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Journal of Photochemistry and Photobiology A: Chemistry 119 (1998) 39–45

Journal of Photochemistry and Photobiology A:Chemistry

Phototransformation of 4-chloro-2-methylphenol in water: influence of humic substances on the reaction

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Received 20 July 1998; accepted 14 September 1998

Abstract

The phototransformation of 4-chloro-2-methylphenol was studied in distilled, natural or humic substances containing waters. Samples were irradiated under different conditions: in monochromatic light at 280 nm, in polychromatic light with lamps emitting within the wavelength ranges 290–350 nm and 300–450 nm and in solar-light. When 4-chloro-2-methylphenol is irradiated in pure water, dechlorination occurs with a good efficiency ($\Phi = 0.66$). Methylbenzoquinone is the main primary photoproduct in oxygenated solution; methylhydroquinone and methylhydroxybenzoquinone are produced via secondary photolysis of methylbenzoquinone, especially in polychromatic light. Humic substances enhance significantly the rate of photodegradation of 4-chloro-2-methylphenol at $\lambda > 300$ nm. The photoinduced reaction yields 3-chloro-*trans–trans*- and 3-chloro-*cis–trans*-1-methyl-1-one-2,4-hexadienoic acids. The opening of the aromatic ring is explained by the abstraction of the phenolic hydrogen atom by reactive species produced by excitation of the humic substances followed by the reaction of the 4-chloro-2-methylphenoxyl radical with $HO_2^{\cdot}/O_2^{-\cdot}$ radicals. When 4-chloro-2-methylphenol is dissolved in natural waters and exposed to solar-light, dechlorinated and ring opening products are produced. It is deduced that under environmental conditions 4-chloro-2-methylphenol can be phototransformed by both direct and photoinduced processes. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: 4-chloro-2-methylphenol; Direct photolysis; Photoinduced transformation; Humic substances

1. Introduction

4-chloro-2-methylphenol (CMP) is a high production volume chemical figuring in the priority list EEC/793/33. It is, therefore, needed to collect data on this molecule for a better knowledge of its fate in natural waters and for the risk assessment. Photochemical transformations are a possible way of degradation of pollutants, especially in the case of chloroaromatic compounds for which biodegradation is generally difficult. The objective of the present work was to obtain information on the phototransformation of CMP in water from an analytical and kinetic point of view.

The photochemical transformation of CMP was investigated under a variety of reaction conditions. In a first step, CMP was photolysed in pure water in order to obtain basic data on the photoreactivity and on the nature of photoproducts. CMP was irradiated with mono- and poly-chromatic light in laboratory conditions and subsequently exposed to solar-light. In a second step, the influence of humic substances, that are naturally-occurring chromophores, was investigated. Finally, phototransformation studies using natural waters sampled in different sites were undertaken.

2. Experimental

CMP, methylhydroquinone ($MeQH_2$) and methylbenzoquinone (MeQ) were purchased from Aldrich. CMP was purified by sublimation before use. Water was purified with a Milli-Q device (Millipore). Methanol (SDS) was HPLC grade and dichloromethane (Aldrich) was of purity 99.6%, free of stabiliser. Humic acids (HA) were extracted by a standard procedure from the surface (A_1) horizons of a mountain acid soil Ranker. Fulvic acids (FA) were extracted from the same Ranker soil [1]. The solutions of humic substances ($10\ \mathrm{mg\ l^{-1}}$) were buffered at $pH = 6.5$ with phosphates and filtered through 0.45 μm Millipore filters prior to irradiation. The samples of natural rivers were obtained the day before the experiments. Sample 1 was collected in the torrent Couze-chambon before Montaigut, sample 2 in river Allier and sample 3 in the lake Pavin.

