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Photochemical behaviour of dichloroanilines in water and formation of aminochlorophenoxazones

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Abstract

The main photochemical reaction of dichloroanilines (DCAs) is photohydrolysis, i.e. a substitution of Cl by OH involving a molecule of water, with initially a relative specificity. The quantum yields lie in the range 0.015–0.060. This reaction was previously reported for 3,4-DCA and 2,6-DCA. It is observed with all other isomers 2,3-DCA, 2,4-DCA, 2,5-DCA and 3,5-DCA. This reaction is not influenced by the presence of oxygen. In contrast to 2-chloroaniline (2-CA), 2,4-DCA and 2,6-DCA do not lead to the contraction of the ring (formation of chlorinated cyclopentadiene carbonitrile). Surprisingly, 2,4-DCA neither reacts as 2-CA nor as 4-CA. A priority order in the site of substitution is deduced from the comparison between the six DCA isomers: *meta* > *ortho* > *para*. In other words, *para* and *ortho* substitutions are minor pathways when the *meta* position is chlorinated. Moreover, the formation of aminochlorophenoxazones was observed with 2,4- and 2,6-DCA. It results from the photochemical transformation of the aminochlorophenols initially formed. With 2,4-DCA, 2-amino-7-chlorophenoxazin-3-one was identified; with 2,6-DCA, 2-amino-1-chloro- and 2-amino-1,9-dichlorophenoxazin-3-one are formed. These reactions involve the intermediate formation of an *o*-benzoquinone monoimine. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Phototransformation; Photohydrolysis; Dichloroanilines; Aminophenoxazones; Aqueous solutions

1. Introduction

Chloroanilines (CAs) may be formed in natural waters by the biodegradation of various phenylcarbamate, phenyurea and acylanilide herbicides [1]. They are toxic for marine organisms and their biodegradability is relatively low. Consequently, photolysis may play a significant role in their elimination.

It was previously observed that the photochemical behaviour of monochloroanilines depends on the position of the halogen on the ring. With 3-CA photohydrolysis, i.e. heterolytic substitution of Cl by OH involving a molecule of water, is almost specific [2]. With 2-CA photohydrolysis competes with the formation of 1,3-cyclopentadiene-1-carbonitrile [3]. 4-CA has a more complex behaviour depending on both oxygenation and concentration. In a deoxygenated solution the main photoproducts are 4-aminophenol and 2,4'-diamino-5-chlorobiphenyl, whereas in the presence of oxygen the main photoproduct was tentatively identified as 4-amino-4'-chloro-diphenylamine [4]. Minor formations of 4-chloro-

nitrobenzene and 4-chloronitrosobenzene have also been reported [5].

Among the DCAs the photochemistry of 3,4-dichlorinated (3,4-DCA) is the most studied. Moilanen and Crosby reported its phototransformation into 3,3',4,4'-tetrachloroazobenzene [6]. Mansour et al. identified 10 photoproducts in irradiated aqueous or methanolic solutions: 4-CA, aniline, 2,4,5-trichloroaniline, chloronitrobenzenes, azobenzene and several derivatives [7,8].

The formation of 3,3',4,4'-tetrachloroazobenzene can be photosensitized by riboflavine-5'-phosphate sodium (FMN). In these conditions 4-(3,4-dichloroanilino)-3,3',4'-trichloroazobenzene was also identified among the products [9]. The most detailed photochemical study of 3,4-DCA was carried out by Miller et al. They reported that irradiation in water at $\lambda > 290$ nm gives 5-amino-2-chlorophenol with a conversion of $78 \pm 5\%$. The quantum yield was evaluated as 0.052 ± 0.003 whatever the pH between 4 and 12. It was suggested that the reaction involves the excited singlet state and proceeds through an aryl cation produced by heterolytic cleavage of the *meta* C–Cl bond [10]. A minor formation (2%) of 3-CA was also observed. Miille and Crosby obtained

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the same products in seawater [11]. According to Miller et al., in natural waters the phototransformation of 3,4-DCA results from both direct and sensitised reactions. A minor formation of 3,3',4,4'-tetrachloroazobenzene was observed in the presence of humic substances but not in pure distilled water [12]. In natural conditions the photochemical half-life of 3,4-DCA ranges from 2 to 125 h [1]. Irradiation favours further biotransformation [13].

