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Phototransformation of 2,6-dichloroaniline in aqueous solution

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Abstract

Three photoproducts were identified in an air-saturated irradiated aqueous solution of 2,6-dichloroaniline (2,6-DCA): 2-amino-3-chlorophenol (**1**), 2-amino-1-chlorophenoxazin-3-one (**2**) and 2-amino-1,9-dichlorophenoxazin-3-one (**3**). **1** is the main primary photoproduct; its initial chemical yield is higher than 65%. Its formation is influenced neither by oxygen nor by pH in the range 3.6–11.2. It results from the photohydrolysis of 2,6-DCA. It may be noted that no formation of chlorocyclopentadiene carbonitrile was observed, whereas the contraction of the ring is a significant pathway with 2-chloroaniline. Two other photoproducts namely 2-aminophenol (**4**) and 2-aminophenoxazin-3-one (**5**) were also formed in deoxygenated solutions. Compounds **2**, **3** and **5** are formed in the second stage and result from the excitation of **1**, but they appear at relatively low conversion extent. A mechanism involving an *o*-benzoquinone monoimine (*o*-BQMI) is proposed to explain their formation. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: 2,6-Dichloroaniline; Phototransformation; Aqueous solution; Photohydrolysis; Aminophenoxazones

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1. Introduction

Mono- and dichloroanilines are listed as priority pollutants of waste waters. They are important chemical intermediates in the production of dyes and agricultural agents. They can be released in the environment as metabolites of anilide and chlorophenylureas herbicides [1]. Their absorption near 300 nm is not negligible and it was experimentally observed that they can be transformed by sunlight even in winter. So it is important to know their photochemical behaviour in aqueous solution.

The phototransformation of monochloroanilines was the subject of several publications. In 1960s Latowski noted that the quantum yield of formation of hydrogen chloride from 4-chloroaniline (4-CA) in alcohols or alcoholic mixtures reaches almost 1 [2]. Miller and Crosby reported that in aqueous solution 4-CA is photooxidized into 4-chloronitrosobenzene and 4-chloronitrobenzene [3]. Very recently it was pointed out that the position of the halogen plays a major role in the orientation of the phototransformation of chloroanilines in aqueous solution. With 3-chloroaniline (3-CA) the transformation into 3-aminophenol and hydrogen chloride is initially almost quantitative and the reaction was attributed to a heterolytic mechanism involving a molecule of water (photohydrolysis) [4]. Similar reaction was previously observed with chlorobenzene [5] and 3-chlorophenol [6]. Photohydrolysis occurs with 2-chloroaniline, but another reaction was reported: the formation of 1,3-cyclopentadiene-1-carbonitrile [7]. This reaction implies the photocontraction of the ring as it was observed with 2-halogenophenols [6,8]. The photochemical behaviour of 4-CA is more complex [9]: it depends on both concentration and presence of oxygen. In deoxygenated solution the main product is 4-aminophenol or 5-chloro-2,4′-diaminobiphenyl according to the concentration. In the presence of oxygen the main product was identified as 4-amino-4′-chlorodiphenylamine.

The phototransformation of dichloroanilines (DCA) was the subject of only a few publications. In alcohols DCA are reduced into chloro- and unsubstituted aniline [10,11]; the formation of chloroazobenzenes was also reported, but the purpose of the present paper is the photochemical behaviour in pure water. Most of results concern 3,4-DCA. It was reported that 3,4-DCA yields 5-amino-2-chlorophenol with a convertion of 78 ± 5%. The quantum yield was evaluated at 0.052 ± 0.003 at 313 nm. A minor amount of 3-chloroaniline (2%) was also produced. The reaction is explained by a heterolytic cleavage of *meta* C–Cl bond [12]. The reaction rate is unchanged in sea water and the same products are formed, but the formation of 3-chloroaniline is higher (5%). Traces of 3,3′,4,4′-tetrachloroazobenzene (TCAB) was also identified [13]. The formation of TCAB and 4-(3,4-dichloroanilino)-3,3′,4-trichloroazobenzene was observed when the transformation of 3,4-DCA was sensitized by riboflavin-5′-

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phosphate sodium (FMN) [1]. Sunlight irradiation of 3,4-DCA in natural water results in both direct and sensitized photoreactions [14].

In the case of 2,6-DCA the substitution of chlorine by a cyano group with KCN in *t*-butanol–water mixture was observed [15], but no study was reported to our knowledge, about the phototransformation of 2,6-DCA in the absence of organic solvent.

