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PII: S1010-6030(18)30898-0
DOI: https://doi.org/10.1016/j.jphotochem.2018.07.043
Reference: JPC 11409

To appear in: *Journal of Photochemistry and Photobiology A: Chemistry*

Received date: 29-6-2018
Revised date: 27-7-2018
Accepted date: 28-7-2018

Please cite this article as: Bououden Z, Halladja S, Sleiman M, Leremboure M, Richard C, Mechanism of Bromoxynil phototransformation: effect of medium and surfactant, *Journal of Photochemistry and amp; Photobiology, A: Chemistry* (2018), https://doi.org/10.1016/j.jphotochem.2018.07.043

Mechanism of Bromoxynil phototransformation: effect of medium and surfactant

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Graphical abstract

Highlights

- Bromoxynil undergoes photoreduction on wax in the presence of H-donor molecules
- On wax, the dehalogenation is partly homolytic and release bromine atoms
- In water, photodehalogenation is heterolytic
- Numerous adducts are generated at high conversion extent

Abstract:

Bromoxynil (BXN, 3,5-dibromo-4-hydroxybenzonitrile) is a herbicide that is classified as a highly hazardous chemical, toxic for the reproduction. The processes and mechanisms regarding the fate of this compound in the environmental compartments subject to solar light are poorly documented. In this work, we investigated the photochemical transformation of BXN and its main photoproducts on two relevant compartments: the surface of plant leaves that are contaminated during the crop treatments and water as the medium receiving pollutions. In a first step, BXN was deposited on wax films mimicking the surface of leaves and exposed to simulated solar light. Deposited as a pure molecule, BXN was photostable whereas deposited in the presence of an ethoxylated surfactant (5-10% in weight) BXN underwent a fast photoreduction yielding 3-bromo-4-hydroxybenzonitrile (MBr) as the unique primary photoproduct. Using muconic acid as a trapping agent for bromine atoms, it was shown that photodebromination was partly homolytic with release of bromine radical. In a second step, we studied the photolyses of BXN and MBr in water, because both should be able to reach surrounding aquatic media by wash off and leaching. The primary reactions were the heterolytic replacement of Br^- by OH^-, but photoreduction, photooxidation and formation of adducts were also observed at higher extent of the reactions. These results demonstrate that the mechanism of phototransformation of BXN depends drastically on the medium. They also stress the potentially important role of surfactants in the fate of BXN on leaves, and the need to investigate the photochemical reactions in a wide range of conditions to cover the diversity of situations.

1. Introduction

Bromoxynil (BXN, 3,5-dibromo-4-hydroxybenzonitrile) is a herbicide that is used for the post-emergence control of annual broad-leaves weeds. Approved in almost all the european countries, it is listed in the Pesticide Action Network as a highly hazardous chemical and classified as toxic for the reproduction. Consequently, its environmental fate is of concern. In the environment, the phototransformation is possible because of the light absorption properties of BXN (Figure 1A). The photolysis of BXN in water was the subject of several studies since the 1990s. They showed that in simulated solar light BXN (pKa = 3.75 ±0.05) undergoes photolysis with a quantum yield lying between 0.008 and 0.064 (1-4). The main primary photoproduct was 3-bromo-4,5-dihydroxybenzonitrile (MBr) [1, 2, 4] and Br^- formation was also detected [4] in accordance with a heterolytic photodebromination (Scheme 1). Photoreduction into MBr and 4-hydroxybenzonitrile (HBZ) was also observed when chloride anions, carbonates or natural organic matter were added to the medium [5-7] (Scheme 1).To our knowledge, product studies mainly focused on photoproducts formed in the very early stages of the reaction and little is known on the intermediates formed at longer stages.

More recently, the photodegradation of BXN immobilized on silica particles was studied because due to its poor solubility in water BXN might be partly adsorbed on particles in surface waters [4]. In these conditions, the quantum yield of photolysis was drastically reduced and bromide ions were not detected suggesting significant changes in the photolytic reactions.

Surface water is not the only compartment in which BXN can be potentially found. Being applied on crops in post-emergence, BXN is also abundantly present on plant leaves. After the fast evaporation of water contained in the spray mixtures, BXN forms dry deposits on the apolar waxes covering the leaves. It is exposed to solar light and can potentially undergo photolysis as observed for many other molecules [8]. Pesticides being always applied in the presence of formulation additives, the dry deposits consist of BXN embedded in the formulants. Formulation agents are generally non-absorbing, but they were shown to enhance the photodegradation of pesticides [9, 10]. In the case of sethoxydim, the adjuvants contained in the formulation Poast® were found to accelerate the photodegradation of the pesticide and the existence of a sensitizing effect was proposed by the authors [9]. The rate of thiram photodegradation was also significantly increased by the inert components of the commercial formulation and again sensitization was proposed [10]. Formulation agents can at least serve as hydrogen atoms donors [11].

Consequently, the photochemical reactivity of BXN on plant leaves may be different from that described in water because (i) water molecules that govern the aqueous photochemical reaction are not or poorly present on leaves and (ii) the phototransformation of halogenated aromatics is greatly affected by H-donor molecules [12]. To our knowledge, the photochemical fate of BXN on leaves was not reported in the literature although this reaction governs the nature of chemicals released in the surface waters through leaching.

The present work aimed to shed light on the fate of BXN in the different environmental compartments focussing on the poorly documented aspects of the reaction. We investigated the photochemical reactivity of BXN on paraffinic wax films mimicking the apolar surface of leaves in the absence and in the presence of surfactants to approach the real conditions. Then, we studied the aqueous photolysis of BXN on a long time scale to identify secondary photoproducts. Phototransformation of MBr, the main photoproduct of BXN on leaves, was also studied on wax and in water because, to our knowledge, the photoreactivity of this molecule was never reported.