Very recently it was reported that the main initial photo-reaction of 2,6-DCA is a photohydrolysis of the C–Cl bond. No photocontraction of the ring was observed whereas this reaction was observed with 2-CA. In a second stage the initially formed 2-amino-3-chlorophenol leads to the formation of 2-amino-1-chlorophenoxazin-3-one and 2-amino-1,9-dichlorophenoxazin-3-one [14].

It may be noted that the main photoreactions of 2,4-, 2,5- and 3,4-DCAs in methanol is the substitution of Cl by H [15]. According to the same authors the reaction occurs more easily in the *para* position than in *meta* and in *meta* than in the *ortho* position.

The aim of the present work is to compare the photochemical behaviour of the different isomeric DCAs (2,3-DCA; 2,4-DCA; 2,5-DCA; 2,6-DCA; 3,4-DCA; 3,5-DCA) in aqueous solution. 3,4-DCA was not the subject of new experiments since its photochemical behaviour is well described in the literature.

2. Material and methods

2.1. Reactants

Dichloroanilines 2,3-DCA 99%; 2,4-DCA 99%; 2,5-DCA 98%; 2,6-DCA 98% and 3,5-DCA 98% were purchased from Aldrich. Two difluoroanilines were studied for comparison: 2,4-DFA 97% from Fluka and 2,6-DFA 97% from Acros.

2-Amino-3-chlorophenol and 2-amino-5-chlorophenol were used to study secondary photochemical reactions. They were isolated from irradiated solutions of 2,6-DCA and 2,4-DCA, respectively, and their structure was confirmed by GC-MS and NMR as detailed in Section 3.

3-CA 99% and 2-amino-4-chlorophenol 97% used as analytical standards were provided by Aldrich.

Water used for solutions was purified with a Milli-Q device.

2.2. Irradiations

For the evaluation of quantum yields solutions were irradiated in a monochromatic parallel beam with a Schoefel monochromator equipped with a xenon lamp (1600 W). The band width was about 10 nm. The quartz cell was cylindrical, the optical path being equal to 1 cm. The incident photon flow was measured by chemical actinometry with ferrioxalate. For comparison some quantum yields were

measured at 253.7 nm using a device consisting of six low pressure mercury lamps surrounded by a cylindrical mirror. A cylindrical reactor in quartz (diameter 2 cm) was placed along the axis of the device. The photon flow received by the reactor was measured with uranyl oxalate.

For isolation and identification of photoproducts solutions were irradiated in the range 290–350 nm with six fluorescent lamps (Duke Sunlamp GL 20), the reactor in Pyrex being centered along the axis.

2.3. Analyses

UV spectra of solutions were recorded on a Cary 3 spectrophotometer (Varian).

Irradiated solutions were analysed with a Waters 996 HPLC chromatograph equipped with a photodiode array detector and Millenium for the treatment of the chromatogram. The column was C₁₈ 250 mm × 4.6 mm and the eluent was a methanol–water mixture usually 70/30 v/v.

Hydroxylated products obtained in irradiated solutions were isolated as follows. An almost saturated solution was irradiated between 290 and 350 nm. After filtration to eliminate insoluble products, unreacted DCA was partly evaporated under reduced pressure and then selectively extracted with trichloro-1,1,2-trifluoroethane. The hydroxylated product was then extracted with diethyl ether. Aminophenoxazones were isolated by preparative HPLC on a Gilson chromatograph (column C₁₈ 100 mm × 20 mm; eluent water–methanol 40/60 v/v).

GC-MS Hewlett-Packard 5985 equipped with a capillary column Machery–Nagel Optima 5 (25 m × 0.25 mm i.d.) was used for the identification of the main photoproducts isolated by HPLC.

¹H NMR 400 MHz spectra of isolated photoproducts were recorded on Bruker AC400. The solvent was usually acetone D₆, but CD₃OD was also used for the primary photoproducts obtained from 2,4-DCA and 2,6-DCA.

