Available online at www.sciencedirect.com
SCIENCE DIRECT®

Journal of Photochemistry and Photobiology A: Chemistry 168 (2004) 15–22

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Phototransformation of 3,5-dihalogeno-4-hydroxybenzonitriles (ioxynil and chloroxynil) in aqueous solution

Moulay A. Malouki[a], Abdennour Zertal[a], Bernadette Lavédrine[b],
Tahar Sehili[a], Pierre Boule[b,*]

[a] Laboratoire des Sciences et Technologies de l'Environnement, Université Mentouri, Route de Aïn El Bey, 25000 Constantine, Algeria
[b] Laboratoire de Photochimie Moléculaire et Macromoléculaire, Université Blaise Pascal - CNRS UMR 6505
(Clermont-Ferrand) 63177 Aubière Cedex, France

Received 8 December 2003; received in revised form 4 January 2004; accepted 4 May 2004

Abstract

The main initial photochemical reaction of ioxynil and chloroxynil in pure water is the photohydrolysis of C–halogen bond, leading, in both cases, to a monohalogenated dihydroxybenzonitrile. Reduction is observed as a minor pathway, especially when irradiation is carried out in the presence of humic acids. In a second stage, similar reactions occur with the remaining C–halogen bond. The photochemical reactivity is not significantly affected by the nature of the halogen Cl, Br or I.

Keywords: Photolysis; Photohydrolysis; Ioxynil; Chloroxynil; Hydroxylated benzonitriles

1. Introduction

Bromoxynil (3,5-dibromo-4-hydroxybenzonitrile) and ioxynil (3,5-diiodo-4-hydroxybenzonitrile) are used as herbicides. They are photosynthetic electron transfer inhibitors at the photosystem II receptor site [1]. For this reason, their photodegradation was the object of several publications, particularly in the case of bromoxynil. Chloroxynil (3,5-dichloro-4-hydroxybenzonitrile) was only briefly reported in two comparative kinetic studies [2,3].

These three substrates have relatively low pK_a values because of the electron-withdrawing effect of the CN group, and in environmental conditions, they are present mainly in the anionic form. They absorb UV light of wavelength shorter than 325 nm for chloroxynil, 330 nm for bromoxynil and 350 nm for ioxynil. Thus, they may be phototransformed by sunlight. The quantum yields of photodegradation are relatively low, and there is some discrepancy in their evaluation: 0.052 ± 0.004 for bromoxynil according to Kochany et al. [4], 0.0060, 0.0093 and 0.0024 for chloroxynil, bromoxynil and ioxynil, respectively, according to Millet et al. [2] It should be noted that in the latter experiments, 0.5% acetonitrile was present in the solution.

The analytical study of the phototransformation of bromoxynil was developed mainly by Kochany and co-workers [5,6] who identified 3-bromo-4-hydroxybenzonitrile and 4-hydroxybenzonitrile as the main photoproducts and proposed a radical mechanism for their formation [5]. They also reported that the reaction is inhibited by chloride ions showing instead substitution of Br by Cl [4,7], and by nitrite ions, the presence of which favours the formation of nitroderivatives [8]. However Machado et al. [9] found 3-bromo-4,5-dihydroxybenzonitrile as the major photoproduct in aqueous solution, and they suggested a heterolytic mechanism as in the case of many halogenoaromatic derivatives [10–13].

The transformation of bromoxynil can also be photoinduced by inorganic species [14] or by fulvic acids [15], but it is a different problem.

The aim of the present work is to study the photochemical behaviour of ioxynil and chloroxynil in order to compare it with that of bromoxynil and other 2-halogenated phenols.

2. Experimental

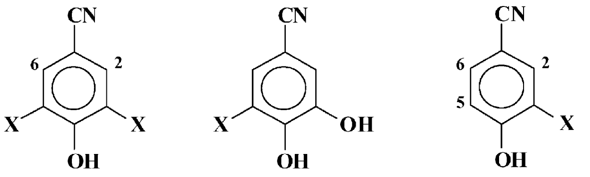
2.1. Chemical and reagents

Ioxynil of high purity was kindly provided by Rhône-Poulenc Agrochimie (France). No meaningful impurity

---

* Corresponding author. Tel.: +33 473407176; fax: +33 473407700.
E-mail address: pierre.boule@univ-bpclermont.fr (P. Boule).

1010-6030/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2004.05.007



substrates	5-halogeno-3,4-dihydroxybenzonitrile	3-halogeno-4-hydroxybenzonitrile
chloroxynil X = Cl	5-Cl DHBN	3-Cl HBN
bromoxynil X = Br	5-Br DHBN	3-Br HBN
ioxynil X = I	5-I DHBN	3-I HBN

was detected on the HPLC chromatogram with detection at 237 nm. Chloroxynil 98.9% was provided by Riedel-de Haën.

Methanol for HPLC was purchased from Fluka or from Carlo-Erba. Water for solutions was purified by Milli-Q system (Millipore) and controlled by its resistivity ($\geq$18 MΩ cm).

Potassium ferrioxalate used for actinometry was prepared from potassium oxalate and ferric chloride, according to the procedure proposed by Calvert and Pitts [16], and carefully stored in the dark.