The aim of the present work is to study the photochemical behaviour of 2,6-DCA in pure water. Surprisingly 2,6-DCA does not react as 2-CA.

2. Experimental

2.1. Materials

2,6-Dichloroaniline 98% was from Aldrich. 2,6-Difluoroaniline 97% was provided by Acros. Water was purified with Milli-Q device (Millipore) and its purity was controlled by its resistivity (>18 MΩ cm).

2.2. Irradiations of solutions

For the determination of quantum yields or for the identification of photoproducts solutions were irradiated in monochromatic light at 254 or 291 nm. At 254 nm the device consisted in six low pressure mercury lamps (germicidal lamps) in a cylindrical mirror, the irradiation cell, in quartz being located along the axis. For irradiations at 291 nm a monochromator Schoeffel equipped with a xenon lamp (1600 w) was used.

Some solutions were irradiated between 290 and 350 nm with lamps Duke Sunlamp GL20w since this UV range is more representative of sunlight.

2.3. Evaluation of quantum yields

The evaluation of quantum yields of disappearance need the measurement of the photon flux absorbed and the titration of the studied compound. The photon flux was evaluated at 291 nm with ferrioxalate actinometry and at 254 nm with uranyl oxalate. The percentage of 2,6-DCA transformed was evaluated by HPLC.

2.4. Analyses

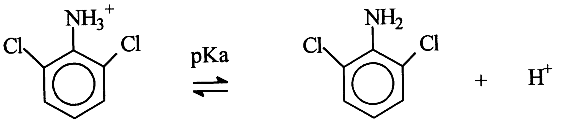
UV spectra were recorded on Cary 3 (Varian) spectrophotometer. Photoproducts were identified by HPLC with chromatograph Waters 996 equipped with a photodiode array detector, a Millennium software version 2.15 and a column C_{18} 250 mm × 4 mm, 5 μm. The eluent was a water–methanol mixture usually 30 : 70 (v/v). Products **2** and **3** were isolated on HPLC Gilson on a column C_{18} 100 mm × 20 mm with a mixture water–methanol 40 : 60 (v/v) as the eluent.

The main photoproducts **1–3** were identified by GC–MS and 400 MHz ^{1}H NMR. GC–MS was Hewlett-Packard 5985. A capillary column Optima 5 (Machery-Nagel) 25 m, i.d. 0.25 mm was used (stationary phase siloxane). NMR spectra were recorded on Bruker AC 400. **1**: *m*/*z* 145 ($M^{\bullet+}$, 100%), 143 ($M^{\bullet+}$, 33), 116 (12), 107 (18), 80 (24), 52 (48). ^{1}H NMR (CD_3OD) δ (ppm): 6.92 (dd, H_4), 6.82 (dd, H_6), 6.70 (t, H_5), 5.08 (2H, s, NH_2). **2**: *m*/*z* 246 ($M^{\bullet+}$, 71%), 248 ($M^{\bullet+}$, 30), most significant fragments 218 (24), 220 (9), 211 (21). ^{1}H NMR (CD_3COCD_3) δ (ppm): 7.83 (dd, H_9), 7.56 (m, H_7), 7.49 (dd, H_6), 7.45 (m, H_8), 6.45 (2H, s, NH_2), 6.32 (s, H_4). **3**: *m*/*z* 280 ($M^{\bullet+}$, 74%), 282 ($M^{\bullet+}$, 49), most significant fragments 252 (19), 254 (13), 245 (21), 247 (7). ^{1}H NMR (CD_3COCD_3) δ (ppm): 7.56 (dd, H_8 or H_6), 7.51 (t, H_7), 7.46 (dd, H_6 or H_8), 6.62 (2H, s, NH_2), 6.35 (s, H_4). (Formulae are given in Section 3.2).

3. Results

3.1. Spectrophotochemical properties of 2,6-dichloroaniline

The solubility of 2,6-DCA in unbuffered water was evaluated at 2.6 mM. The neutral form of 2,6-DCA absorbs at wavelengths shorter than 325 nm with a maximum located at 291 nm. The molar absorption coefficient at this wavelength was evaluated at 2680 M^{-1} cm^{-1}. As it can be seen in Fig. 1 that the protonated form is significantly less absorbing and that its maximum is located at shorter wavelengths.