3. Results

3.1. UV absorption and pKa

The UV spectrum of 2,5-DCA at various pH is given in Fig. 1 as an example. The pKa of the protonated form was deduced from the influence of pH on the absorption at 294 nm (Fig. 1, insert). It was evaluated at 1.45. Similar results were obtained with the other DCAs. The UV spectra of 2,5- and 3,4-DCA are compared in Fig. 2 to the sunlight spectrum. The other DCAs have similar spectra.

Values of pKa and the main features of the UV spectra are gathered in Table 1. The data for the second absorption band of the neutral forms were not reported since it is located at $\lambda < 250$ nm and it is not involved in the photolysis in environmental conditions. It appears in Table 1 that the excitation of protonated forms can be neglected for the following reasons: (i) the pKas are near 2 or lower; (ii) the

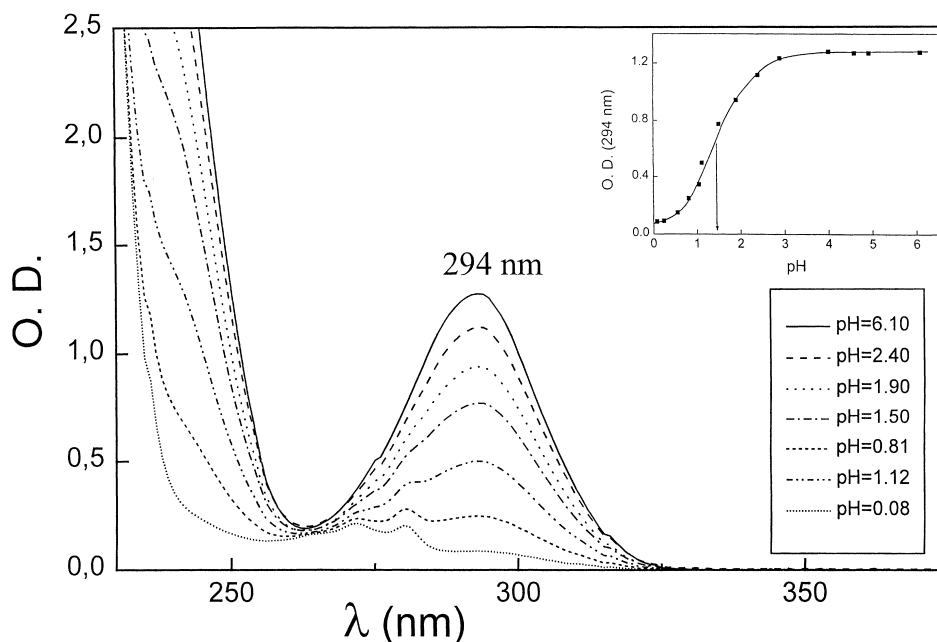


Fig. 1. UV spectrum of a solution of 2,5-DCA 4.9×10^{-4} M at various pH. Insert: Determination of the pKa of the protonated form from the variation of the absorption at 294 nm vs. pH.

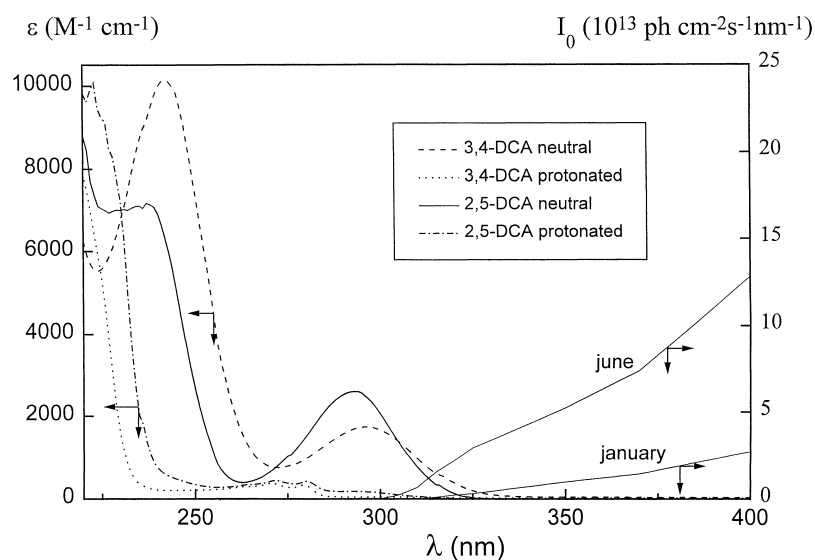


Fig. 2. UV spectra of 3,4- and 2,5-DCA in aqueous solution compared to the sunlight spectrum according to Frank and Klöpffer [16].