For pK_a determination, the pH of the solution was adjusted with perchloric acid or phosphate buffer in concentration ten times higher than that of the substrate.

2.2. Photoreactors and light sources

For the determination of quantum yields, solutions were irradiated in monochromatic parallel beam in a cylindrical quartz cell (optical length 1.00 cm). The light source was a high-pressure mercury lamp Osram HBO 200 W associated with a monochromator Bausch and Lomb or Jobin Yvon. The irradiation wavelength was 313 nm for ioxynil and 296 nm for chloroxynil. The photon flux was evaluated with potassium ferrioxalate at 8.68×10^{14} photon cm^{-2} s^{-1} at 313 nm and at 3.20×10^{14} photon cm^{-2} s^{-1} at 296 nm. The low light intensity provided by this device does not allow the isolation of sufficient quantities for the identification of photoproducts. For this purpose, solutions were irradiated in the range 275–365 nm in a device consisting of six fluorescent lamps Duke Sunlamp FL20 surrounded by a cylindrical mirror. Solutions were put into a quartz reactor for chloroxynil and a Pyrex reactor for ioxynil. The reactor was placed along the axis of the device. The use of Pyrex limits the irradiation range reaching the solution to $\lambda \geq 290$ nm. It may be noted that chloroxynil does not absorb beyond ca. 325 nm.

Solutions were also exposed to sunlight in horizontal Pyrex tubes ($\Phi_i = 40$ mm) filled up to approximately the third of their capacity in order to have a large ratio of surface over volume. They were exposed in Clermont-Ferrand (latitude 46°N, altitude 420 m) either in April or in July. Exposition to sunlight was carried out only on sunny days at 12 GMT ±4 h.

2.3. Analyses

UV–Vis spectra of solutions were recorded on a Cary3 (Varian) spectrophotometer using quartz cells. A pH-meter Jenway 3310 was used to measure the pH of solutions. The disappearance of substrates and the formation of products were monitored by HPLC on a Waters 990 or 996 apparatus, both of which are equipped with a photodiode array detector. The column was a Waters Spherisorb ODS-2, 5 μm, 250 × 4.6 mm, and the eluent was a methanol/water mixture in 60/40 (v/v) proportion. A small amount (0.1%) of phosphoric acid was added to water to prevent the ionisation of phenolic compounds. For identification, the main photoproducts were isolated using the following method: 3 L of a 10^{-4} M solution was irradiated in the range 290–365 nm. Ioxynil and its photoproducts were extracted with ethylacetate and then the organic phase was concentrated. The solution of chloroxynil was directly evaporated under reduce pressure. After evaporation of the solvent, the solid residue was dissolved in a small volume of a water/methanol mixture and injected in an analytical HPLC column. The acidification of the eluent was accomplished by acetic acid, which is easy to eliminate by evaporation. A total of 40 or 50 injections were necessary for the isolation of sufficient amounts of different photoproducts for NMR analysis. ^{1}H NMR spectra in acetone D_6 were recorded on Bruker DPX 300 MHz or Bruker Advance 500 MHz. Mass spectra were obtained on Hewlett-Packard 5989B by direct introduction and chemical ionisation with methane. Iodide ions were evaluated by HPLC after calibration with standard solutions of sodium iodide.

3. Results

3.1. Solubility and pK_a values

According to Tomlin [1], the solubility of bromoxynil in water is 130 mg L^{-1}. Whereas, ioxynil is practically insoluble in water. It was however possible to evaluate solubility of the latter at 42 mg L^{-1} in unbuffered solution by comparison of the UV absorbance of a saturated solution with that of a standard solution containing a low percentage of methanol. The solubility is lower in acidic solution: at pH 1, it is lower than 7.4 mg L^{-1} (i.e. 2×10^{-5} M). Chloroxynil was sufficiently soluble for the present study, and its solubility was not precisely determined. For illustration, the spectrophotometric determination of the pK_a of chloroxynil is presented in Fig. 1.

The values of pK_a reported in the literature for chloroxynil, bromoxynil and ioxynil or measured in the present work are gathered in Table 1. The value of pK_a obtained for chloroxynil (3.78) is close to the values published by Tomlin

