Photochemical behaviour of 1,4-dichlorobenzene in aqueous solution

Laurence Meunier, Jean-François Pilichowski, and Pierre Boule

Abstract: Several photoproducts were identified in the direct photolysis of 1,4-dichlorobenzene (1,4-DCB) in air-saturated aqueous solution, namely 4-chlorophenol, hydroquinone, hydroxybenzoquinone, and 2,5-dichlorophenol. In the absence of oxygen the latter is not formed and phenol was detected, but the unexpected formations of 4,4′-dichlorobiphenyl, 2,4′,5-trichlorobiphenyl, and a terphenyl derivative are observed. Mechanisms are proposed to explain the formations of identified photoproducts. The phototransformation of 1,4-DCB may be photoinduced by NO_3^- or Fe^{III} salts. The main primary product is 2,5-dichlorophenol, which results from a hydroxylation without dechlorination. Some other products have been identified in particular 4-chlorophenol and 2,5-dichlorobenzoquinone in the case of Fe^{III} salts.

Key words: 1,4-dichlorobenzene, photolysis, aqueous solution, induced phototransformation.

Résumé : Plusieurs photoproduits ont été identifiés lors la photolyse du 1,4-dichlorobenzène (1,4-DCB) en solution aqueuse aérée : le 4-chlorophénol, l'hydroquinone, la benzoquinone et le 2,5-dichlorophénol. En absence d'oxygène ce dernier ne se forme pas, mais il apparaît du phénol et surtout on observe la formation de 4,4′-dichlorobiphényle, de 2,4′,5-trichlorobiphényle et d'un dérivé de type terphényle. Des mécanismes réactionnels sont proposés pour expliquer la formation des divers produits identifiés. La phototransformation du 1,4-DCB peut aussi être photoinduite par des ions nitrate ou des sels ferriques. Le principal produit initialement formé est le 2,5-dichlorophénol qui résulte d'une hydroxylation sans déchloration. Quelques autres produits ont été identifiés en particulier le 4-chlorophénol et la 2,5-dichlorobenzoquinone dans le cas des sels ferriques.

Mots clés : 1,4-dichlorobenzène, photolyse, solution aqueuse, transformation photoinduite.

Introduction

1,4-Dichlorobenzene (1,4-DCB) is produced in very large amounts and its use is very popular in many homes. Most often it is used without any precaution as an insect repellant or to eliminate bad smells. It is included in the list of Priority Substances to be assessed under the Canadian Environmental Protection Act (1). Its LD_{50} (500 mg kg^{-1} orally in rats) (2) is a little lower than that of chlorophenols (3). Special attention was focussed on the population exposure in Ontario (1), and its physico-chemical and biological properties were the subject of many studies (4).

The photochemical behaviour of chlorobenzenes in water is interesting since photochemical pathways depend on the solvent and very little is known about the transformation of 1,4-DCB in water. To our knowledge, the direct photolysis of 1,4-DCB in water was briefly reported by Boule et al. (5). The main initial photoreaction was assumed to be photohydrolysis leading to 4-chlorophenol, but products (hydroquinone and hydroxybiphenyls) resulting from secondary reactions were also detected by fluorescence even at low conversions. The quantum yield of disappearance was evaluated at 0.010. The yield of formation of the triplet state in methanol was evaluated at 0.95 by Alfassi and Previtali (6). The same authors measured the rate constant of disappearance of the triplet state in methanol ($[3.0 \pm 0.4] \times 10^5\ s^{-1}$) that corresponds to a lifetime equal to 3.3 μs.

It may be assumed that the mechanism of this reaction is similar to the mechanism of monochlorobenzene transformation into phenol, which was the subject of some controversies. According to Previtali and Ebbesen (7), the main reaction observed when monochlorobenzene is photolyzed in pure water is the transformation into phenol, but the reduction into benzene is also detected. These reactions are assumed to result from two competitive pathways: a singlet state photosubstitution reaction with the radical cation as an intermediate, and a homolytic C—Cl bond cleavage in both excited singlet and triplet states. On the other hand, Tissot et al. (8) observed a quantitative transformation into phenol, which was attributed to the photohydrolysis of a polarized short-lived triplet state that was not directly observed. The transformation of monochlorobenzene induced by hydroxyl radicals was reported by Merga et al. (9). The major prod-

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ucts are the three isomeric chlorophenols. This reaction implies the intermediate formation of an $OH^•$ adduct. No results were reported about the transformation of monochloro- or dichlorobenzenes induced by excitation of photoinducers such as nitrate ions or ferric salts that produce hydroxyl radicals under irradiation.

The aim of the present work is to study the mechanism of the direct phototransformation of 1,4-DCB in pure water. The reactions induced by excitation of nitrate ions and Fe^{III} salts are also considered.