protonated forms absorb at shorter wavelength than neutral forms; (iii) the absorption coefficients of the protonated forms are low; (iv) it can be deduced from Förster's cycle that the protonation of the excited state occurs only at very high H^+ concentration. Consequently the phototransformation of DCAs in natural conditions is due to the excitation of neutral forms which generally absorb up to 330 nm.

3.2. Quantum yields

The quantum yields of disappearance were evaluated at a low conversion extent in aqueous solutions irradiated near maximum absorption (280–300 nm) in various conditions of

pH, oxygenation and concentration. No effect of pH was observed in the range 4–11, no difference between solutions purged with argon, air and oxygen was noted and no influence of concentration appeared in the range 10^{-3} – 10^{-4} M. Consequently only one average value is reported for each compound in Table 2. They are consistent with the value obtained by Miller et al. with 3,4-DCA [10]. Quantum yields were also measured at 253.7 nm; most often they are slightly higher than near 290 nm. Two DFAs were studied for comparison in order to argue the mechanism of the reaction. It is worthy of note that the quantum yields of 2,4-DFA and 2,6-DFA are significantly higher than those of DCAs.

Table 1
Main features about UV absorption of DCAs in an aqueous solution

	2,3-DCA	2,4-DCA	2,5-DCA	2,6-DCA	3,5-DCA
Solubility (10^{-3} mol l^{-1})	6.8	3.0	3.0	2.6	5.0
pKa	1.77	2.00	1.45	0.40	2.14
<i>Neutral form</i>					
λ (nm)	291	296	294	291	293
ϵ (M^{-1} cm^{-1})	2060	1880	2300	2680	1640
<i>Protonated form</i>					
λ (nm)	276	278	280	277	278
ϵ (M^{-1} cm^{-1})	390	290	420	330	190
λ (nm)	269	270	272	268	270
ϵ (M^{-1} cm^{-1})	420	350	440	390	250

s: Solubility in water.

pKa of protonated form.

λ : Wavelength of the first absorption band (or of the two first maxima when the band is structured).

ϵ : Molar absorption coefficient at maximum absorption.

Table 2
Quantum yield of disappearance of DCAs and some DFAs irradiated in the aqueous solution (concentration 10^{-3} – 10^{-4} M)

Compound	λ_{nm}	$\phi_{disp.}$
2,3-DCA	296	0.015 ± 0.002
	254	0.015 ± 0.002
2,4-DCA	296	0.017 ± 0.002
	254	0.027 ± 0.003
2,5-DCA	294	0.020 ± 0.005
	254	0.053 ± 0.005
2,6-DCA	291	0.016 ± 0.002
	254	0.028 ± 0.003
3,4-DCA ^a	313	0.052 ± 0.003
3,5-DCA	293	0.042 ± 0.002
	254	0.059 ± 0.003
2,4-DFA	282	0.12 ± 0.01
2,6-DFA	270	0.13 ± 0.01

^aAccording to reference [10].

3.3. Analytical study

3.3.1. Phototransformation of 2,3-DCA, 2,5-DCA and 3,5-DCA

The phototransformation of 2,5-DCA is presented with some more detail than the phototransformation of the two isomers, as an example, but the three titled compounds have similar photochemical behaviour.