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PII: S1010-6030(98)00401-8

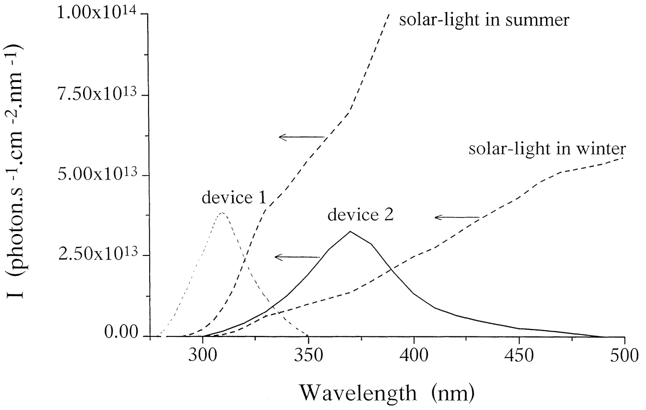


Fig. 1. Spectral photon irradiancies for solar light in summer and in winter [given by R. Franck and W. Klöppfer Chemosphere 17 (1988) 985–994] and for devices 1 and 2.

Samples were filtered through 0.45 μm Millipore filters and stored at 4°C.

Monochromatic irradiations of CMP at 280 nm were performed using a xenon lamp equipped with a Schoeffel monochromator. Solutions containing CMP (1.0×10^{-4} M) in distilled or natural waters and in the presence of the humic substances (10 mg l^{-1}) were irradiated with polychromatic light in two different devices. The first one was equipped with six fluorescent tubes (DUKE sun lamp FL20E) emitting within the range 280–350 nm with a maximum located at 310 nm (Fig. 1). The wavelengths shorter than 290 nm were cut off using a pyrex-glass reactor. The second device was equipped with a fluorescent lamp (Philips TLAD 15 W/05) emitting within the wavelength range 300–450 nm with a maximum of emission at 365 nm (Fig. 1). Samples were also exposed to solar-light in pyrex-glass reactors. Irradiations were performed in February and June. The solutions containing CMP in pure water and in mixture with HA and FA were irradiated simultaneously. In this way, the same amount of photons was received by each solution and it was possible to determine the influence of the humic substances on the rates of CMP disappearance.

UV spectra were recorded on a Cary 3 (Varian) spectrophotometer. ^{1}H NMR spectra were taken on a Brucker AC400 spectrometer. A Hewlett-Packard model 5985 GC–MS at a ionization potential of 70 eV was used to obtain the mass spectra. Products were introduced directly or after GC separation on a Supelco capillary column PTE-5 (30 m × 0.25 mm i.d.). The injector, the transfer line and the ion source were maintained at 250°C. The temperature of the column was programmed from 70 to 220°C at 20°/min. Helium was used as carrier gas. The HPLC–MS–MS analyses were performed with a Therma Separation Product Spectra series gradient pump P400 equipped with a 25 cm × 4.6 mm column packed with a 5 μm Alltima C_{18} reversed-phase material (Alltech). The MS system for HPLC–MS–MS analyses consisted of a Finnigan MAT LCQ mass spectrometer equipped with a Finnigan MAT atmospheric pressure chemical ionisation (APCI) and an electrospray ionisation (ESI) source. For HPLC–ACPI–MS, the eluent was water–methanol (40%–60%) delivered at 1.0 ml/min. Nitrogen was used as shealth gas at 80 ml/min and helium as auxiliary gas at 10 ml/min. Vaporiser and capillary temperatures were set at 450 and 150°C respectively, and corona discharge at 5 μA. The MS operated in positive ionisation mode. For HPLC–ESI–MS analyses, a mixture water–acetic acid–methanol (40%–0.1%–60%) was used at a flow of 0.8 ml/min. At the end of the chromatographic column, the eluent was splitted, and the MS inlet flow rate was 0.2 ml/min. Nitrogen was used as shealth gas at 81 ml/min and helium as auxiliary gas at 9 ml/min. The capillary temperature was set at 265°C and the spray voltage was 4 kV. Analytical HPLC was carried out on a Waters apparatus equipped with a photodiode array detector (model 996) using a C_{18} reverse phase column Lichrospher (Merck). The eluent was a mixture water–orthophosphoric acid–methanol (40%–0.1%–60%). Preparative HPLC was performed on a Gilson apparatus with UV detection using a semi-preparative microsorb 3 μm column and a mobile phase water–orthophosphoric acid–methanol (50%–0.02%–50%). Potassium ferrioxalate was used as chemical actinometer. DOC measurements were performed by Institut Louise Blanquet (Clermont-Ferrand, France) using a standard method.