Experimental

Reactants and analytical standards

1,4-Dichlorobenzene (99+%) from Aldrich was used without further purification. The following compounds were used as analytical standards: 4-chlorophenol 99+% (Aldrich), 2,5-dichlorophenol >98% (Fluka), hydroquinone >99.5% (Merck), benzoquinone 99% (Merck), 2,5-dichlorohydroquinone (Kodak). Potassium nitrate, used as photochemical inducer, was obtained from Prolabo RP Normapur, while ferric perchlorate nonahydrate (>97%) was purchased from Fluka.

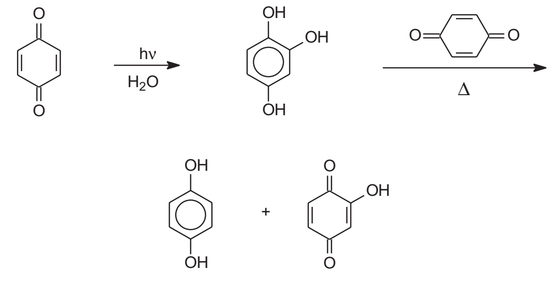
2,5-Dichlorobenzoquinone was obtained by oxidation of 2,5-dichlorohydroquinone by ferric perchlorate in excess. The mixture was heated at 60°C overnight. 2,5-Dichlorohydroquinone was quantitatively transformed and the reaction mixture was directly used for the calibration of HPLC.

4′-Chlorophenyl-*p*-benzoquinone was synthesized from 4-chloroaniline and *p*-benzoquinone. The procedure, which was proposed by Brassard and L'Ecuyer (10) and reported by Carlson and Miller (11), involves the diazotation of 4-chloroaniline. The crude product was recrystallized from an ethanol–acetone mixture. Its structure was supported by mass spectrometry results ((70 eV) *m*/*z*: 218–220, main fragment at 183).

4′-Chloro-2,5-dihydroxybiphenyl-(4′-chlorophenylhydroquinone) (4′-ClPhQH_2) was obtained by reduction of previous compound by sodium dithionite ($Na_2S_2O_4$). The crude product was purified by HPLC. Its formula was supported by mass spectrometry results (*m*/*z*: 220–222, main fragment at 185).

Hydroxybenzoquinone was obtained by irradiation of benzoquinone in solution. Actually, irradiation leads to two main products, hydroquinone and hydroxybenzoquinone, in approximately equal amounts (12).

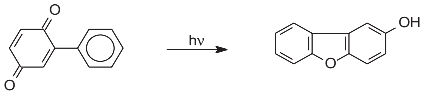
[1]



From the HPLC evaluation of benzoquinone transformed and hydroquinone formed, it is possible to deduce an approximate value of the concentration of hydroxybenzoquinone present.

2-Hydroxydibenzofuran was obtained by photocyclization of phenylbenzoquinone in aqueous solution. Phenylbenzoquinone was provided by Eastman. The reaction is quantitative by irradiation at 365 nm (13):

[2]



Solutions were prepared with water purified with Milli-Q device and controlled by its resistivity (>18 MΩ cm).

Irradiations

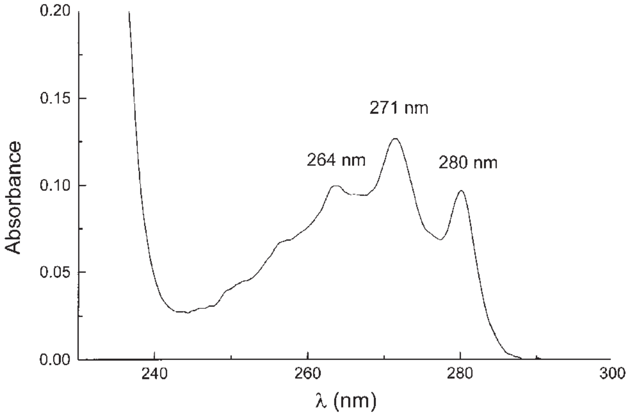
Direct phototransformation of 1,4-DCB was studied by irradiating aqueous solutions at 254 nm in a quartz reactor with a low pressure mercury lamp (germicidal lamp). Reactor and lamp were located on both focal axes of a cylindrical mirror with an elliptic base. The number of photons received was evaluated at 7.09×10^{15} photons cm^{-3} s^{-1} using uranyl oxalate as a chemical actinometer (14).

This device is appropriate for the analysis of products since incident photon flow is relatively intense. However it is not appropriate for the determination of quantum yields since the optical path is not well defined and it is not possible to calculate the percentage of light absorbed. For determination of quantum yields solutions were irradiated in quasi-parallel beam using one germicidal lamp. The incident photon flow was evaluated at 1.33×10^{14} photons cm^{-3} s^{-1} using potassium ferrioxalate as the chemical actinometer (14), since it is much more sensitive than uranyl oxalate.