When the unbuffered solution 10^{-3} M of 2,5-DCA was irradiated between 290 and 350 nm four peaks P_1^{25} – P_4^{25} appeared on the HPLC chromatogram (Fig. 3), P_3^{25} and P_4^{25} were identified as 2-amino-4-chlorophenol and 3-CA, respectively, by comparison of UV spectra and HPLC

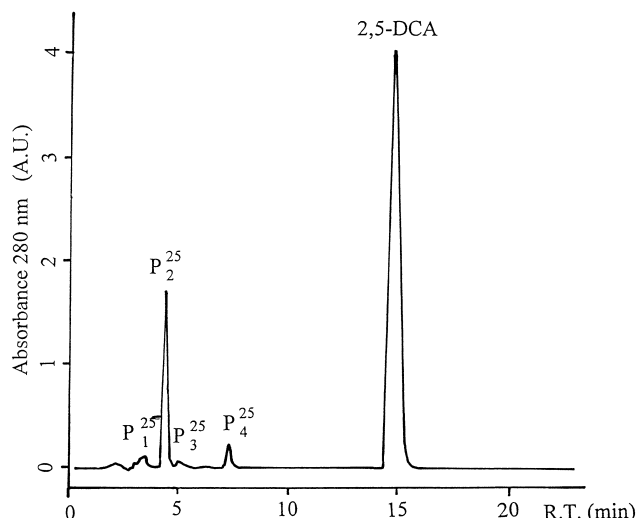


Fig. 3. HPLC chromatogram of a solution of 2,5-DCA 10^{-3} M irradiated in the range of 290–350 nm up to 18% of transformation. Column C_{18} 250 mm \times 4.6 mm. Eluent methanol–water 60/40 v/v.; detection 280 nm.

retention times of commercial standards. 3-CA accounted for 3% of the transformation in air-saturated solution and 5% in the absence of oxygen. Formation of P_3^{25} was not quantified. The order of magnitude is lower than 1%.

Product P_2^{25} was isolated and identified as 3-amino-4-chlorophenol by MS and 1H NMR spectra:

Isolated P_2^{25} was then used for the calibration of the HPLC. Its initial formation accounts for more than 70% of the 2,5-DCA transformed (Fig. 4).

Product P_1^{25} has the kinetics of a secondary photoproduct. It was observed that it can be formed by the photooxidation

m/z	143 (M^+ , 100%); 145 (M^+ , 33%); 114 (6%); 80 (42%); 52 (23%)
1H NMR (CD_3 CO CD_3) δ ppm	8.15 (s, OH); 6.96 (d, H_3); 6.35 (d, H_2); 6.11 (dd, H_6); 4.80 (s, NH_2)

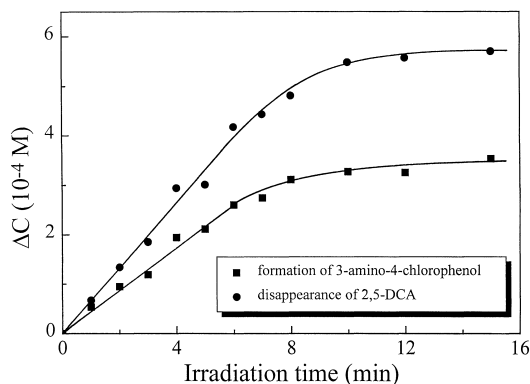
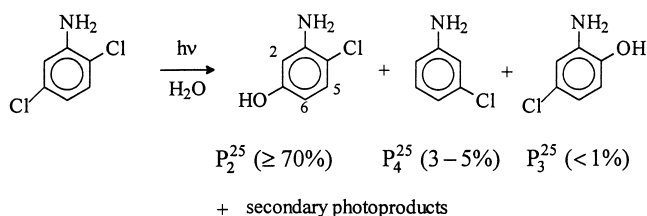


Fig. 4. Kinetic of 2,5-DCA disappearance and 3-amino-4-chlorophenol formation at 254 nm (initial concentration 10^{-3} M).

of 2-amino-4-chlorophenol or 3-amino-4-chlorophenol. It is not formed in the absence of oxygen. A possible structure might be aminobenzoquinone; it is consistent with its UV spectrum (maximum absorption at 263 and 483 nm):



Similar reactions were observed with 2,3-DCA and 3,5-DCA, but the reaction was a little more specific. After filtration to eliminate a slight precipitate, only one peak was observed on the HPLC chromatogram at a low conversion extent. With 2,3-DCA the main photoproduct was identified with 3-amino-2-chlorophenol. It accounts for about 80% of the DCA transformed.

