1**–**3** in the range $2–4 \times 10^{-4}$ M, chosen because this allowed effective micelles incorporation.

Table 1. Anionic, cationic, and nonionic surfactants used.

Surfactants	
$CH_3(CH_2)_{10}CH_2OSO_3^- Na^+$	**4** (SDS)
$(C_{10}H_{21})_2(CH_3)_2N^+Cl^-$	**5**
$C_{12-18}H_{(12-18)2+1}(OCH_2CH_2)_7H$	**6**
 Sum of *w* + *x* + *y* + *z* = 20	**7** (Tween 80)

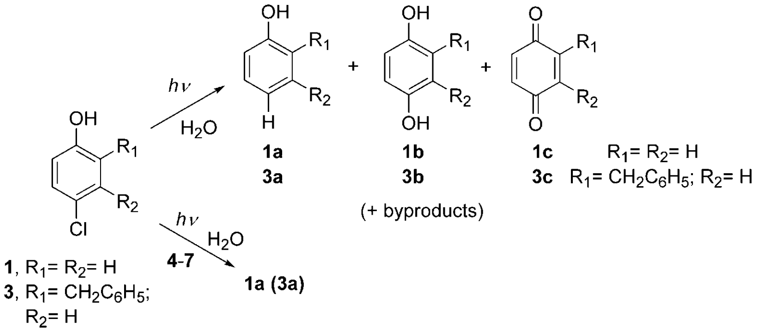
Irradiations were carried out under both deaerated and aerated conditions in neat water in the absence or in the presence of the chosen surfactant. A multilamp apparatus equipped with six phosphor coated lamps centered at 310 nm was adopted (see Experimental Section). Two kinds of experiments were carried out: 1) 10 min irradiation led to the almost complete consumption of the starting chlorophenols; after photolysis, the products formed and the pH of the solution were assessed; and 2) the decomposition quantum yield (Φ_r) of compounds **1**–**3** was measured in separate, low conversion experiments on an optical bench under all of the conditions tested.

The results with 4-chlorophenol **1** (4×10^{-4} M) are summarized in Table 2. In neat water, the quantum yield of decomposition (Φ_r 0.6 to 0.8) was lower in aerated than in nitrogen-equilibrated aqueous solutions, but the addition of a cationic or nonionic surfactants obliterated the difference and the anionic surfactant made Φ_r (air) > Φ_r (N_2). Detailed analysis of the high conversion (>90%) experiments showed that chloride was stoichiometrically liberated and the pH decreased from the initial value (ca. 6), more markedly in aerated solution (down to 3.4 with 2% **6**) than in deaerated solution (down to 4.4 with 2% **7**). Under air, the main product was hydroquinone **1b** (Scheme 3 and Table 2). The result was already apparent from the strong band at 260 nm (Figure 1) and was confirmed by

Table 2. Quantum yield of reaction and course of the photochemical reaction of 4-chlorophenol (4×10^{-4} M) in water and in the presence of surfactants (10 min irradiation).

Surfactant, amount	Conditions	pH		Consumption [%], 10 min	Φ_r	Products yield [%][a]
		Starting	Final			
none	deaerated	5.8	5.4	93	0.83[b]	**1a**, 25; **1b**, 17; **1c**, <1
none	aerated	5.8	3.5	96	0.62[c]	**1b**, 47; **1c**, 1
4, 3×10^{-2} M	deaerated	5.9	5.5	98	0.74	**1a**, 54; **1b**, 5
4, 3×10^{-2} M	aerated	5.9	3.9	93	0.84	**1a**, 42; **1b**, 3; **1c**, 1
4, 3×10^{-2} M	aerated[d]	n.d.	n.d.	37[e]	n.d.	**1a**, 40; **1b**, 2; **1c**, 1
4, 10^{-3} M	aerated	n.d.	n.d.	98	n.d.	**1a**, 15; **1b**, 43; **1c**, 1
5, 2% w/w	deaerated	5.7	5.0	99	0.58	**1a**, 48; **1b**, 8
5, 2% w/w	Aerated	5.7	3.5	97	0.60	**1a**, 36; **1b**, 3
6, 2% w/w	deaerated	6.3	4.5	99	0.60	**1a**, 49
6, 2% w/w	aerated	6.3	3.4	92	0.58	**1a**, 26; **1b**, 1; **1c**, <1
7, 2% w/w	deaerated	5.9	4.4	95	0.57	**1a**, 50; **1b**, 1
7, 2% w/w	aerated	5.9	3.8	93	0.57	**1a**, 30; **1b**, 1