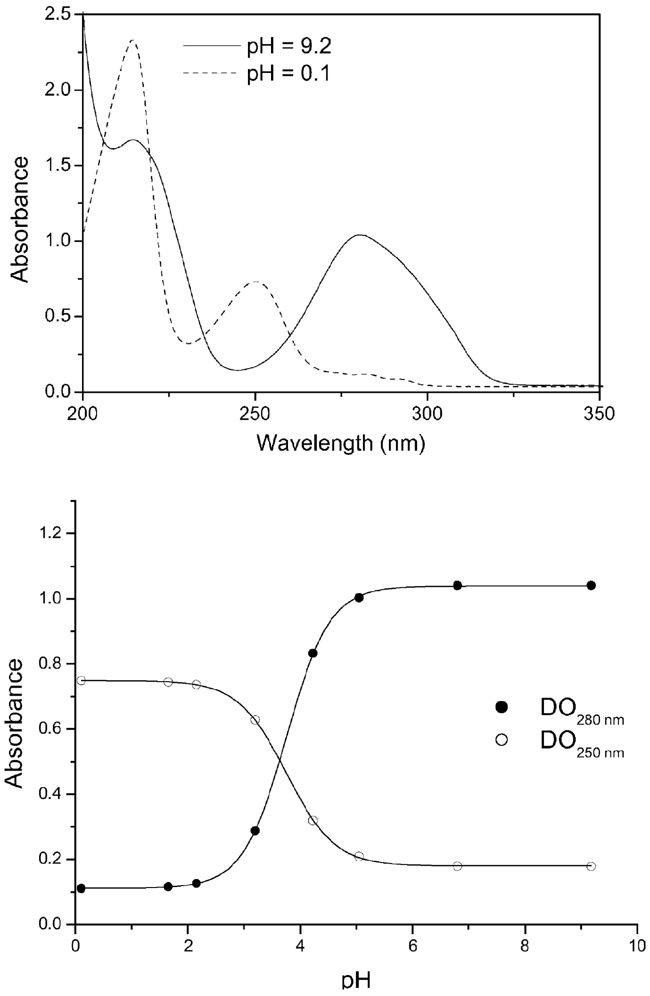


Fig. 1. Absorption spectrum of aqueous solution of chloroxynil 1.4×10^{-4} M for various values of pH, and determination of the pK_a from absorption at 250 and 280 nm.

for bromoxynil and ioxynil [1], and a little lower than the values given by Nolte et al. [3] for the three substrates. It may be noted that these compounds are more acidic than acetic acid, due to the strong electron-withdrawing effect of nitrile group. In environmental conditions, these compounds are thus present mainly in the anionic form.

Table 1
pK_a of studied compounds

	pK_a	Reference
Chloroxynil	4.9	[3]
	3.78	Present work
Bromoxynil	3.86	[1]
	4.3	[3]
	3.75	[9]
Ioxynil	3.96	[1]
	4.5	[3]

Table 2
Spectrophotometric parameters of substrates

	Molecular form		Anionic form	
	λ_{max} (nm)	ε ($M^{-1}\,cm^{-1}$)	λ_{max} (nm)	ε ($M^{-1}\,cm^{-1}$)
Chloroxynil[a]	215	33 500	215	24 200
	250	10 500	280	15 070
Chloroxynil [2]	216	42 190	218	26 760
	251	12 510	281	19 650
Chloroxynil [3]	250		280	
Bromoxynil [17]	251	10 540	283	18 270
Bromoxynil [3]	253		283	
Ioxynil[a]	235	34 100[b]	237	25 670
			285	17 320
Ioxynil [2]	235	32 820	237	25 400
			285	17 300
Ioxynil [3]	258		284	

[a] Present work.

[b] This value is not very accurate (±10%) because of the low solubility in acidic solution ($<2 \times 10^{-5}$ M)).

3.2. Spectrophotometric study

The main characteristics of the UV spectra of chloroxynil, bromoxynil and ioxynil are given in Table 2. It can be noted that the anionic form absorbs at longer wavelengths than the corresponding molecular form. The latter absorbs only very little sunlight (wavelengths longer than 300 nm). Consequently, only the anionic form should play a role in the environmental phototransformation. When either an air-saturated or a deoxygenated solution of chloroxynil 10^{-4} M, buffered at pH 6.3, was irradiated at 296 nm, the spectral characteristics of the solution changed in the course of irradiation. The time-dependent UV spectrum (Fig. 2) shows three isosbestic points at 234, 264 and 314 nm, respectively. This indicates that the stoichiometry remains constant up to a conversion extent higher than 50%. A similar evolution of the spectrum of irradiated solution of ioxynil was observed, in good

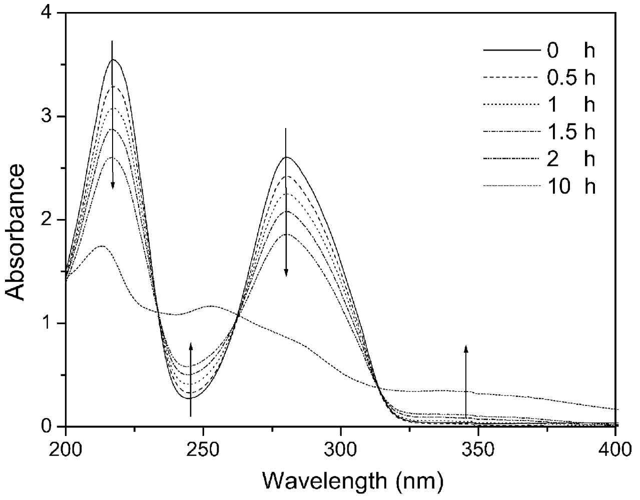


Fig. 2. Evolution of the UV spectrum of an air-saturated solution of chloroxynil 10^{-4} M irradiated at 296 nm.

agreement with the results of Millet et al. [2]. The formation of chloride ions with the former and iodide ions with the latter was also evidenced by HPLC.