To study the photochemical degradation induced by excitation of nitrate ions solutions were irradiated with 6 fluorescent lamps Duke GL20E. These lamps emit light not only between 275 and 350 nm with a maximum near 310 nm but also on the mercury lines located at 365, 405, and 436 nm. Wavelengths shorter than 290 nm were cut off using a Pyrex reaction chamber. The number of photons received in the range 290–350 nm was roughly evaluated at 6×10^{15} photons cm^{-3} s^{-1} by uranyl oxalate. It is difficult to obtain an accurate value since the actinometer absorbs a low percentage of photons emitted on mercury lines.

Reactions photoinduced by excitation of Fe^{III} were studied by irradiating solutions with three Mazda MAW125 lamps. These lamps consist of filtered medium pressure mercury arc. Actually, according to the spectrum given by the manufacturer, they emit about 87% of photons at 365 nm, about 6% at 334 nm, and 3% at 313 nm. Emission at 313 nm is perhaps lower after use, therefore, direct excitation of 1,4-DCB is completely excluded. The reactor in Pyrex was placed along the central axis of the device and the solution maintained at room temperature by a cooling jacket. With this device the photon flow received by the solution was evaluated at 1.2×10^{16} photon cm^{-3} s^{-1} using Aberchrome 540 as the actinometer (15), because uranyl oxalate is not sufficiently absorbing at this wavelegth and potassium ferrioxalate is too sensitive for this device.

Fig. 1. UV spectrum of an aqueous solution of 1,4-dichlorobenzene (1,4-DCB) (4.0×10^{-4} M).



Deoxygenation

To control the influence of oxygen on the formation of photoproducts some solutions were deoxygenated. Argon bubbling cannot be used with diluted solutions because of the high vapor pressure of 1,4-DCB. Water contained in the photochemical reactor in the presence of some crystals of 1,4-DCB was deoxygenated by argon bubbling before dissolution of the reactant. After closing the reactor with a septum, the water was magnetically stirred to dissolve the 1,4-DCB. The concentration was evaluated from HPLC according to a reference solution of known concentration.

Analyses

The UV spectra were recorded on Cary 3 (Varian) spectrophotometer. Irradiated solutions were analysed by HPLC on Waters 996 equipped with a photodiode array detector or on Merck L-6200 equipped with fluorescent detection. In both cases the column was C_{18} 250 mm × 4 mm, and the eluent water–methanol (30:70 or 25:75, v/v).

Several photoproducts were identified by GC–MS on Hewlett-Packard 5989 equipped with a capillary column Machery Nagel Optima 5 (25 m × 0.25 mm i.d.). Products were detected by electronic impact (70 ev) mass spectrometry (EI-MS). Nuclear magnetic resonance (NMR) spectra were obtained on samples dissolved in acetone-d_6 (internal reference) with a Bruker AC400 spectrometer. ^{1}H and H–H COSY (2D) classical sequences were used.

The formation of chloride ions in irradiated solutions was measured with a specific electrode after calibration with standard aqueous solutions of NaCl.

Isolation of photoproducts V and VI

About 100 mL of a deoxygenated solution of 1,4-DCB almost saturated was irradiated for 30 min with 6 low pressure mercury lamps. This process was repeated 20 times. The irradiated solutions were filtered to remove remaining crystals of 1,4-DCB and purged with nitrogen to completely eliminate unreacted 1,4-DCB from the solution. The products were extracted with ether and, after evaporation, isolated by HPLC (Column C_{18}, eluent water–methanol (25:75 v/v)).

Table 1. Formation of H^+ and Cl^- in a solution of 1,4-DCB (4.5×10^{-4} M) irradiated at 254 nm.

1,4-DCB converted	$[H^+]$	$[Cl^-]$
2.7×10^{-4} M (59%)	$(3.6 \pm 0.2) \times 10^{-4}$	$(4.0 \pm 0.2) \times 10^{-4}$

Results

Physico-chemical properties of 1,4-DCB

1,4-DCB is a white crystalline solid. According to the Handbook of Chemistry and Physics, its density at 20°C is 1.2475. It is often classified as insoluble in water. Nevertheless, its solubility is sufficient to record its UV spectrum in aqueous solution. The solubility was evaluated by comparing the UV spectrum of an aqueous saturated solution with the spectrum of a solution of known concentration in a mixture MeOH–H_2O (5:95 v/v), and it was evaluated at $(4.8 \pm 0.3) \times 10^{-3}$ M (i.e., 71 ppm), which is in good agreement with literature data (74–80 ppm (4)). It was checked that the molar absorption coefficient of 1,4-DCB is not influenced by low percentage of MeOH.

The UV spectrum of 1,4-DCB is given in Fig.1. The absorption band has several maxima located at 264, 271, and 280 nm. The corresponding molar absorption coefficients were evaluated at 246, 310, and 236 M^{-1} cm^{-1} respectively. No absorption was detected at $\lambda > 290$ nm.