From the variation of the absorbance versus acidity function H_0, the pK_a was evaluated at 0.40. Moreover the pK_a^* of the first excited singlet state of the conjugated acid

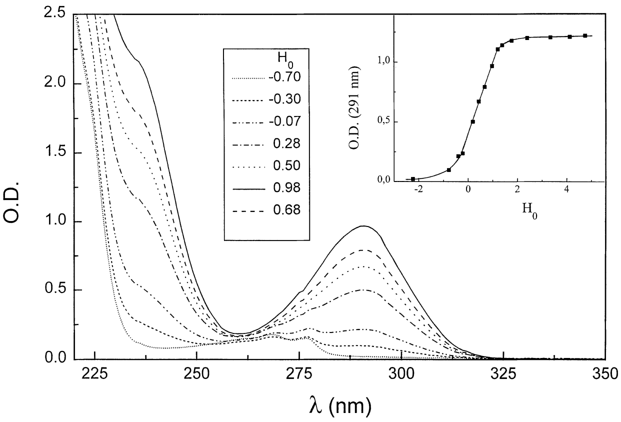


Fig. 1. UV absorption spectrum of an aqueous solution of 2,6-DCA 4.55 × 10^{-4} M vs. acidity function H_0.

2,6-DCAH$^+$ may be estimated from Förster's cycle:

$$\mathrm{p}K_a^* = \mathrm{p}K_a - 2.1 \times 10^{-3}\left(\frac{1}{\lambda_p} - \frac{1}{\lambda_n}\right)$$

where λ_p and λ_n are the wavelengths (in cm) of maximum UV absorption of protonated and molecular forms respectively. It was deduced that protonation is completely negligible in the singlet excited state. Consequently only the neutral form plays a role in the environmental phototransformation of 2,6-DCA.

3.2. Product study

A significant change was observed in UV absorption when a solution was irradiated at 254 nm (Fig. 2). An increase of absorbance was observed near 260 nm and between 400 and 450 nm. The irradiation produced a decrease of pH attributed to the release of hydrochloric acid. Three main photoproducts (**1–3**) appeared on the HPLC chromatogram of air-saturated irradiated solutions (detection at 280 nm). Using a mixture water–methanol 30 : 70 (v/v) as the eluent, **1** had a shorter retention time, **2** and **3** a longer retention time than 2,6-DCA. The same products were obtained when solutions were irradiated at 291 nm or in the range 290–350 nm. **1** is a primary product and its formation is unaffected by oxygen, pH and initial concentration. **2** and **3** are not formed in the first stage of the reaction, but they appear at relatively low conversion extent. In contrast to **1** and **2** the formation of **3** needs the presence of oxygen. The UV spectra of **1** and 2,6-DCA are similar (maximum absorption at 290 nm). It is not the case of **2** and **3**: both of them have a strong absorption band between 380 and 470 nm with a maximum near 430 nm.

Products **1–3** were isolated according the following procedure, from a solution 2×10^{-3} M irradiated at 254 nm and about 50% transformed. The solution was evaporated under reduced pressure. 2,6-DCA which has a higher vapor pressure with respect to the other compounds, was eliminated in the gas phase; **2** and **3** were then separated one from the other by semi-preparative HPLC.

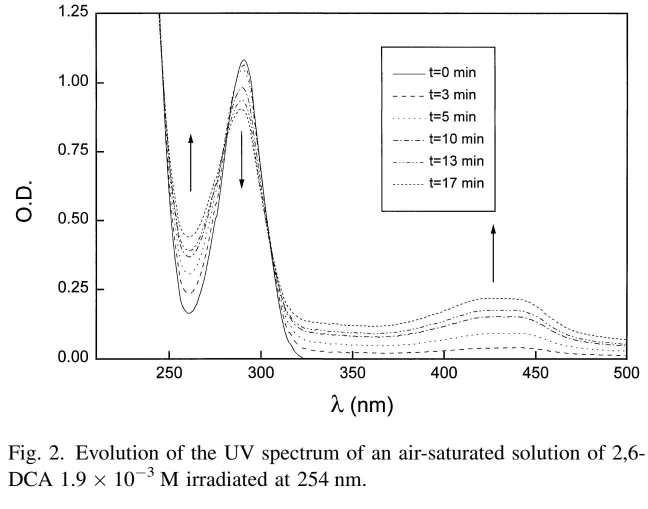
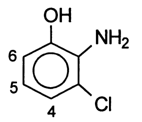
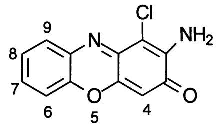


Fig. 2. Evolution of the UV spectrum of an air-saturated solution of 2,6-DCA 1.9×10^{-3} M irradiated at 254 nm.