[a] HPLC yields based on consumed **1** [b] See Ref. [13]. [c] See Ref. [12]. [d] Reaction carried out in a quartz tube in a solar simulator (SolarBox, Xe lamp, see text). [e] 4 h irradiation.



Scheme 3. Effect of surfactants on the photochemistry of compounds **1** and **3**

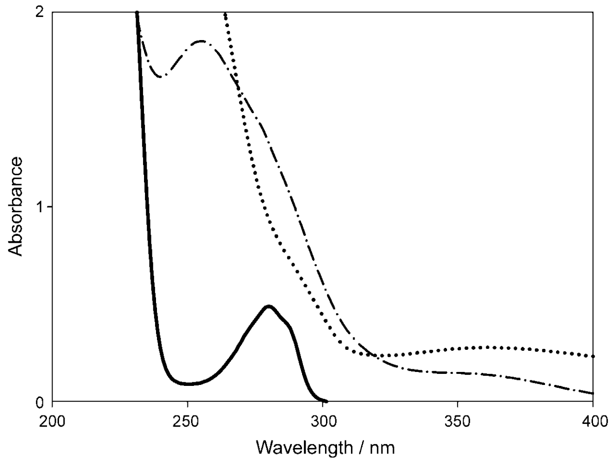


Figure 1. Absorption spectra of a 4×10^{-4} M water solution of **1** (solid line); same after 10 min irradiation under deaerated (dashed line) and air-equilibrated conditions (dotted line).

HPLC analysis (see Experimental Section); a trace of benzoquinone (**1c**) was also detected. Under nitrogen, phenol **1a** was the main product, with a **1a**/**1b** ratio of 1.45.

Whereas in neat water the irradiated solution was slightly yellow, in the presence of any of the surfactants, it remained colorless. Under these conditions, the formation of **1b** was inhibited (compare Figure 2 and Figure 1) and made **1a** the main product independent of the presence of oxygen, with a **1a**/**1b** ratio >5 and in most cases >10.

An aerated solution of **1** containing **4** (3×10^{-2} M) was likewise irradiated in a SolarBox equipped with a xenon lamp to mimic the solar irradiation. After 4 h irradiation, 4-chlorophenol was partially consumed (37%) with the same product distribution as when an UV lamp was used. When **4** was added in 10^{-3} M amount (eight times lower than its cmc),[18] some phenol was formed (ca. 15%) but **1b** was by far the main product.

4-Chloro-3-methyl sodium phenate (**2**) was present as the anion, but the photochemical behavior was quite similar to that of **1**. The starting pH was slightly basic (ca. 9, one unit below in the presence of the cationic surfactant). Acidity liberation upon irradiation decreased the pH and gave almost neutral or slight acidic solutions. The reaction quantum yield was slightly lower than that of **1**, with Φ_r (**2**) of about 0.65 for a 4×10^{-4} M solution in neat water, in this case independent of the presence of oxygen. The addition of any of the surfactants uniformly reduced Φ_r to about 0.45, but the main effect under these conditions was on the product distribution. In neat water, a complex mixture was formed, containing a small amount of **2a** (under nitrogen) or **2b** (under air; Table 3 and Scheme 4), whereas a much cleaner reaction course was observed in the presence of any of the surfactants **4**–**7**, with cresol **2a** as the major product both in aerated and deaerated solutions. The highest amount of **2a** (up to 60%) was detected when ammonium salt **5** was used, whereas the presence of the other surfactants allowed the formation of **2a** (at least 40%). Irradiation in neat water led to the formation of a species highly absorbing around 260 nm, particularly under oxygen, while this was not the case with any of the surfactants, which gave almost superimposable UV spectra (see the Supporting Information, Figures S1 and S2).