3.3. Identification of photoproducts

The HPLC chromatogram of an air-equilibrated solution of ioxynil (10^{-4} M) irradiated between 290 and 350 nm up to approximately 90% conversion is presented in Fig. 3. It may be noted that long irradiation times are required for the gathering of appropriate amounts for NMR analysis of P_{i1} and P_{i2}, which appear as secondary products, while shorter times are more opportune for P_{i3}, which is almost specifically formed at low conversion extent. These three photoproducts were isolated as described in Section 2.3, by HPLC after extraction and concentration. P_{i3} was identified as 5-iodo-3,4-dihydroxybenzonitrile (5-I DHBN) from its mass spectrum with chemical ionisation and its ^{1}H NMR spectrum: $m/z + 1 = 262$, $m/z + 29 = 290$; δ_{ppm} acetone D_6: 9.5 (broad, 2 protons), OH; 7.63, d, H_6 ($J = 1.7$ Hz); 7.18, d, H_2 ($J = 1.7$ Hz). The relatively higher amount of product that has been gathered confirmed that it is the main photoproduct.

Product P_{i2} was identified as 3,4-dihydroxybenzonitrile: $m/z + 1 = 136$, $m/z + 29 = 164$, δ_{ppm} acetone D_6: 9 (broad 2 protons), OH (disappears in the presence of D_2O); 7.15, d ($J = 1.8$ Hz); 7.14, dd, ($J = 1.7$ and 8.7 Hz); 6.97, d ($J = 8.7$ Hz).

The mass spectrum of P_{i4} indicates that this photoproduct is most probably 3-iodo-4-hydroxybenzonitrile (3-I HBN): $m/z + 1 = 246$, $m/z + 29 = 274$. Unfortunately, the isolated amount was not sufficient for an NMR analysis. Similarly, the mass spectrum of P_{i1} is consistent with that of 3,4,5-trihydroxybenzonitrile: $m/z + 1 = 152$, $m/z + 29 = 180$, $m/z + 41 = 192$.

Peak P_{i0} probably corresponds to a mixture of dearomatised products, resulting from the phototransformation of P_{i1}. The values of 183, 139 and 113 were observed on the mass spectrum but not definitively attributed.

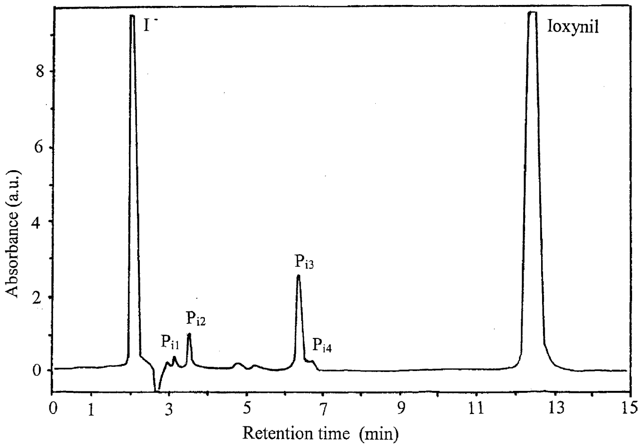


Fig. 3. HPLC chromatogram of aqueous solution of ioxynil 10^{-4} M irradiated between 290 and 365 nm up to approximately 90% conversion. Column C_{18}; eluent $MeOH/H_2O$ 60/40; detection at 237 nm (absorption maximum of ioxynil).

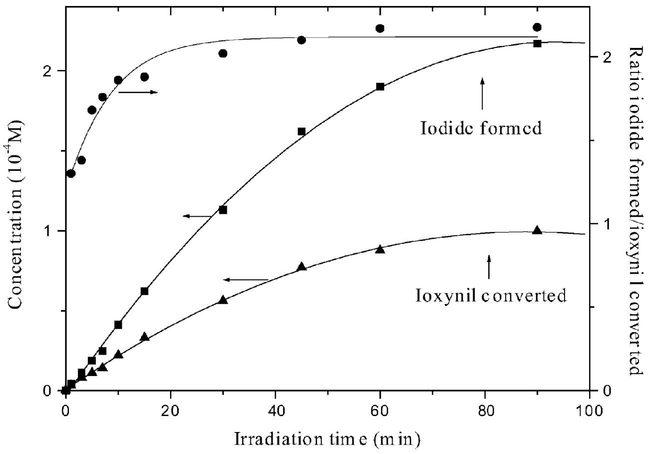


Fig. 4. Ratio of iodide formed to ioxynil transformed in a solution of 1.1 × 10^{-4} M irradiated in the range 290–365 nm.

The scission of the C–I bond was confirmed by HPLC titration of iodide ions formed during the photolysis of ioxynil. As it appears in Fig. 4, the ratio between the formation of I^- and the disappearance of ioxynil, which is initially just a little higher than 1 as expected, increases up to 2 in later stages. The same photoproducts were detected when the solution was exposed to sunlight.