Direct photolysis at 254 nm

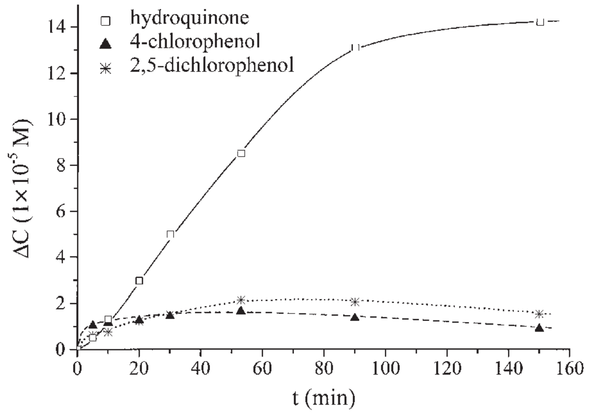
Air-saturated solutions

A solution (4.7×10^{-4} M) was irradiated for a few hours at 254 nm. The quantum yield, calculated by HPLC measurement of the amount of 1,4-DCB transformed, was determined to be $\phi = 0.050 \pm 0.01$. This value is significantly higher than the previous evaluation (0.01) (5). The significant increase of absorbance during the irradiation complicates the evaluation of absorbed light and, consequently, the calculation of the quantum yield.

The disappearance of 1,4-DCB can be compared with the formation of H^+ and Cl^- evaluated from the pH decrease and specific electrode measurements, respectively (Table 1). It was experimentally proved that the relative formation of H^+ and Cl^- increases with increasing conversion, which may be related to the elimination of the second chlorine atom in a secondary reaction.

The main products identified on the HPLC chromatogram are hydroquinone (**II**), 4-chlorophenol (**III**), 2,5-dichlorophenol (**IV**), and hydroxybenzoquinone (**I**). Their formations were quantified using commercial compounds (Fig. 2) except for hydroxybenzoquinone, which was only qualitatively identified. It was noted that the formation of 2,5-dichlorophenol is twice as high in oxygen-saturated solution as compared to the air-saturated solution. The major product initially formed is 4-chlorophenol, but it does not accumulate and its formation reached a stationary concentration after a few minutes. This phenomenon is related with a short delay observed in the formation of hydroquinone, which is due to the high transformation quantum yield of 4-chlorophenol, higher than 0.6 according to Grabner et al. (16). Therefore, it was not possible to establish an accurate

Fig. 2. Quantification of the main photoproducts identified in an air-saturated aqueous solution of 1,4-DCB (3.7 × 10^{-4} M) irradiated at 254 nm (one germicidal lamp).

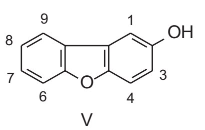


initial mass balance. To prove that 4-chlorophenol cannot accumulate in the solution, 4-chlorophenol (1.4 × 10^{-5} M) was added to a solution of 1,4-DCB (8.9 × 10^{-5} M), and after 10 min irradiation the concentration of 4-chlorophenol was only 1.2 × 10^{-6} M.

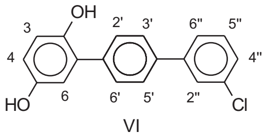
The phototransformation of 1,4-DCB was also observed in solutions irradiated in the range 275–350 nm, along with the formation both of hydroxybenzoquinone and trace amounts of hydroquinone. 4-Chlorophenol and 2,5-dichlorophenol are formed in a first stage as it appears in Fig. 2, but do not accumulate in these conditions due to the fact they absorb at longer wavelengths than 1,4-DCB.

Deoxygenated solutions

Solutions of 1,4-DCB (3.7 × 10^{-4} M), deoxygenated as reported in *Experimental* section, were irradiated at 254 nm. The formation of 2,5-dichlorophenol was not observed, but two unexpected photoproducts **V** and **VI** appeared on the HPLC chromatogram. These two products were not observed in irradiated diluted solutions (6.7 × 10^{-5} M). They were isolated as described in the *Experimental* section and identified by MS and ^{1}H NMR spectroscopy, respectively, as 2-hydroxydibenzofuran (2-HDBF) and 3″-chloro-2,5-dihydroxy-*p*-terphenyl (CDTP):



V



VI

Product **V**: MS *m*/*z* (%): 184 ($M^{\bullet+}$, 100), 128. ^{1}H NMR (CD_3COCD_3) δ: 8.37 (s, OH), 8.00 (dd, *J* = 7.0, 1.3 Hz, H6), 7.55 (dd, *J* = 7.9, 0.9 Hz, H9), 7.47 (dt, *J* = 7.9, 1.3 Hz, H8), 7.47 (d, *J* = 2.5 Hz, H1), 7.44 (d, *J* = 8.8 Hz, H4), 7.33 (dt, *J* = 7.5, 0.9 Hz, H7), 7.01 (dd, *J* = 8.8, 2.5 Hz, H3).

The identification of **V** was corroborated by its typical UV spectrum (maxima at 251, 289, 310–320 nm) and by comparison of its HPLC retention time with those of an authentic sample of 2-HDBF obtained by photolysis of phenylbenzoquinone.