3. Results

3.1. Irradiation of CMP in pure water

The maximum of absorption of molecular CMP is located at 280 nm. At this wavelength, the molar extinction coefficient is equal to 1750 $mol^{-1}\,l\,cm^{-1}$ (see Fig. 2). At wavelengths longer than 300 nm, the absorption of CMP is very weak (inset of Fig. 2).

The irradiation of aerated solutions of CMP (1.0×10^{-4}–7.0×10^{-4} M) by monochromatic light at 280 nm led to the formation of MeQ (chemical yield = 86%) and to the

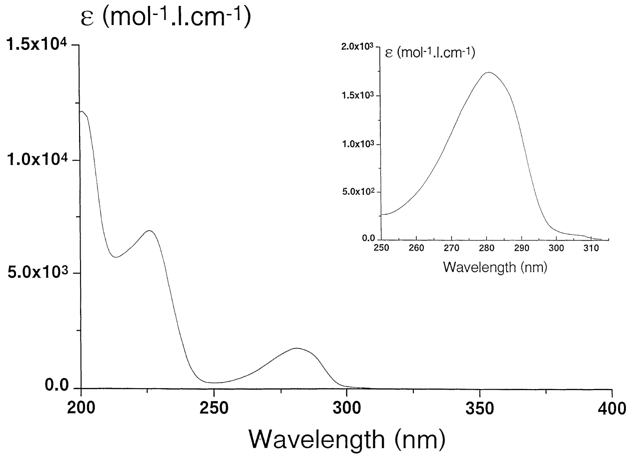


Fig. 2. Absorption spectrum of molecular CMP in water.

release of HCl. The quantum yield of photolysis was evaluated as 0.66. In the absence of oxygen, MeQ was not formed. $MeQH_2$ was produced with a chemical yield depending on the CMP concentration: 57% for $[CMP] = 1.0 \times 10^{-4}$ M and 13% for $[CMP] = 7.0 \times 10^{-4}$ M. The quantum yield of CMP disappearance increased with the CMP concentration: 0.70 ± 0.05 for $[CMP] = 1.0 \times 10^{-4}$ M and 0.88 ± 0.05 for $[CMP] = 7.0 \times 10^{-4}$ M. Aerated solutions of CMP were also irradiated by polychromatic lamps emitting within the wavelength range 290–350 nm. In these conditions, several photoproducts were detected, and MeQ was found in traces. The reaction mixture was analysed by GC–MS after extraction with dichloromethane. The two following photoproducts were characterized: $MeQH_2$ ($m/e = 124$, $\lambda_{max} = 290$ nm) and methylhydroxybenzoquinone (MeQOH) ($m/e = 138$, $\lambda_{max} = 254$ and 395 nm in acidic medium). CMP was also irradiated in the range 300–450 nm. Long irradiation times were necessary to observe a transformation because CMP absorbs weakly in this wavelength range. $MeQH_2$ and MeQOH were the main photoproducts. Finally, CMP was exposed to solar-light and these two products were produced again.

MeQ (5×10^{-4} M) was irradiated alone at $\lambda > 300$ nm. In these conditions, $MeQH_2$ and MeQOH were formed in equimolar amounts. It can be, therefore, deduced that $MeQH_2$ and MeQOH produced upon irradiation of CMP solutions by polychromatic light or in solar-light were secondary photoproducts resulting from the photolysis of MeQ.