m/z 143 (M^+ , 100%); 145 (M^+ , 33%); 114 (10%); 80 (21%); 52 (48%)
 1H NMR (CD_3 CO CD_3) δ ppm 8.35 (s, OH); 6.83 (t, H_5); 6.35 (dd, H_4); 6.26 (dd, H_6); 4.87 (s, NH_2)

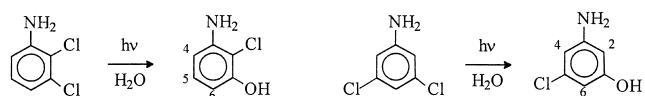
With 3,5-DCA the main photoproduct is 3-amino-5-chlorophenol. Its formation is almost quantitative.

m/z 143 (M^+ , 100%); 145 (M^+ , 33%); 114 (7%); 80 (43%); 52 (14%)

After acetylation to improve MS analysis $m/z = 185-187$.

1H NMR (CD_3 CO CD_3) δ ppm 8.30 (s, OH); 6.19 (t, H_2); 6.10 (d, H_4, H_6); 4.83 (s, NH_2)

This reaction is consistent with the phototransformation of 3-chloroaniline into 3-chlorophenol previously reported [2]:



3.3.2. Phototransformation of 2,4-DCA and 2,6-DCA

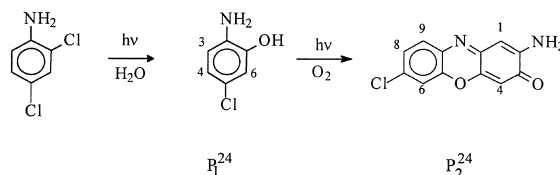
The photochemical behaviour of 2,4- and 2,6-DCA is a little more complex since an influence of oxygen was observed. When an air-saturated or deoxygenated solution of 2,4-DCA was irradiated at 290 nm the main primary photoproduct P_1^{24} had a HPLC retention time shorter than the retention time of 2,4-DCA. From MS and NMR spectra it was identified as 2-amino-5-chlorophenol.

m/z 143 (M^+ , 100%); 145 (M^+ , 33%); 114 (10%); 80 (23%); 52 (10%)
 1H NMR (CD_3 OD) δ ppm 7.49 (d, H_3); 7.22 (d, H_6); 7.16 (dd, H_4); 5.10 (s, NH_2)

The formation of 4-amino-3-chlorophenol (commercial product) was not observed, but another photoproduct P_2^{24} , with a longer HPLC retention time, was detected in an air-saturated solution, but not in the deoxygenated medium. P_2^{24} was identified as 2-amino-7-chlorophenoxazin-3-one.

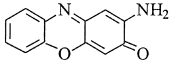
m/z 246 (M^+ , 100%); 248 (M^+ , 33%); 219 (50%); 221 (19%)
 1H NMR (CD_3 CO CD_3) δ ppm 7.70 (d, H_9 or H_6); 7.53 (d, H_6 or H_9); 7.41 (dd, H_8); 6.48 (s, H_4); 6.32 (s, H_1)

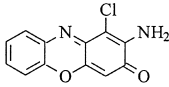
The formation of P_2^{24} has the kinetics of a secondary photoproduct. Product P_1^{24} was isolated from an irradiated solution and it was experimentally proved that P_2^{24} results from the photooxidation of P_1^{24} .

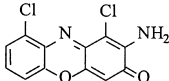


m/z 143 (M^+ , 100%); 145 (M^+ , 33%); 114 (10%); 80 (21%); 52 (48%)
 1H NMR (CD_3 CO CD_3) δ ppm 8.35 (s, OH); 6.83 (t, H_5); 6.35 (dd, H_4); 6.26 (dd, H_6); 4.87 (s, NH_2)

With 2,6-DCA the main primary photoproduct P_1^{26} is 2-amino-3-chlorophenol. This accounts for more than 65% of the 2,6-DCA transformed, but in a second stage amino-chlorophenoxazin-3-ones are formed. Three derivatives were identified [14].