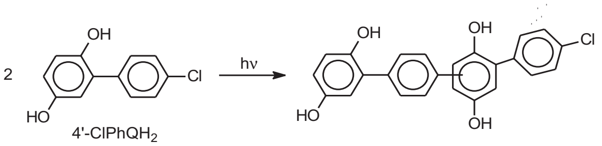
Product **VI**: MS *m*/*z* (%): 296 ($M^{\bullet+}$, 100), 298 ($M^{\bullet+}$, 33), consistent with $C_{18}H_{13}ClO_2$. ^{1}H NMR (CD_3COCD_3) δ: 7.83 (s, OH), 7.82 (s, OH), 7.72 (t, *J* = 1.9 Hz, H2″), 7.70 (s, 4H, H2′, 3′, 5′, 6′), 7.67 (m, H6″), 7.49 (t, *J* = 7.9 Hz, H5″), 7.39 (m, H4″), 6.86 (d, *J* = 3.0 Hz, H6), 6.84 (d, *J* = 8.75 Hz, H3), 6.69 (dd, *J* = 8.75, 3.0 Hz, H4).

It was deduced from the H–H COSY spectrum that the four protons 2′, 3′, 5′, and 6′ are fortuitously equivalent and generate a single absorption (δ = 7.70 ppm) without any apparent coupling constant.

Three other photoproducts were identified as phenol (*m*/*z* = 94), 4,4′-dichlorobiphenyl (*m*/*z* = 222, 224, 226) and 2,4′,5-trichlorobiphenyl (*m*/*z* = 256, 258, 260) from GC–MS analysis of the crude product of phototransformation after evaporation of water.

The formations of 2-HDBF and terphenyl derivative were also observed in deoxygenated solutions of 1,4-DCB irradiated between 275 and 350 nm. Some complementary experiments were carried out to explain the formation of 2-HDBF in deoxygenated solution. (*i*) A deoxygenated solution of hydroquinone (6.7 × 10^{-4} M) and 1,4-DCB ($c \approx 4 \times 10^{-3}$ M) was irradiated in the range 290–350 nm. In these conditions the excitation of 1,4-DCB is negligible compared to the excitation of hydroquinone. It was observed that 2-HDBF appears as one of the main photoproducts. (*ii*) 4′-Chloro-2,5-dihydroxybiphenyl (4′-ClPhQH$_2$), synthesized as described in the *Experimental* section, was irradiated in the range 290–350 nm in various conditions. 2-HDBF was the main photoproduct on HPLC chromatogram of a deoxygenated dilute solution ($c \approx 6 \times 10^{-5}$ M) irradiated for a few minutes. This reaction was not observed in the presence of oxygen and it is a minor pathway when the concentration of 4′-ClPhQH$_2$ is as high as 1.4 × 10^{-3} M. In relatively concentrated solutions irradiation leads to the formation of an insoluble product identified as an adduct resulting from elimination of HCl between two molecules (CI-MS *m*/*z* = 404, 405 [M + 1], and 433 [M + 29]).

[3]

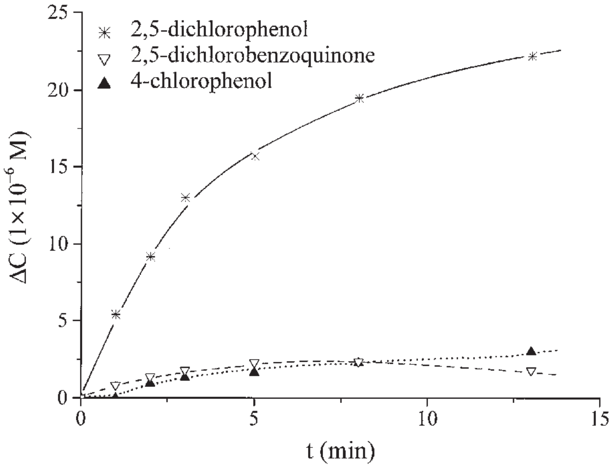


Reactions induced by excitation of nitrate ions or ferric ions

Nitrate ions absorb at wavelengths shorter than 340 nm with a maximum at 302 nm (molar absorption coefficient ε = 7.2 M^{-1} cm^{-1} at 302 nm), hence, when solutions are irradiated in the range 290–350 nm, NO_3^- is excited without excitation of 1,4-DCB.

An air-saturated solution of 1,4-DCB (3.3 × 10^{-4} M) and KNO_3 (1 × 10^{-2} M) was irradiated between 290 and 350 nm. The incident photon flow was roughly 6 × 10^{15} photons cm^{-3} s^{-1} (see *Experimental* section), but the solution absorbs only a fraction of this energy (probably less than 20%). The main photoproduct detected on the HPLC chromatogram of a solution irradiated for 165 min was 2,5-dichlorophenol. The formation of 4-chlorophenol was also observed, but in such minor amounts that it could not be quantified. Nitrate ions

Fig. 3. Quantification of the main photoproducts identified in an air-saturated aqueous solution of 1,4-DCB (3.6×10^{-4} M) irradiated at 365 nm in the presence of ferric salts (1×10^{-3} M).



are converted into nitrite. 2,5-Dichlorophenol presents a kinetics of formation of primary photoproduct.