3.2. Irradiation of CMP in the presence of humic substances

The influence of the humic substances on the phototransformation of CMP in different irradiation conditions was studied. Results are reported in Table 1. When CMP was irradiated by the polychromatic lamps (within the wavelength range 290–350 nm), the rate of phototransformation was almost the same in the absence as in the presence of humic substances. By contrast, when solutions were irradiated within the wavelength range 300–450 nm, the rate of CMP loss was about 40 times higher in the presence of HA or FA than in their absence. The humic substances increased, therefore, significantly the rate of transformation of CMP in these irradiation conditions. When solutions were exposed to solar-light, a significant enhancing effect of humic substances on the rate of CMP loss was observed too.

The irradiation at $\lambda > 300$ nm or in solar-light of solutions containing CMP (10^{-4} M) and HA or FA ($10\ mg\ l^{-1}$) yielded four photoproducts: $MeQH_2$, MeQOH, I and II. I and II were detected at very low extent of the reaction and seemed to be primary products. It must be noted that I and II were retained on the HPLC column only when the mobile phase was acidified. It means that the pK_a value of these compounds is lower than 5. In order to identify I and II, we proceeded as follows. Two portions of 100 ml were exposed to solar-light until the conversion extent of CMP reached 60%. The irradiated samples were evaporated to 10 ml, acidified with phosphoric acid and filtered to remove unsoluble CMP and HA. For NMR identification, photoproducts I and II were separated by preparative HPLC. In order to perform HPLC–MS analyses, photoproducts I and II were extracted from the aqueous solution with dichloromethane (yield 75%). Part of this solution was evaporated to dryness under a stream of nitrogen. The sample was reconstituted with 1 ml of water/methanol (50 : 50, v/v) and analysed by HPLC–ESI–MS–MS (see Fig. 3). The remaining dichloromethane solution was esterified by treatment with 300 µl BF_3-methanol at 50°C for 30 min. The sample was evaporated to dryness and treated as before. The methylester of photoproducts I and II were analysed by HPLC–APCI–MS–MS (see Fig. 3). Analyses by NMR and HPLC–MS gave the following results:

Photoproduct I

$\lambda_{max} = 276$ nm in H_2O, pH = 3; ^1H NMR ($CDCl_3$, ppm) 7.34 (d, 1H, $J = 15.3$ Hz), 6.63 (d, 1H, $J = 15.3$ Hz), 6.6 (s, 1H), 2.5 (s, 3H), HPLC–ESI–MS–MS, $t_r = 3.54$ min, mass $m/z = 173$ corresponding to $[M - H]^-$, product ion mass $m/z = 155$ corresponding to $[M - H_2O - H]^-$.

Methyl ester derivative

HPLC–APCI–MS–MS, $t_r = 4.81$ min, mass $m/z = 189$ corresponding to $[M + H]^+$, product ions mass $m/z = 171$ corresponding to $[M - H_2O + H]^+$, mass $m/z = 161$ corresponding to $[M - CO + H]^+$, mass $m/z = 143$ corresponding to $[M - CO - H_2O + H]^+$.

Photoproduct II

$\lambda_{max} = 280$ nm in H_2O, pH = 3; ^1H NMR ($CDCl_3$, ppm) 8.44 (d, 1H, $J = 15.1$ Hz), 6.64 (s, 1H) 6.6 (d, 1H, $J = 15.1$ Hz), 2.35 (s, 3H), HPLC–ESI–MS–MS, $t_r = 4.08$ min, same results as for photoproduct I.