The structure of **1–3** were deduced from MS and ^{1}H 400 MHz NMR:



1



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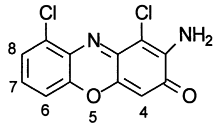


3

1: 2-amino-3-chlorophenol; **2**: 2-amino-1-chlorophenoxazin-3-one; **3**: 2-amino-1,9-dichlorophenoxazin-3-one.

The amount of **1** isolated was sufficient to calibrate HPLC and to obtain an approximate evaluation of the chemical yield of the initial reaction. The problem is that at very low conversion extent there is a poor experimental accuracy for the evaluation of disappearance, and that at conversion extent higher than 10% the formation of aminophenoxazones is not negligible. The chemical yield was evaluated at ca. 65%. It is most likely higher at low conversion extent since at 254 nm the absorbance of **1** ($\varepsilon \approx 1220$ M^{-1} cm^{-1}) is higher than the absorbance of 2,6-DCA ($\varepsilon \approx 790$ M^{-1} cm^{-1}) and their quantum yields are similar ($\approx$0.03). Consequently secondary reactions play a significant role even at low conversion extent. A solution of **1** was irradiated at 254 nm. In the presence of oxygen both products **2** and **3** were formed that confirms their secondary formation in the phototransformation of 2,6-DCA. In the absence of oxygen **3** was not formed, but the formation of 2-aminophenol (**4**) and 2-aminophenoxazin-3-one (**5**) was observed. The latter was identified by comparison with products resulting from the irradiation of 2-aminophenol in aqueous solution [16].

Besides a methanolic solution of 2,6-DCA 2×10^{-3} M was irradiated at 254 nm. The main photoproduct was 2-chloroaniline. No formation of **1**, **2** and **3** was observed. In these conditions the main primary reaction is a photoreduction by methanol.

In order to confirm the mechanism of phototransformation of 2,6-DCA in aqueous solution, 2,6-difluoroaniline (2,6-DFA) was irradiated at 270 nm in solution 1.5×10^{-3} M. Similar photochemical behaviour was observed; the main product initially formed was 2-amino-3-fluorophenol. In a second step aminofluorophenoxazones were formed. As it appears in Table 1 the reaction is significantly more efficient than with 2,6-DCA.

3.3. Quantum yield measurements

The quantum yield of disappearance of 2,6-DCA was measured in various conditions. Results are gathered in Table 1. It can be deduced that oxygen and pH have no influence on the kinetics of the transformation. The reaction is significantly more efficient at 254 nm than at 291 nm. This phenomenon can be related to the fact that both wavelengths

Table 1
Quantum yield of photolytic disappearance of 2,6-DCA and 2,6-DFA (only last line) in various conditions

Concentration (10^{-3} M)	λ (nm)[a]	pH	Oxygenation	Φ_{disp}[b]
2.0	254	5.5	Argon purged	0.030
			Air	0.030
			Oxygen	0.025
1.5	254	3.6	Air	0.027
2.0		6.4		0.030
1.5		12.2		0.029
0.5	291	5.5	Air	0.017
2.2	291	5.5	Air	0.015
2.0 (in MeOH)	254		Air	0.009
1.5 (2,6-DFA)	270	5.5	Air	0.13

[a] Irradiation wavelength.
[b] Quantum yield of disappearance.

correspond to different absorption bands. The reaction is more efficient by excitation in the band of higher energy.

It is noteworthy that 2,6-DFA has similar photochemical behaviour, but with significant higher efficiency and that the photolysis of 2,6-DCA is less efficient in methanol than in water (different reaction).

4. Mechanism and discussion

4.1. Formation of aminochlorophenol

No photocontraction of the ring was observed with 2,6-DCA, whereas with 2-chloroaniline the formation of 1,3-cyclopentadiene-1-carbonitrile is a significant photochemical pathway [7] as well as the formation of 2-aminophenol. The formation of 2-amino-3-chlorophenol from 2,6-DCA is attributed to a heterolytic reaction for the following reasons:

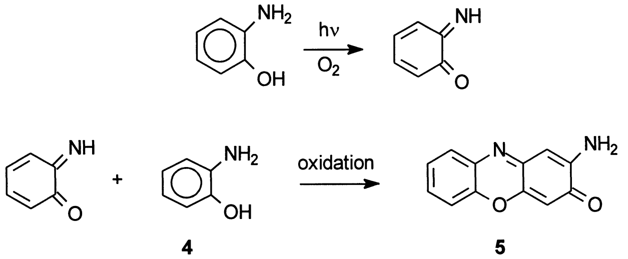
1. The reaction is initially relatively specific, the formation of aminophenoxazones resulting from secondary reactions, and no influence of oxygen was observed for the formation of 2-amino-3-chlorophenol. The involvement of Cl$^{\bullet}$ and aminochlorophenyl radical should lead to the formation of other products.
2. The same reaction was observed with 2,6-DFA in spite of the much stronger covalence of C–F bond compared to C–Cl bond. The fact that the quantum yield is higher with 2,6-DFA than with 2,6-DCA, whereas C–F bond strength (523 KJ mol^{-1}) is higher than the energy of a photon at 270 nm (443 KJ mol^{-1}) is inconsistent with a homolytic bond scission.

Besides the reaction is probably not a substitution of Cl$^-$ by OH$^-$, but involves a molecule of water since it is not influenced by pH between 3.6 and 6.4.

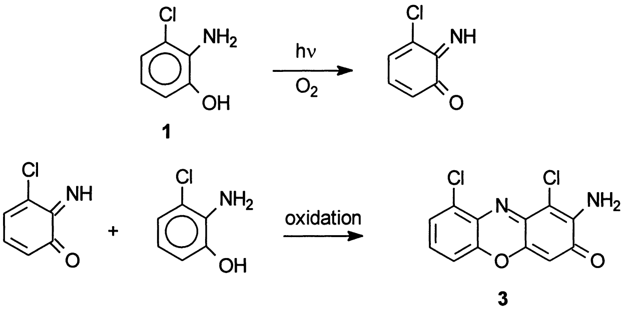
In the case of 3-chlorophenol which have the same photochemical behaviour, no influence of pH was observed at pH as low as 0.5 [6].

4.2. Formation of aminochlorophenoxazones

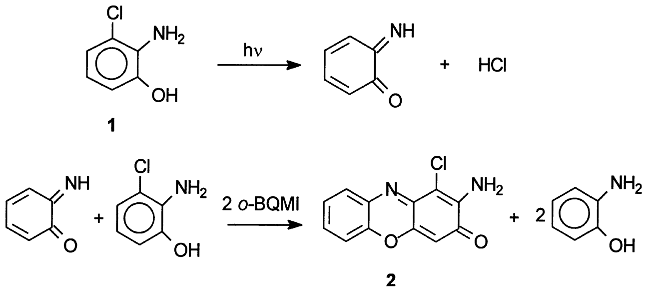
The formation of **2** and **3** is due to the excitation of **1** initially formed. It was observed with a solution of **1** isolated by HPLC. Such a reaction was previously observed in the photooxidation of 2-aminophenol [16]; it is due to the intermediate formation of *o*-benzoquinone monoinine (*o*-BQMI) [17].



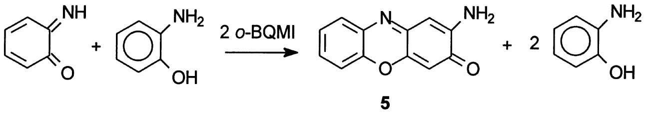
Product **3** was observed only in the presence of oxygen. Its formation is attributed to the oxidation of **1** in 3-chloro-*o*-benzoquinone monoimine:



In the absence of oxygen *o*-BQMI may be formed by elimination of hydrochloric acid. The formation of **2** is attributed to the addition of *o*-BQMI on **1** followed by the oxidation of the adduct, most likely by *o*-BQMI, as suggested by Nogami et al. [17]. The following mechanism is consistent with the observed formation of 2-aminophenol in deoxygenated solution:



The formation of 2-aminophenoxazin-3-one observed only in the absence of oxygen may be explained by a similar mechanism:



It can be concluded that photohydrolysis is the main initial photochemical reaction of 2,6-DCA. No contraction of the ring was observed as it was reported for 2-CA. In a second stage aminochlorophenoxazones are formed. They result from the phototransformation of 2-amino-3-chlorophenol (**1**) initially formed. It can be noted that 2-amino-1-chlorophenoxazin-3-one (**2**) and 2-aminophenoxazin-3-one (**5**) may be formed in the absence of oxygen whereas the formation of 2-amino-1,9-dichlorophenoxazin-3-one (**3**) needs the presence of oxygen.

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