2-Benzyl-4-chlorophenol (**3**, 2×10^{-4} M) was likewise decomposed with liberation of hydrochloric acid with a quantum yield of approximately 0.6 in neat water and about 0.45 in the presence of surfactants with virtually no oxygen effect. However, a dramatic change occurred in product distribution. Thus, a complex mixture was obtained upon irradiation in neat water with **3a** (15% under nitrogen, 9% under air) as the main product accompanied by traces of **3c**; however, the photoreaction showed a high mass balance (up to 90%) in the presence of surfactants, with *o*-benzylphenol (**3a**) as the exclusive product (Scheme 3, Table 4). The addition of surfactants led again to a reduction of the 260 nm absorption (see the Supporting Information, Figures S3 and S4), although the effect was less uniform in this case.

In the experiments above, the amount of surfactants added has been above the critical micelle concentration, under conditions that may deeply affect chemical reactions with respect to neat (aqueous) solvent.[20,21] Thus, the solubility of nonpolar substrates is enhanced, but because these are located in a nonpolar and highly viscous environment within the micelles, the conditions differ from both protic and aprotic media and major effects on the reaction rate, the product distribution, the mechanism, and the overall selectivity intervene.[20a] The affinity of chlorophenols for surfactants is well established.[22] Notice further that zeolites[23] and montmorillonite[24] have been shown to be effective sorbents for the removal of chlorophenol contaminants in aqueous systems when the surface is modified by a cationic surfactant.

No significant effects of surfactants **4**–**7** (that are transparent in the λ interval used) on the absorption spectrum of phenols **1**–**3** were observed (Figures 2; see the Supporting Information, Figures S2 and S4) and the quantum yield of the reaction underwent only a limited decrease. These pieces of evidence support that the primary photochemical reaction remains the same in micelles as in neat water, despite the very large