Table 1
Percentage of CMP loss in solutions containing CMP (10^{-4} M) alone or the presence of HA ($10\ mg\ l^{-1}$) or FA ($10\ mg\ l^{-1}$) irradiated in several devices

Conditions	Percentage of CMP loss (%)		
	$290 < \lambda < 350$ nm $t_{irr} = 15$ min	$300 < \lambda < 450$ nm	Solar-light (in June) $t_{irr} = 6$ h
CMP	42 ± 4	4 ± 2 in 40 h	2 ± 1
CMP + HA	39 ± 4	18 ± 2 in 4 h	37 ± 4
CMP + FA		16 ± 2 in 4 h	18 ± 2

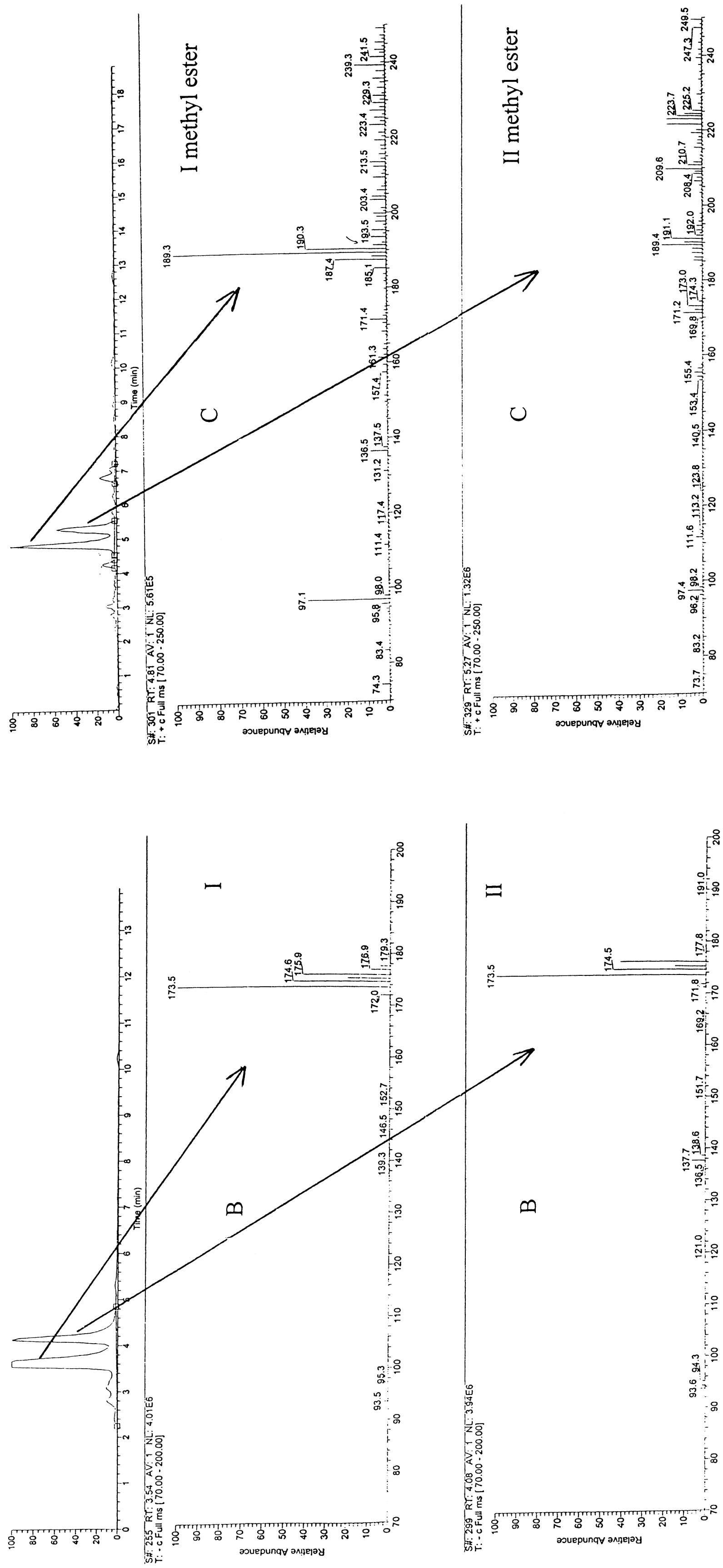
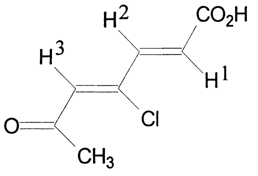


Fig. 3. HPLC–MS spectra of I, I methyl ester, II and II methyl ester (A) UV chromatogram (B) ESI–MS spectra, negative ionization mode (C) APCI–MS spectra, positive ionization mode.