The HPLC chromatogram of a solution of chloroxynil 10^{-4} M irradiated in the same conditions than ioxynil is presented in Fig. 5. As observed with ioxynil, the reaction is initially almost specific. The main photoproduct is P_{c3}. The other products P_{c1} and P_{c2} appear as secondary products. P_{c1} was identified as 3,4,5-trihydroxybenzonitrile by mass and ^{1}H NMR spectrometries: $m/z + 1 = 152$; $m/z + 29 = 180$; $m/z + 41 = 192$. NMR (acetone D_6): singlet at 6.83 ppm. It is then identical to P_{i1} obtained with ioxynil and it will

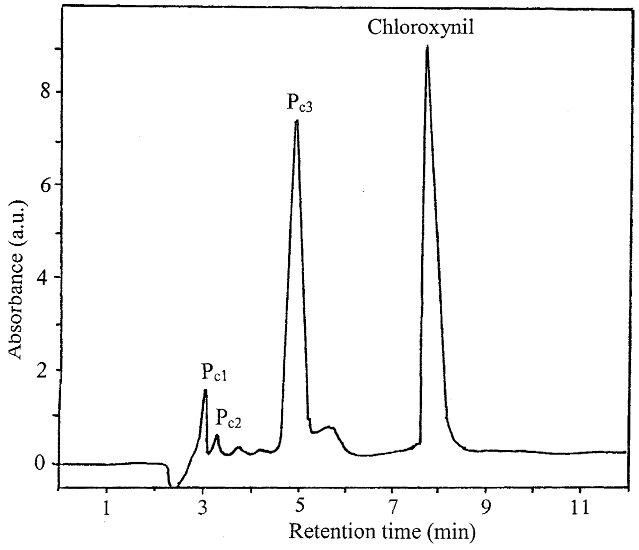


Fig. 5. HPLC chromatogram of a solution of chloroxynil 10^{-4} M irradiated between 290 and 365 nm. Detection at 216 nm.

be abbreviated into P_1). P_{c2} is identical to P_{i2} obtained with ioxynil. It will be abbreviated into P_2.

P_{c3} was identified by mass spectrometry and ^1H NMR as 5-chloro-3,4-dihydroxybenzonitrile (5-Cl DHBN): $m/z + 1 = 170$; $m/z + 29 = 198$; $m/z + 41 = 210$. The presence of a peak at 172 in the ratio 1/3 with the peak at 170 is consistent with a monochlorinated compound. In the NMR spectrum (acetone D_6), two aromatic protons are visible at 7.45 ppm (H_6) and 7.25 ppm (H_2), respectively. P_{c4} was identified from mass spectrometry as 3-chloro-4-hydroxybenzonitrile (3-Cl HBN): $m/z + 1 = 154/156$ (ratio 3); $m/z + 29 = 182$.

It was noted from the amount of isolated products that the yield of P_2 is higher with ioxynil than with chloroxynil, whereas the reverse order was observed with P_1.

3.4. Kinetic study

3.4.1. Quantum yield

The quantum yields of disappearance of ioxynil and chloroxynil at 313 and 296 nm, respectively, were evaluated at 0.005 and 0.013. These values are in good agreement with these previously reported for solutions irradiated with filtered polychromatic light [2]. It can be noted that the quantum yield is higher with chloroxynil than with ioxynil in spite of a higher energy bond of C–Cl compared with C–I. A similar result has been reported for fluorophenols and fluoroanilines, which displayed higher quantum yields than their chlorinated counterparts [12,18]. This observation is consistent with a heterolytic mechanism for the reaction of photohydrolysis, which is the main transformation pathway.

3.4.2. Kinetics of formation of photoproducts

The amounts of isolated photoproducts were not sufficient for the calibration of HPLC. Kinetics of formation of photoproducts in solutions of ioxynil and chloroxynil irradiated in artificial UV light or in sunlight were then studied using HPLC peaks' areas. In both cases, the product of photohydrolysis (P_{i3} or P_{c3}) appears as a primary photoproduct. In contrast, the di- and tri-hydroxylated products (P_1 and P_2) appear as secondary products. Kinetics of formation of the main photoproducts in a solution of ioxynil 1.10×10^{-4} M in pure water irradiated in artificial UV light and in a solution of chloroxynil 1.17×10^{-4} M exposed to sunlight in water collected in the artificial lake of Villerest on Loire (French river) and exposed to sunlight, are presented as examples in Fig. 6a and 6b respectively.

3.4.3. Irradiation in methanolic solution

A solution of ioxynil 10^{-4} M was irradiated in pure methanol and in a mixture of water/methanol 95:5 v/v. The same products, namely P_{i2}, P_{i3} and P_{i4}, were obtained, but another product P_{i5} was also formed and identified as 4-hydroxybenzonitrile from its mass spectrum, obtained by chemical ionisation with CH_4: $m/z + 1 = 120$, $m/z + 29 = 148$, $m/z + 41 = 160$. As expected, in pure methanol, P_{i4} (the product of reductive dehalogenation) was widely