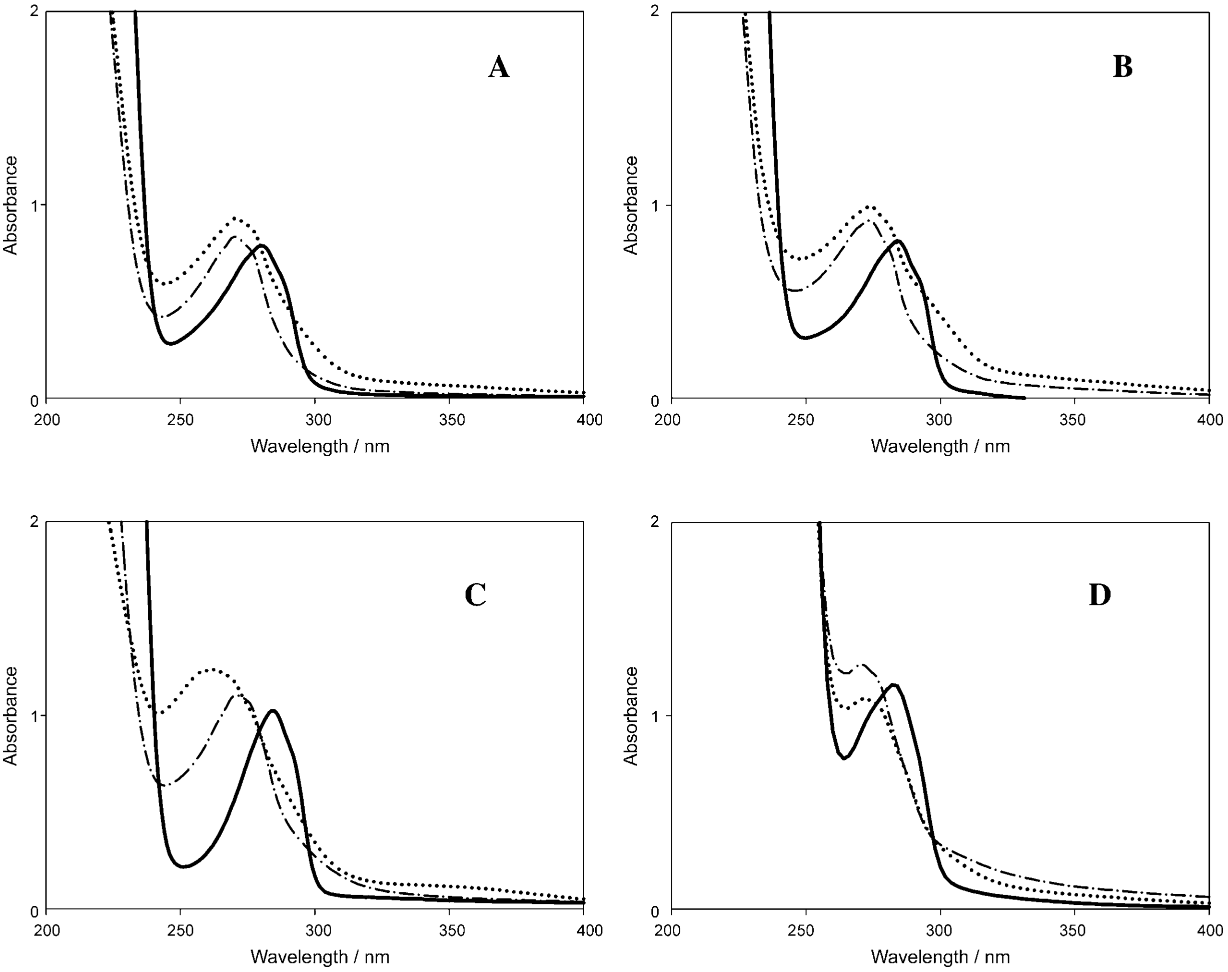


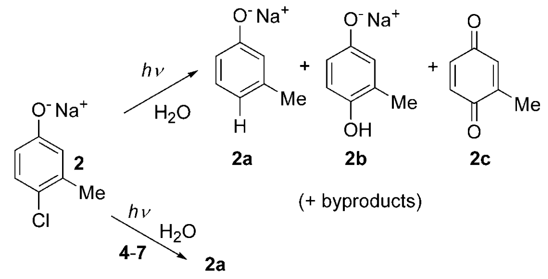
Figure 2. Absorption spectra (solid lines) of a 4×10^{-4} M water solution of **1** in the presence of surfactant **4** (A), **5** (B), **6** (C) and **7** (D) and after 10 min irradiation under deaerated (dashed lines) and aerated (dotted lines) conditions, respectively.

Table 3. Quantum yield of reaction and course of the photochemical reaction of sodium 4-chloro-3-methylphenate (4×10^{-4} M) in water and in the presence of surfactants (10 min irradiation).

Surfactant, amount	Conditions	pH		Consumption [%], 10 min	Φ_r	Products yield [%][a]
		Starting	Final			
none	deaerated	9.1	7.0	95	0.64[b]	**2a**, 14; **2b**, 2
none	aerated	9.1	5.7	90	0.68[b]	**2b**, 14; **2c**, 1
4, 3×10^{-2} M	deaerated	9.3	7.1	100	0.35	**2a**, 46; **2b**, 2
4, 3×10^{-2} M	aerated	9.3	5.8	100	0.40	**2a**, 41; **2b**, 1
5, 2% w/w	deaerated	7.9	6.4	100	0.40	**2a**, 60
5, 2% w/w	aerated	7.9	5.3	100	0.42	**2a**, 53
6, 2% w/w	deaerated	9.0	6.6	100	0.45	**2a**, 52
6, 2% w/w	aerated	9.0	6.7	100	0.47	**2a**, 53
7, 2% w/w	deaerated	9.0	6.7	100	0.46	**2a**, 39
7, 2% w/w	aerated	9.0	6.6	100	0.46	**2a**, 40

[a] HPLC yields based on consumed **2**. [b] Complex mixture formed.

change in product distribution toward a clean dechlorination, particularly with compounds **2** and **3**, which occurred independent of the surfactant (up to 90% with **3**, a result similar to what was reported for the case of 2-chlorophenol).[18]