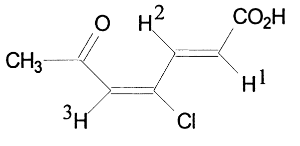
Methyl ester derivative

HPLC–APCI–MS–MS, $t_r = 5.27$ min, same results as for methyl ester derivative of product I.

Obviously, I and II were chlorinated compounds with very close structures since they exhibited similar absorption and mass spectra. Moreover, the only difference in the NMR spectra was the chemical shift of the proton H^2: 7.34 ppm in I and 8.44 ppm in II. The coupling constant between H^1 and H^2 was equal to 15.3 Hz. This high value is characteristic of a *trans* coupling between two vinyl hydrogen atoms and showed that I and II were ring opening products. The chemical shifts of H^1 and H^2 measured in muconic esters were 6.15 and 7.28 ppm, respectively for the *trans–trans* isomer with $J_{H1–H2} = 15.8$ Hz and 6.12 and 8.4 ppm for the *cis–trans* isomer with $J_{H1–H2} = 16.0$ Hz [2]. These data resembled those found for I and II. The surprisingly high chemical shift of H^2 in the *cis–trans* isomer was attributed to the fact that this proton is in the close environment of the carbonyl group. A significant difference in the chemical shift of H^2 was also observed in the case of *trans–trans* and *trans–cis*-2,4-hexadienic-6-oxo-6-phenyl acid [3]. Based on the NMR and mass spectra data, we concluded that I and II have the following structures:



I



II

The absorption spectra confirm the structures too: the broad bands centered around 280 nm are characteristic of a highly conjugated structure. By comparison, the maximum of absorption of muconic acid which is a diacid is located at 254 nm.

The distribution of the four photoproducts depended on the conditions of irradiation. When solutions containing CMP and humic substances were irradiated within the range 290–350 nm, $MeQH_2$ and MeQOH were the main photoproducts (chemical yields around 37%) and photoproducts I and II were detected as traces. When the solutions were irradiated by the lamps emitting within the range 300–450 nm, the chemical yields of $MeQH_2$ and MeQOH decreased to 20% and 10%, respectively and the photoproducts I and II were formed in greater amounts than in the previous case. The irradiation of CMP-humic substances mixtures in solar-light in June gave results very similar to those obtained in the latter device. On the other hand, we noticed that the formation of $MeQH_2$ and MeQOH was drastically reduced when the irradiations were performed in February, i.e. in conditions where the solar spectrum is shifted to longer wavelengths.

Table 2
Percentage of CMP loss upon irradiation in the presence of FA (10 mg l^{-1}) or in natural waters sampled in February in three rivers

Conditions	DOC (mg l^{-1})	Percentage of CMP loss
Distilled water	0	4 ± 2% en 40 h
Distilled water + FA; $OD_{365} = 0.075$	4.00	16 ± 2% in 4 h
Sample 1; $OD_{365} = 0.071$	2.45	9 ± 2% en 40 h
Sample 2; $OD_{365} = 0.083$	2.00	10 ± 2% en 40 h
Sample 3; $OD_{365} = 0.016$	1.20	6 ± 2% en 40 h

(CMP) = 10^{-4} M. OD_{365}: absorbance measured at 365 nm in a 5 cm-path cell.