 P_2^{26} 2-amino-7-chlorophenoxazin-3-one by comparison with the photooxidation of 2-aminophenol [17]

 P_3^{26} 2-amino-1-chlorophenoxazin-3-one, by MS and 1H NMR [14]

 P_4^{26} 2-amino-1,9-dichlorophenoxazin-3-one, by MS and 1H NMR [14]

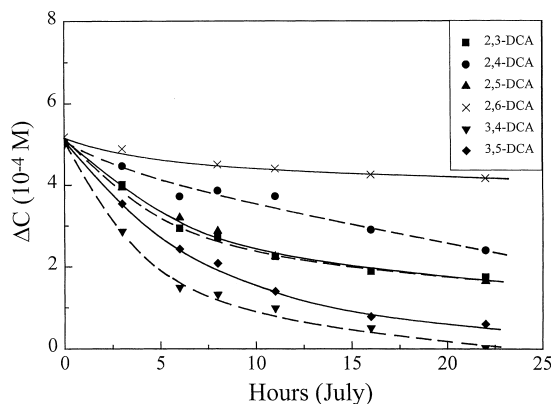


Fig. 5. Kinetics of degradation of DCAs in sunlight (Clermont-Ferrand: latitude 46°N, altitude 400 m).

The formation of P_4^{26} needs the presence of oxygen whereas P_2^{26} is formed in the absence of oxygen. P_3^{26} is formed in both cases.

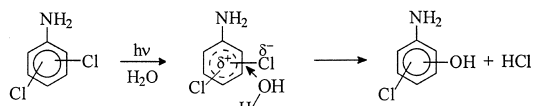
3.4. Irradiation in sunlight

Solutions of DCAs 5×10^{-4} M were exposed in sunlight in summer and in winter. It appears from Fig. 5 that the transformation rate is highly dependent on the position of the halogens on the ring. The initial rate is about 10 times higher with 3,4-DCA than with 2,6-DCA. The other DCAs have intermediate transformation rates. The faster transformation of 3,4-DCA is due to both, its higher absorption at $\lambda > 300$ nm and its relatively high quantum yield (compared to *ortho*-chlorinated DCAs). In winter the transformation rate is roughly 10 times slower than in summer (in irradiation hours); this means that 3,4-DCA is completely transformed in ca. 20 days.

4. Discussion and mechanisms

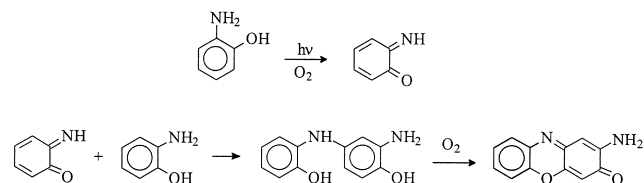
4.1. Photohydrolysis

The formation of phenolic compounds almost specific in some cases, associated with the release of hydrochloric acid (the decrease of pH and formation of Cl^- were controlled) is attributed to a heterolytic photohydrolysis as it was previously proposed for chlorobenzene [17] and 3-chlorophenol [18]. The fact that the reaction has a higher quantum yield with DFAs than with DCAs rules out a homolytic C-halogen scission, since the energy strength is significantly higher for C–F than for C–Cl, and higher than the energy of a photon at 290 nm. The fact that the reaction is not influenced by oxygen is also consistent with a heterolytic mechanism. The reaction involves a molecule of water and it is not a substitution of Cl^- by OH^- since no effect of pH was observed between pH 3 and pH 12 with 2,5-DCA.

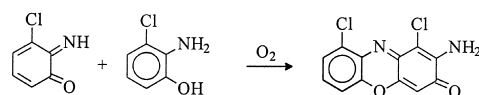


4.2. Formation of aminophenoxazines

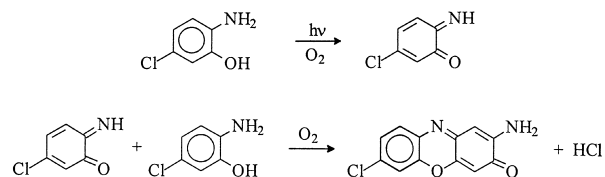
It was deduced from the kinetic study that the formation of aminophenoxazines results from a secondary reaction. Actually it was confirmed that this reaction occurs with 2-amino-3-chlorophenol and 2-amino-5-chlorophenol isolated from irradiated solutions of 2,6-DCA and 2,4-DCA, respectively, and irradiated in UV light. Previously such a reaction was observed by Ikekawa et al. [19]. It was suggested that the first step is the oxidation of 2-aminophenol into *o*-benzoquinone monoimine (*o*-BQMI), this intermediate being assumed to react with 2-aminophenol. The following mechanism was proposed [19]:



This mechanism may be applied for the formation of 2-amino-1,9-dichlorophenoxazin-3-one from 2-amino-3-chlorophenol:



and to the formation of 2-amino-7-chlorophenoxazin-3-one, from 2-amino-5-chlorophenol, with this difference that the addition involves the elimination of hydrochloric acid:



However, the formation of 2-amino-1-chlorophenoxazin-3-one and 2-aminophenoxazin-3-one occurs in the absence of oxygen and it may be assumed that *o*-BQMI may result from the elimination of hydrochloric acid from 2-amino-3-chlorophenol.

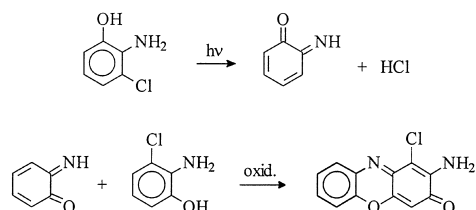


Table 3
Main photoproducts in the photolysis of CAs and DCAs in an aqueous solution

Reactant	Primary photoproducts	Secondary photoproducts	Reference
2-CA	2-aminophenol 1,3-cyclopentadiene-1-carbonitrile		[3]
3-CA	3-aminophenol	resorcinol+...	[2]
4-CA	2,4'-diamino-5-chlorobiphenyl 4-amino-4'-chlorodiphenylamine 4-aminophenol (depending on conditions)	2,4'-diamino-5-hydroxybiphenyl	[4]
2,3-DCA	3-amino-2-chlorophenol		This work
2,4-DCA	2-amino-5-chlorophenol	2-amino-7-chlorophenoxazin-3-one	This work
2,5-DCA	3-amino-4-chlorophenol		This work
2,6-DCA	2-amino-3-chlorophenol	2-aminophenoxazin-3-one and chlorinate derivatives	[14] and this work
3,4-DCA	5-amino-2-chlorophenol		[10]
3,5-DCA	3-amino-5-chlorophenol		This work

The second reaction is an oxidative step. *o*-BMQI is most likely to be the oxidant as suggested by Nogami et al. [20] since the formation of 2-aminophenol (its reduction product) was observed in deoxygenated irradiated solutions.

Similarly the formation of 2-aminophenoxazin-3-one observed only in the absence of oxygen results from the addition of *o*-BQMI on 2-aminophenol, the necessary elimination of hydrogen being attributed to the reduction of *o*-BQMI.

5. Conclusions. Comparison of the photochemical behaviour of CAs and DCAs

The following features can be deduced from the results reported in Table 3. With 3-CA and all DCAs the main reaction is photohydrolysis leading to the corresponding substituted phenol. This reaction has a high chemical yield. It is noteworthy that with DCAs the reaction in the *meta* position has priority on the reaction in *ortho* position and the latter has priority on the reaction in the *para* position. *Para* photohydrolysis was only observed with 4-CA, more efficiently in the absence of oxygen.

The formation of 1,3-cyclopentadiene-1-carbonitrile observed with 2-CA does not occur with *ortho*-chlorinated DCAs.

When photohydrolysis leads to 2-aminophenol derivatives, aminophenoxazones are formed by secondary reactions involving *o*-BQMI. These intermediates may be formed by the oxidation or elimination of hydrochloric acid.

The presence of a second chlorine on the ring disfavours photohydrolysis: the quantum yield was evaluated at 0.12 with 3-CA and lies between 0.015 and 0.060 with the DCAs.

In contrast the quantum yields are higher with DFAs than with DCAs. Both results are consistent with a heterolytic mechanism.

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