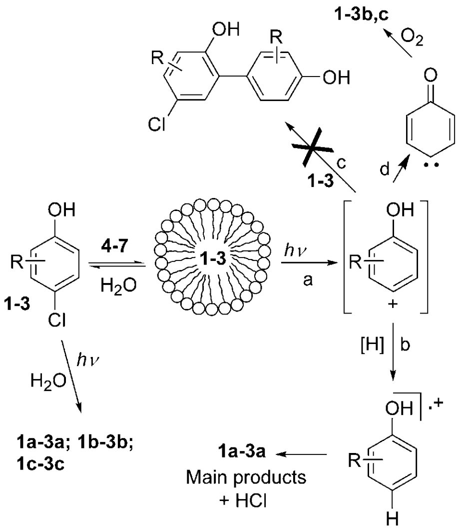
Scheme 4. Effect of surfactants on the photochemistry of compound **2**

The mechanism depicted in Scheme 5 can thus be proposed. Reasonably, chlorophenols molecules are disposed in the micelles with the polar OH group pointed towards the aqueous medium. Thus, despite the low polarity of the inner environment in micelles,[21c] the characteristic photoreaction of chlorophenols in water occurs, namely heterolytic cleavage of the Ar–Cl bond from the triplet state (path a),[10,11,15,18] resulting in hydrochloric acid release.[15] In this way, a phenyl cation is formed, which is a strong but chemoselective electrophile that smoothly adds to π nucleophiles (including olefins, alkynes,

Table 4. Quantum yield of reaction and course of the photochemical reaction of 2-benzyl-4-chlorophenol (2×10^{-4} M) in water and in the presence of surfactants.

Surfactant, amount	Conditions	pH		Consumption [%], 10 min	Φ_r	Product yield [%][a]
		Starting	Final			
none	deaerated	6.2	6.1	98	0.61	**3a**, 15[b,c]
none	aerated	6.2	3.8	95	0.63	**3a**, 9[b,c]
4, 3×10^{-2} M	deaerated	6.3	6.2	100	0.42	**3a**, 56
4, 3×10^{-2} M	aerated	6.3	4.4	100	0.46	**3a**, 49
5, 2% w/w	deaerated	5.5	5.4	100	0.48	**3a**, 75
5, 2% w/w	aerated	5.5	3.7	100	0.46	**3a**, 60
6, 2% w/w	deaerated	6.3	6.1	100	0.44	**3a**, 90
6, 2% w/w	aerated	6.3	4.0	100	0.45	**3a**, 75
7, 2% w/w	deaerated	5.8	4.5	100	0.43	**3a**, 69
7, 2% w/w	aerated	5.8	3.9	100	0.42	**3a**, 68

[a] HPLC yields based on consumed **3**. [b] Complex mixture formed. [c] Compound **3c** also detected by GC–MS analysis (see Experimental Section).



Scheme 5. Photochemistry of substituted chlorophenols in micelles

and aromatics), but not to n donors (water, alcohols), except with the charged ones (e.g., iodide anion).[15,25]

In fact, when generated in methanol, 4-hydroxyphenyl cation does not give 4-hydroxyanisole but rather dihydroxychlorobiphenyls by electrophilic attack on the starting material and phenol by homolytic hydrogen abstraction from the alcohol C–H bond.[10] Another known process is OH deprotonation and trapping of the ylide by oxygen leading to quinone and hydroquinone. In water, under diluted conditions (2×10^{-4} M), neither of the first two processes is viable and a complex mixture is formed, including oxidation products when the irradiation is carried out under oxygen. On the other hand, in micelles, the intermediate is generated (path a) with the divalent carbon directed toward the inner, aliphatic part of the surfactant, so hydrogen abstraction (path b) completely overwhelms other processes, such as coupling (path c) or oxygen trapping (path d). With 4-chlorophenol, some vestige of the aqueous photochemistry remains with the formation of some **1b** under oxygen, at least with surfactants **4** and **5** that lack activated hydrogen to donate,[26] in contrast to the case of **6** and **7** in which ether moieties are present.[12,27] However, introducing a methyl or, better, a benzyl group directs more strictly the positioning of the phenol in the micelle, so that, particularly with phenol **3**, path a is exclusive and high-yielding.