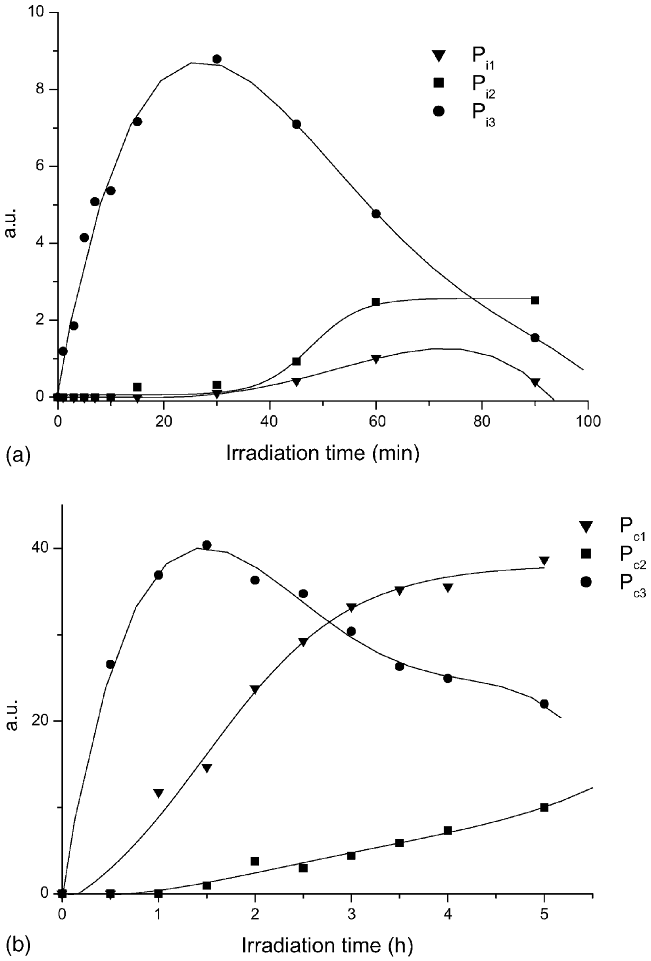


Fig. 6. Kinetics of formation of the main photoproducts in a solution of ioxynil 1.10×10^{-4} M in pure water irradiated in artificial UV light, detection at 237 nm (a), and in a solution of chloroxynil 1.17×10^{-4} M in lake water exposed to sunlight, detection at 216 nm (b).

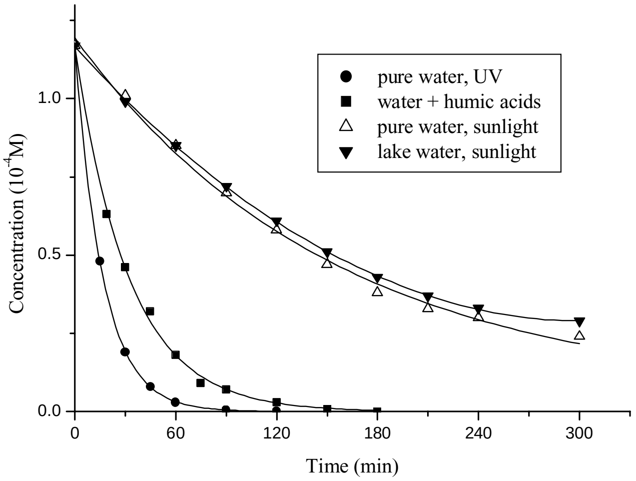
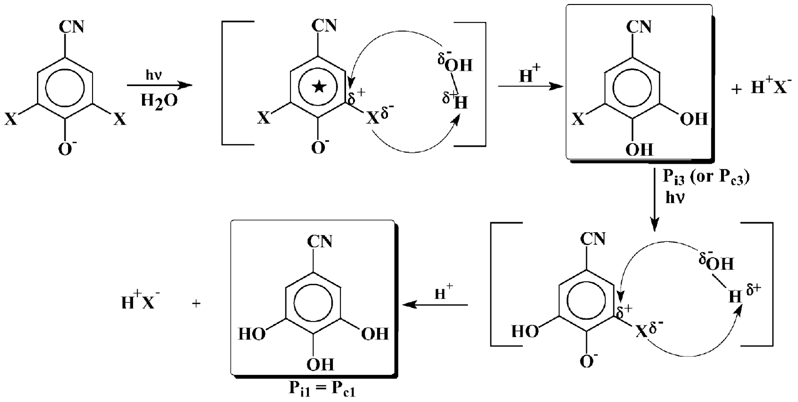


Fig. 7. Influence of humic acids on the photodegradation rate of chloroxynil 1.17×10^{-4} M exposed to UV light (290–365 nm).



Scheme 1. Photohydrolysis of ioxynil and chloroxynil.

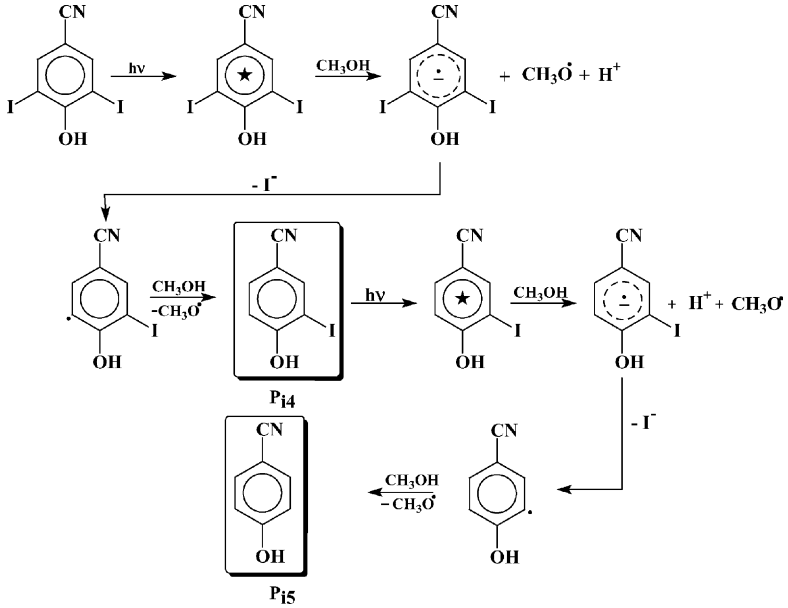
predominant. The minor formation of P_{i2} and P_{i3} may be attributed to the presence of traces of water in methanol. In aqueous solution containing 5% v/v methanol, photohydrolysis and photoreduction have similar rates. It can be deduced that the reaction with methanol is easier than the reaction with water.