3.3. Irradiation of CMP in natural waters

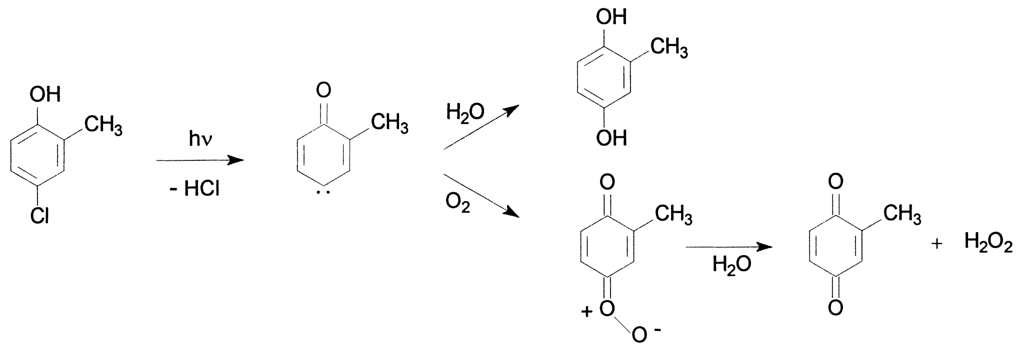
In order to have a better insight into the mechanism of phototransformation in natural conditions, CMP was irradiated in waters sampled in different sites using the lamps emitting within the wavelength range 300–450 nm. These irradiation conditions were chosen because, as it was shown in the previous paragraph, they simulated the best solar-light exposures. Quantitative results are given in Table 2. With the three water samples, the rates of CMP phototransformation were higher than that measured in distilled water and slower than that measured in the presence of FA. The rate of CMP photodegradation was the lowest in the water sample 3, for which the DOC and the OD_{365} values were the lowest. Irradiation of CMP in the three natural waters and in FA solutions yielded $MeQH_2$, MeQOH, I and II. The proportions of I and II were lower with the sample 3 than with samples 1 and 2.

4. Discussion

The mechanism of direct and humic substances-mediated phototransformations of CMP are clearly different as indicated by the fact that the photoproducts are distinct. The direct photolysis leads to dechlorination whereas the photoinduced reaction yields chlorinated ring opening products.

The direct phototransformation of CMP exhibits the same characteristics than that of 4-chlorophenol [4,5]. It was shown that by excitation of 4-chlorophenol HCl is released and a carben is formed [6]. Based on these previous results, the production of MeQ in aerated solution and $MeQH_2$ in the absence of oxygen can be explained by the Scheme 1.

The irradiation of aerated CMP with polychromatic light yields different protoproducts due to the fact that MeQ absorbs photons and is photolysed in turn. Hydroquinone and hydroxybenzoquinone are produced upon irradiation of benzoquinone in water [7]. Similarly, we find $MeQH_2$ and MeQOH as secondary photoproducts of MeQ. These compounds absorb also at $\lambda > 300$ nm and are, therefore, phototransformed in secondary reactions. As a consequence, the reaction mixture becomes very complex as soon as the



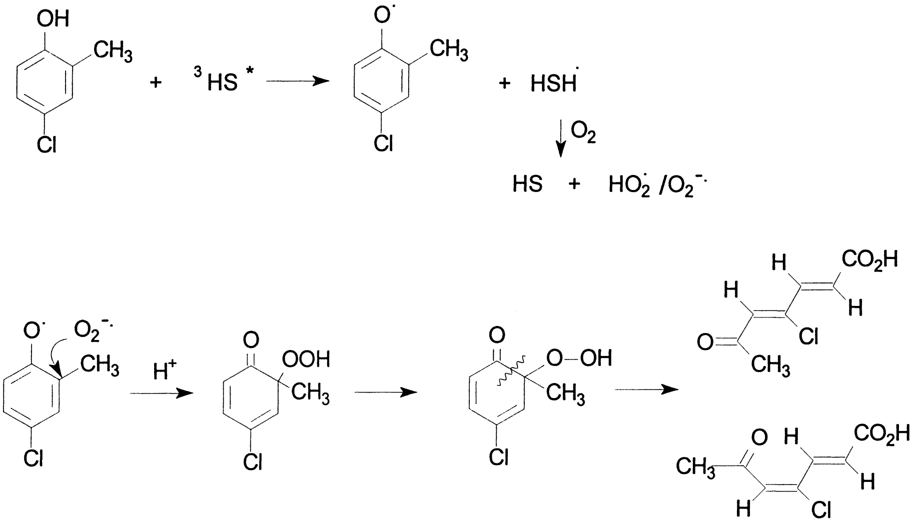
Scheme 1.