The mass balance was not expected to be very good since irradiations were long and in a range where most of photoproducts, such as 2,5-dichlorophenol, 4-chlorophenol, hydroquinone, benzoquinone (not quantified but necessarily formed from 4-chlorophenol), absorb.

Ferric salts absorb at longer wavelengths than nitrate ions and can be excited at 365 nm without excitation of 1,4-DCB. In our experimental conditions, only quinones are expected to absorb at this wavelength. However, it can be noted that the lamps used for the irradiation have a minor emission at 313 nm (about 3% of photons) and at 334 nm (about 6%). A solution of 1,4-DCB (2.6×10^{-4} M) with added ferric salt (1×10^{-3} M) was irradiated under these conditions. The main photoproducts detected by HPLC are 2,5-dichlorophenol, 2,5-dichlorobenzoquinone, and 4-chlorophenol. These products present a kinetics of primary photoproducts (Fig. 3). A small amount of benzoquinone was also detected at 250 nm.

The absence of hydroquinone and 2,5-dichlorohydroquinone result from their oxidation by Fe^{III}, as it was checked that Fe^{III} easily oxidizes these two compounds into 1,4-benzoquinone and 2,5-dichloro-1,4-benzoquinone, respectively.

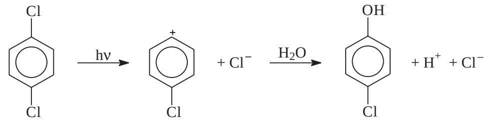
Discussion and mechanisms

Direct photolysis

Formation of 4-chlorophenol and hydroquinone

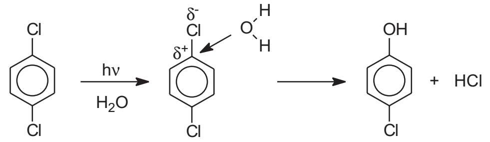
In previous work the main initial reaction was assumed to be a photohydrolysis leading to the formation of 4-chlorophenol (5). This mechanism is most likely since it also agree with the phototransformation of monochlorobenzene and several other chloroaromatic derivatives, such as 3-chlorophenol (17), 3-chloroaniline, and one derivative used as a pesticide (18). The intermediate formation of a carbocation may be suggested (eq. [4]),

[4]



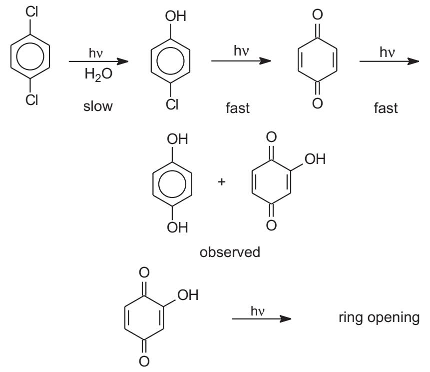
but a concerted mechanism is more likely since, in the case of 3-chlorophenol and 3-chloroaniline, no transient was observed in laser flash photolysis (eq. [5]).

[5]

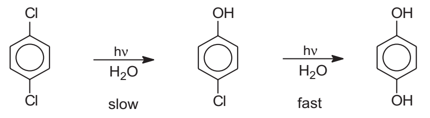


Photohydrolysis may be assumed to occur either from the excited singlet state or from the triplet state. The triplet state is more likely for the following reasons: (*i*) Alfassi and Previtali (6) experimentally proved that the yield of formation of 1,4-DCB triplet state is about 0.95 in methanol; (*ii*) the photohydrolysis of monochlorobenzene can be sensitized by acetone-d_6 (19); and (*iii*) the photohydrolysis of monohalogenophenols can also be sensitized (20).

4-Chlorophenol does not accumulate much since it absorbs at the irradiation wavelengths and its quantum yield of disappearance is high. It does, however, accumulate a little better when solutions are irradiated at 254 nm as compared to 275–350 nm, because it absorbs more at longer wavelengths when compared to 1,4-DCB. According to the concentration of oxygen, it is transformed into hydroquinone (20–22). The reaction involves the intermediate formation of a carbene (20, 23). *p*-Benzoquinone cannot be observed when solutions are irradiated at 254 nm since it has a strong absorption band at 245 nm and it is easily phototransformed into hydroquinone (12). Thus, the formation of hydroquinone in air-saturated solutions is attributed to the following sequence controlled by the first step (eq. [6]), whereas in the absence of oxygen hydroquinone is formed by photohydrolysis (eq. [7]) (21).