3.4.4. Irradiation in the presence of humic acids or in natural surface water

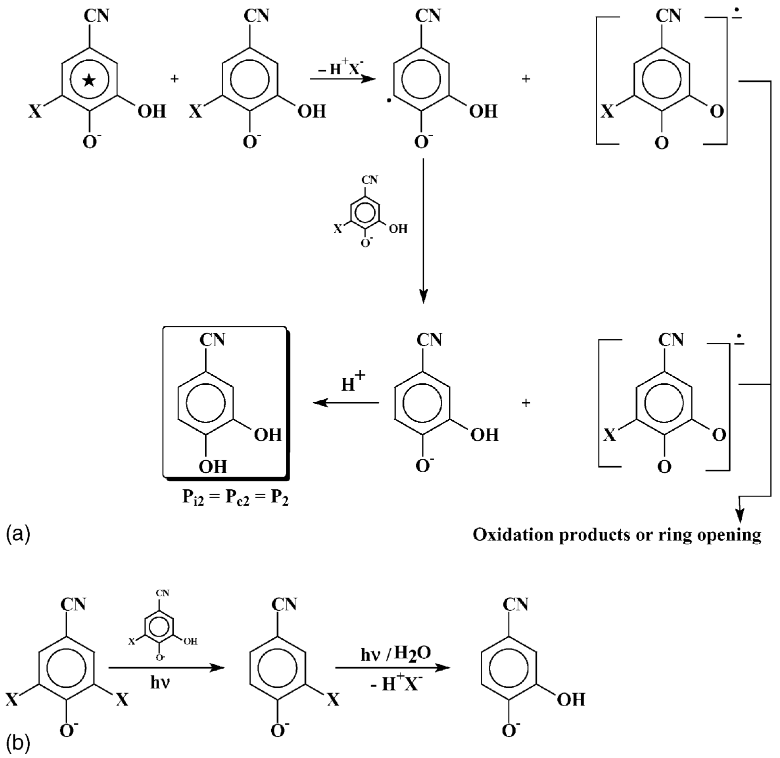
Solutions of chloroxynil 1.17×10^{-4} M were also irradiated in the presence of humic acids Aldrich (26 mg L^{-1}) and in lake water (pH = 7.2). Changing Milli-Q water to lake water had no significant influence on the degradation rate. It can be seen from Fig. 7 that humic acids have an inhibiting effect on the degradation. This means that, at this concentration, their screening effect is more efficient than their inducing effect on the degradation. It was also observed that the presence of humic substances slightly favours the formation of P_2, which involves a reduction process.

4. Discussion and mechanisms

The main initial pathway in UV-irradiated aqueous solutions of ioxynil and chloroxynil is the photohydrolysis of a C–halogen bond. The highest yields were indeed obtained for P_{i3} and P_{c3}. The same phenomenon was previously reported for bromoxynil [9]. This reaction is explained by a heterolytic mechanism involving the scissions, probably concerted, of a C–halogen bond and a molecule of water as it was previously suggested in the case of 3-chlorophenol [10] and 3,4- and 3,5-dichlorophenols [11]. The formation of 3,4,5-trihydroxybenzonitrile from 5-halogeno-3,4-dihydroxybenzonitrile may be described by the same mechanism (Scheme 1). It is noteworthy that no ring contraction was observed whereas this reaction is reported with the 2-halogenophenols, especially when they are presented in their anionic form [10–13]. This is due to the electron-withdrawing effect of the CN group, which inhibits the release of a halide ion when it is not



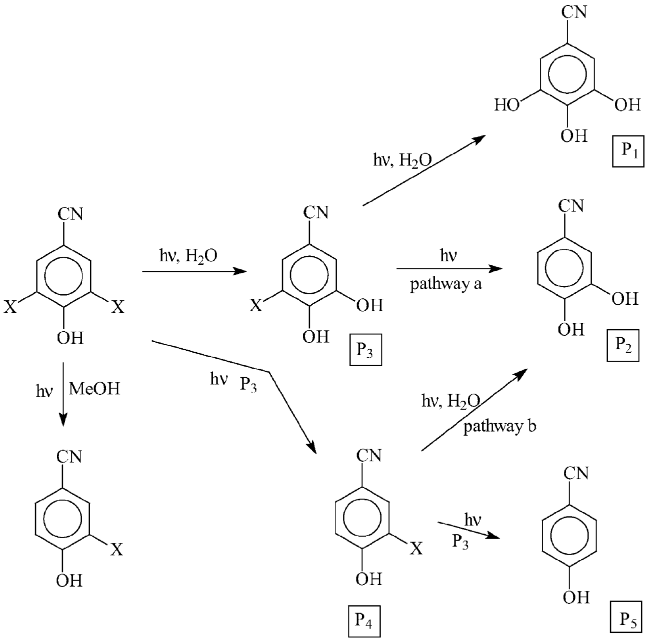
Scheme 2. Photoreduction of ioxynil in methanol.