conversion extent exceeds 30%–40%. When CMP is irradiated within the wavelength range 300–450 nm or exposed to sunlight, the direct photolysis occurs and yields $MeQH_2$ and MeQOH, as previously observed. However, the phototransformation process is slow because CMP absorbs weakly above 300 nm.

On the other hand, the formation of ring opening products in the presence of humic substances is likely to be due to the oxidation of CMP by reactive species generated by excitation of the humic substances. Previous studies [1,8] have shown that the irradiation of humic substances produces reactive triplet states capable of abstracting the phenolic hydrogen atoms. This hydrogen atom is further transferred onto oxygen with formation of $HO_2^{\cdot}/O_2^{-\cdot}$ and regeneration of the starting humic substances chromophores. The formation of I and II might, therefore, result from the reactions shown in Scheme 2.

When CMP is irradiated in the presence of humic substances, both direct photolysis and photoinduced reactions can occur. The relative importance of the two pathways depends on the experimental conditions. When the irradiations are performed at $\lambda < 300$ nm, the direct photolysis predominates due the high quantum yield of the reaction. On the other hand, at $\lambda > 300$ nm, the direct photolysis is unimportant because of the very weak absorption of light by CMP and the photoinduced transformation is the main route. This influence of the irradiation wavelength is noticeable in the case of solar-light irradiations. As a proof, the chemical yields of $MeQH_2$ and MeQOH are smaller when solar-light irradiations are performed in February than in June because of the wavelength red-shift in winter.

Humic substances and especially fulvic acids account for as much as 50% of the dissolved organic matter contained in the natural waters. We clearly demonstrated that FA photoinduced the transformation of CMP. As a result it is expected to observe higher rates of CMP degradation in natural than in distilled water. With the sample 3, the DOC and the OD_{365} values were small reflecting low contents in dissolved organic matter and hence in humic materials. In accordance, the photoinduced transformation was a minor pathway and the direct photolysis was the main photodegradation process. With the samples 1 and 2 more heavily loaded in dissolved organic matter, direct and photoinduced processes occurred in similar proportions.



Scheme 2.

5. Conclusions

Direct photolysis and humic substances-photoinduced transformation of 4-chloro-2-methylphenol proceed by two different mechanisms. In the former case, dechlorination occurs with the final primary formation of MeQ or $MeQH_2$. In the latter case, 4-chloro-2-methylphenol is likely to be oxidized by reactive species produced by excitation of humic substances into the 4-chloro-2-methylphenoxyl radical. 3-chloro-*trans–trans*- and 3-chloro-*cis–trans*-1-methyl-1-one-2,4-hexadienoic acids are finally produced. The ring scission may occur by reaction of the phenoxyl radical with $HO_2^{\cdot}/O_2^{-\cdot}$. When CMP is irradiated in the presence of humic substances, both types of reaction take place. At $\lambda < 300$ nm, the direct photolysis predominates whereas at $\lambda > 300$ nm, the photoinduced transformation is the main route of phototransformation. Despite a weak absorptivity at $\lambda > 300$ nm, CMP is likely to undergo a direct photolysis in solar-light, but the rate of CMP degradation is significantly enhanced by humic substances. The phototransformation of CMP is faster in natural than in distilled water. This enhancing effect is attributed to the photoinductive properties of the humic materials contained in the natural waters.

Acknowledgements

Authors acknowledge the financial support given to this work by the EC-JRC-Environment Institute under contract n^{o} 13294-97-10 F1PEI ISP F, and they wish to thank Dr. B. Larsen and Mr. M. Duane for their help and assistance with HPLC–MS–MS analysis.

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