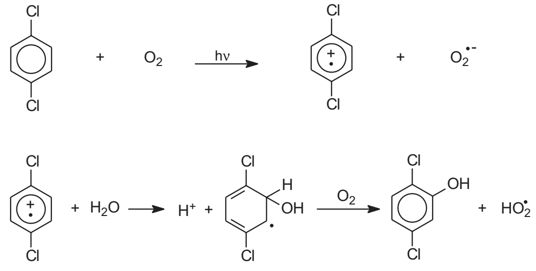
[6]



[7]

Formation of 2,5-dichlorophenol

The formation of 2,5-dichlorophenol is not negligible when 1,4-DCB is irradiated in pure water. It was not observed in the absence of oxygen, which is not surprising since it implies the oxidation of the ring. It can be explained either by the photoionization of the excited singlet state or by the oxidation of triplet state by oxygen or by the oxidation of the ground state by singlet oxygen resulting from the deactivation of 1,4-DCB. The latter may be ruled out because the rate of deactivation of singlet oxygen in water is 5×10^5 s^{-1} (24) and the rate of reaction of 1,4-DCB is ca. 1.7×10^5 M^{-1} s^{-1} or lower, since it is 1.7×10^5 with 9,10-dichloroanthracene in $CHCl_3$ (24). With a concentration of 1,4-DCB equal to 4.7×10^{-4} M, the rate of reaction of $^1O_2$ is expected to be ca. 6000 times lower than the rate of deactivation. In contrast, both other mechanisms are consistent with experimental results. If the formation of 2,5-dichlorophenol results from the photoionization of the singlet state, the effect of oxygen is explained by a competition between the trapping of ejected electron by oxygen and the recombination electron–cation. On the other hand the oxidation of the triplet state of 1,4-DCB by oxygen is consistent with the lifetime of the triplet state. It can be noted that the lifetime of the triplet state of 1,4-DCB is most likely shorter in water than in methanol (3.3 μs according to ref. 6), since Previtali and Ebbesen (7) reported that the triplet state of monochlorobenzene is about 10 times shorter in water than in methanol.



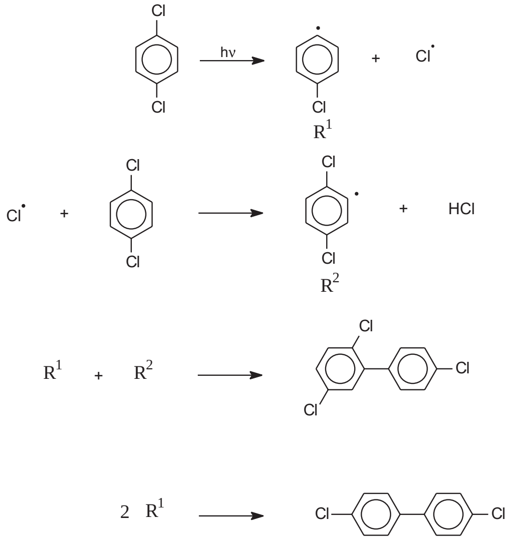
[8]

$$HO_2^{\bullet} \rightleftharpoons O_2^{\bullet-} + H^+ \qquad pK_a = 4.8 \quad (25)$$

$$HO_2^{\bullet} + O_2^{\bullet-} + H^+ \longrightarrow H_2O_2 + O_2$$

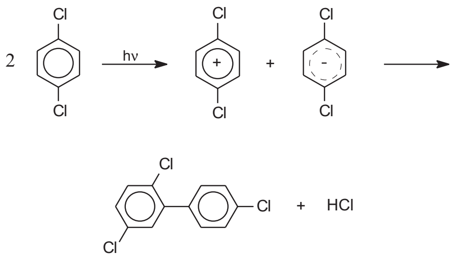
In a second stage, 2,5-dichlorophenol may be formed by $OH^{\bullet}$ radicals resulting from the excitation of H_2O_2.

In the absence of oxygen the formation of 4,4′-dichlorobiphenyl and 2,4′,5-trichlorobiphenyl may be explained by the C–Cl bond homolysis in the triplet state:



[9]

However, the charge transfer from the triplet state, disregarded in the case of monochlorobenzene (7), cannot be excluded here since the triplet state has a high yield of formation (0.95) and a longer lifetime (6).

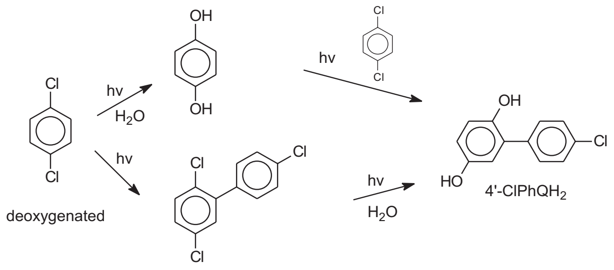


[10]