In summary, contrary to other reported photoreactions,[21] micelles are not innocent bystanders in this case. Actually, micelles act as H donors, which is similar to what was previously reported for cyclodextrin.[12] It is interesting to compare the course of the present photoreactions induced by direct irradiation with photocatalytic degradation, often carried out by using titania.[28] The latter process is equally efficient as far as the degradation goes, but does not lead to the clean dechlorination observed here, but rather to complex ring oxidation processes (and finally to mineralization).

Conclusions

The present work demonstrated that a deep modification on the photochemical behavior of chlorophenol disinfectants is achieved when a sufficient amount (reaching the cmc) of surfactant is present in solution. The co-presence of phenolic antimicrobials and detergents in commercial preparations can allow their concomitant release in natural aquatic systems. In this case, reductive photodechlorination of chlorophenols occurs upon absorption of the UV component of solar light. This is not sufficient for an effective depollution. As an example, phenol has a toxicity comparable to (or even higher) than that of 4-chlorinated analogue and this should foster more attention to the actual conditions of photochemical processes occurring in complex aquatic systems in order to predict the effect on the environment.

Experimental Section

General: 4-Chlorophenol (**1**, Carlo Erba), 4-chloro-3-methyl sodium phenate (**2**, grant from Eurospital), and 2-benzyl-4-chlorophenol (**3**) were purified by crystallization before use. SDS (**4**, Fluka), chloride **5**, and ether **6** were used as received. Tween 80 (**7**, Aldrich) was preliminarily treated to eliminate most of the color. Thus, active charcoal was added to a portion of **7** dissolved in CH_2Cl_2 and the solution was brought to reflux overnight. After elimination of the charcoal by filtration and the solvent by evaporation, the resulting surfactant appeared slightly yellow in color. All the solvents were of HPLC purity grade and were used as received. The UV absorption spectra were recorded with a JASCO V-550 spectrophotometer. A SolarBox 1500e (CO.FO.ME.GRA s.r.l., Milan) Xe lamp set at 500 $W m^{-2}$, equipped with an outdoor filter (cutoff 280 nm) and IR treatment to avoid sample heating, has been used in the present work as the solar simulator.

Photochemical reactions: The water solutions containing **1**–**3** (2–4×10^{-4} M) and (when required) the surfactants **4**–**7** (1–2% w/w) were placed in 1 cm diameter quartz tubes and flushed with nitrogen for 10 min (when appropriate), serum capped and irradiated at

295 K in a multilamp apparatus fitted with six 15 W phosphor coated lamps (center of emission 310 nm). Conversion of the starting material and formation of the photoproducts were monitored by HPLC by using a SUPELCO C18 column (250 mm×4.6 mm, 5 μm), MeCN/water as the eluant (40:60 for **1** and **2** or 60:40 for **3**, flux 1 mL min^{-1}) with UV detection at $\lambda = 270$ nm. The attribution of the products formed was determined by comparison with commercial samples and the corresponding amounts were determined by using calibration curves.

o-Benzylbenzoquinone was detected (by comparison with literature data)[29] by GC–MS analysis of the chloroform extract of both aerated and deaerated **3** water irradiated solutions: MS (m/z +1): 199 (100), 182 (45), 170 (20), 142 (22), 116 (20).

Quantum yield measurements: Quantum yield measurements were carried out with an optical bench fitted with a focalized high-pressure mercury arc (150 W) and an interference filter (transmission maximum at 281 nm). Solutions of **1**–**3** ($2–4\times10^{-4}$ M) in 1 cm optical path cuvettes after flushing with nitrogen (when appropriate) were used. The course of the reaction was again monitored by HPLC and the conversion was limited to <20 %. Potassium ferrioxalate was used as the actinometer.

Acknowledgements

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Keywords: alcohols · cations · micelles · photochemistry · surfactants

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