Scheme 3. Mechanisms proposed for the formation of dihydroxybenzonitrile.

assisted by the heterolytic scission of a molecule of water.

The photoreduction of ioxynil in methanol is attributed to an electron transfer from methanol to ioxynil in the excited state. A similar reaction is expected with bromoxynil and chloroxynil. (Scheme 2).



Scheme 4. Photochemical behaviour of 3,5-dihalogenated-4-hydroxybenzonitriles.

The photoreduction in pure water of ioxynil and chloroxynil into 3-iodo- and 3-chloro-4-hydroxybenzonitrile, respectively, is a minor pathway. A similar behaviour is most likely with bromoxynil. In the absence of added organic matter, 5-halo-DHBN may be assumed to act as the reductant agent, as it is well known that the reductant properties of hydroxylated aromatic derivatives increase with the number of OH groups on the ring.

3,4-Dihydroxybenzonitrile can be formed either by reduction of 5-I DHBN and 5-Cl DHBN (Scheme 3a) or by photohydrolysis of 3-I HBN and 3-Cl HBN (Scheme 3b). Pathway 'a' is more likely since 3-I HBN (P_{i4}) and 3-Cl HBN (P_{c4}) are a very minor intermediates. The fact that the formation of 3,4-dihydroxybenzonitrile (P_2) is easier with 5-I DHBN than with 5-Cl DHBN is attributed to the lower polarity of the C–I bond compared to the C–Cl bond. In contrast, 5-Cl DHBN is more specifically photohydrolysed than photoreduced. The general photochemical behaviour of 3,5-dihalogeno-4-benzonitrile is summarized in Scheme 4.

5. Conclusion

Results obtained with chloroxynil and ioxynil are in good agreement with those previously obtained with bromoxynil. The nature of the halogen has no significant influence on the photoreaction. In pure water, the main photolytic pathway of 3,5-dihalogeno-4-hydroxybenzonitriles irradiated in artificial UV light or in sunlight is a heterolytic photohydrolysis, as observed with 3-chlorophenol, and

3,4- and 3,5-dichlorophenols, but differently from 2-halogenophenols. In a second step, the 5-halogeno-3,4-dihydroxybenzonitriles initially formed are photohydrolysed (most efficiently with chlorinated derivative) or photoreduced into 3,4-dihydroxybenzonitrile (mainly with the iodo derivative). The presence of humic acids slightly reduces the transformation rate of chloroxynil by a screening effect. Photoreduction of ioxynil is a minor pathway in pure water, but it is the main reaction in alcohols.

Acknowledgements

The authors acknowledge the Centre National de la Recherche Scientifique (CNRS), Coopération Internationale No. 10093), and the Ministère Algérien de l'Enseignement et de la Recherche, for their financial support. They are grateful to the firm Rhône-Poulenc Agrochimie for providing ioxynil of high purity. They are also grateful to Othman Abida for his collaboration in HPLC analyses.

References

[1] C.D.S. Tomlin, The Pesticide Manual, 12th ed., British Crop Protection Council, Farnham, UK, 2000, pp. 110 and 548.

[2] M. Millet, W.-U. Palm, C. Zetzsch, Ecotox. Environ. Safety 41 (1998) 44.

[3] J. Nolte, F. Heimlich, B. Graβ, N. Zullei-Siebert, G. Preuss, Fresenius J. Anal. Chem. 351 (1995) 88.

[4] J. Kochany, G.G. Choudhry, G.R.B. Webster, Environ. Sci. Res. 42 (1991) 259.

[5] J. Kochany, G.G. Choudhry, G.R.B. Webster, Pestic. Sci. 28 (1990) 69.

[6] J. Kochany, Chemosphere 24 (1992) 1119.

[7] J. Kochany, G.G. Choudhry, G.R.B. Webster, Arch. Environ. Contam. Toxicol. 19 (1990) 325.

[8] J. Kochany, G.G. Choudhry, Toxicol. Environ. Chem. 27 (1990) 225.

[9] F. Machado, L. Collin, P. Boule, Pestic. Sci. 45 (1995) 107.

[10] P. Boule, C. Guyon, J. Lemaire, Chemosphere 12 (1982) 1179.

[11] P. Boule, C. Guyon, J. Lemaire, Chemosphere 13 (1984) 603.

[12] P. Boule, L. Meunier, F. Bonnemoy, A. Boulkamh, A. Zertal, B. Lavédrine, Int. J. Photoenergy 4 (2002) 69, references therein.

[13] C. Guyon, P. Boule, J. Lemaire, Nouv. J. Chim. 8 (1984) 685.

[14] I. Texier, C. Giannotti, S. Malato, C. Richter, J. Delaire, Catal. Today 54 (1999) 297.

[15] J. Kochany, G.G. Choudhry, G.R.B. Webster, Int. J. Environ. Anal. Chem. 39 (1990) 59.

[16] J.G. Calvert, J.N. Pitts Jr, Photochemistry, John Wiley & Sons, New York, 1966, p. 783.

[17] L. Collin, F. Machado, unpublished results.

[18] K. David-Oudjehani, P. Boule, New J. Chem. 19 (1995) 199.