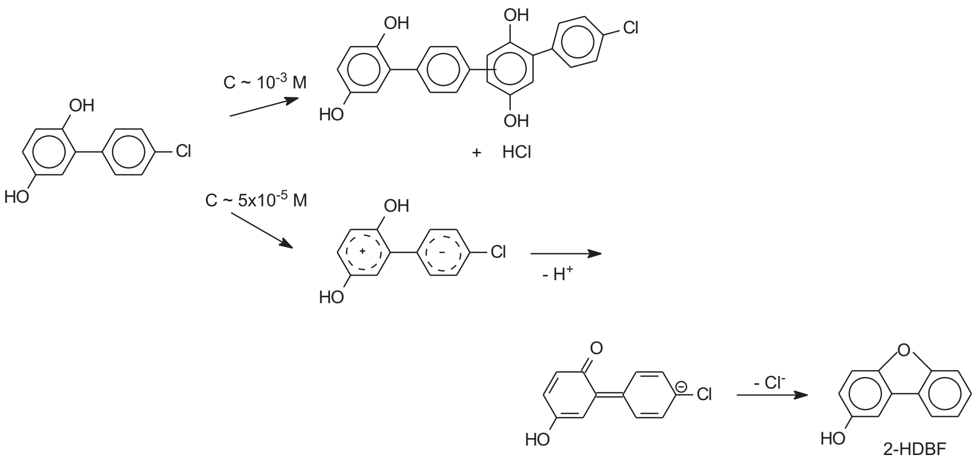
Formation of 2-hydroxydibenzofuran (2-HDBF) and 3″-chloro-2,5-dihydroxy-p-terphenyl (CDTP)

It was previously reported that phenylbenzoquinone photocyclizes with a high yield into 2-HDBF (13). In our experimental conditions it is difficult to explain the intermediate formation of phenylbenzoquinone. In addition, the following features can be noted: (*i*) the formation of 2-HDBF was observed when a deoxygenated solution of hydroquinone is excited in the presence of 1,4-DCB; (*ii*) the excitation of a deoxygenated mixture hydroquinone and 4-chlorophenol leads to the formation of 2,4′,5-trihydroxybiphenyl (20); (*iii*) 2,4′,5-trichlorobiphenyl is expected to be photohydrolyzed into 4′-chloro-2,5-dihydroxybiphenyl (4′-$ClPhQH_2$) (other products are not excluded); and (*iv*) it was observed (present work) that 4′-$ClPhQH_2$ irradiated in diluted deoxygenated solution leads to the formation of 2-HDBF. Therefore, the formation of 2-HDBF may be attributed to an internal charge transfer in excited 4′-$ClPhQH_2$. In relatively concentrated solutions an intermolecular charge transfer leads to the formation of a four-ring adduct (eq. [11*b*]).

[11a]

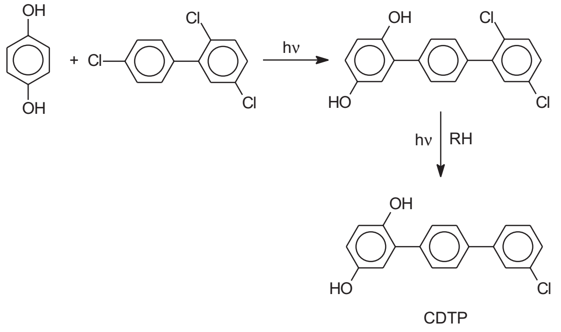


[11b]



The formation of CDTP may be explained similarly by the addition of hydroquinone on 2,4′,5-trichlorobiphenyl followed by a reductive elimination of one chlorine atom.

[12]



Induced phototransformation

The excitation of nitrate ions or ferric salts leads to the formation of hydroxyl radicals:

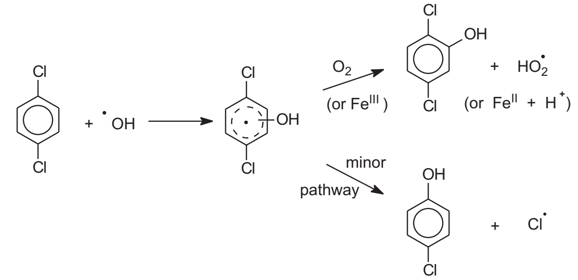
[13]

$$NO_3^- + H_2O \xrightarrow{h\nu} {}^{\bullet}NO_2 + {}^{\bullet}OH + {}^{-}OH \qquad (26)$$

$$Fe^{III}-OH \xrightarrow{h\nu} Fe^{II} + {}^{\bullet}OH \qquad (27)$$

The formation of 4-chlorophenol and 2,5-dichlorophenol result from the hydroxylation of the ring with or without dechlorination:

[14]



Hydroquinone observed in the case of excitation of nitrate ions may result from the further photohydrolysis of 4-chlorophenol or from the substitution of Cl by $OH^{\bullet}$. In the case of the excitation of Fe^{III}, hydroquinone and 2,5-dichlorohydroquinone cannot be observed since they are oxidized by Fe^{III}. The observed formation of benzoquinone and 2,5-dichlorobenzoquinone result from this oxidation.

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