2. Experimental Section

2.1 Materials

BXN (Pestanal), MBr (97%) and HBZ (95%) were purchased from Sigma Aldrich and used as received. Synperonic® 10/6, an ethoxylated primary branched C_9 – C_{11} alcohol with full saturation, water soluble and nonionic surfactant was provided by Uniquema. Paraffinic wax (melting point 70-80°C) was obtained from Aldrich. Acetonitrile (Hipersolv) was obtained from VWR Chemicals. The other reactants and HPLC solvents were of the highest grade available. Water was purified using a reverse osmosis RIOS 5 and Synergy (Millipore) device (resistivity 18 MΩ cm, DOC < 0.1 mg L^{-1}). Stock solutions of BXN (2×10^{-4} M) and MBr (10^{-4} M) were prepared in acetonitrile and stored at 4°C. They were used directly or diluted with purified water to obtain a concentration of 5×10^{-5} M. pH was adjusted using NaOH or $HClO_4$.

2.2 Irradiations

The dishes of 9 cm^2 containing paraffinic wax films were prepared according to (8). BXN or MBr dissolved in pure acetonitrile or in acetonitrile containing Synperonic (10% in weight) were deposited on wax as 10 μL droplets using a micropipet (Eppendorf, Montesson, France). The solvent was allowed to dry overnight at room temperature in the dark. After drying, the surface concentrations of BXN and MBr were 0.6 μg cm^{-2} and 0.2 μg cm^{-2} respectively. Dishes were irradiated in a Suntest CPS solar simulator (Atlas, Elancourt, France) equipped with a xenon arc lamp. A filter was used to cut off wavelengths shorter than 290 nm. The intensity of the lamp was set at 500 W m^{-2} within the wavelength range 290-800 nm to simulate the sunlight average intensity in June in France. Water at 10°C was flowed through the bottom of the solar simulator in contact with the dishes. The surface temperature of the dishes was measured with an infrared thermometer gun. It remained below 25°C during the irradiations. Dishes were covered with a quartz plate as a protection against the air cooling system. 24 dishes could be irradiated simultaneously in the solar simulator and three dishes were removed at each selected irradiation time. The dishes were each rinsed with 1 mL of a methanol-water (50:50, v/v) mixture. This mixture was chosen because it gives a recovery yield of 94 ± 3 %, as previously determined on non-irradiated dishes. The three solutions were injected for analysis in HPLC and the quantification of the substrate loss was based on the average of the three analyses. Aqueous solutions and solutions in acetonitrile were irradiated in a cylindrical device equipped with six TLAD 15W/05 fluorescent tubes emitting within the wavelength range 300-450 nm with a maximum of emission at 365 nm. The Pyrex glass reactor (14 mm inner diameter) was placed in the center of the device. The reactor was filled with 10 mL of solution. The 1 ml-aliquots were withdrawn after selected irradiation times and analyzed by UV-visible and HPLC. HPLC analyses were made in duplicate. To accelerate reactions, irradiations were also performed in a device equipped with six fluorescent tubes DUKE GL 20E emitting between 280 and 380 nm. Quantum yield measurements were performed by irradiating solutions in parallel beam using a mercury arc lamp and an Oriel monochromator. The photon flux was measured by a radiometer QE65000 from Ocean optics.

2.3 Analytical methods

The irradiated solutions of BXN and MBr were analyzed using a Waters HPLC system consisting in an autosampler (Waters 717 plus), a degasser (Agilent 1100 series), a solvent delivery system (Waters 600) and a photodiode array detector (Waters 996). An Agilent Zorbax Eclipse XDB-C_{18} (250mm×4.6mm, 5µm particle size) was used as the analytical column. The eluent was a mixture of methanol and water containing 0.5% phosphoric acid (55:45, v/v). The flow rate was set at 1 mL.min^{-1} and the injection volume was of 30 µL. High resolution mass spectrometry (HRMS) was performed on an Orbitrap Q-Exactive (Thermoscientific) coupled to an ultra-high performance liquid chromatography (UHPLC) instrument Ultimate 3000 RSLC (Thermoscientific). Analyses were made simultaneously in negative (ESI^-) and positive (ESI^+) electrospray modes. The column was a Kinetec EVO C18 (100 mm×2.1 mm) with a particule size of 1.7 μm (Phenomenex). The binary solvent system was composed of acetonitrile and acidified water by formic acid. The gradient elution started with 5% of acetonitrile and reached 95% after 9 min. The flow was set at 0.45 mL min^{-1}. UV-visible spectra were recorded on a Cary 3 (Varian) spectrophotometer in quartz cuvettes.

3. Results and discussion

3.1 Irradiations on paraffinic wax films

Figure 2 shows the consumption profile of BXN when it was deposited on paraffinic wax films alone or in the presence of Synperonic® (10% in weight) and irradiated in the solar simulator. Alone (Figure 2, curve 1), BXN was rather photostable while in the presence of the surfactant (Figure 2, curve 2) it underwent photolysis ($t_{1/2}$~ 100 min) yielding MBr and HBZ as the main detected photoproducts (Table 1). The accumulation of MBr was limited to 5% (Figure 2, curve 3), suggesting it was photodegraded in turn. We checked this by irradiating MBr in the same conditions as BXN. Deposited pure on wax MBr did not undergo phototransformation whereas in the presence of Synperonic (Figure 2, curve 4) MBr was phototransformed at a rate similar to that of BXN. This photodegradation explains the moderate accumulation of MBr during the irradiation of BXN. The main photoproduct of MBr was HBZ. MBr was produced by the substitution of Br by H in BXN and similarly HBZ was formed by the substitution of Br by H in MBr.

Another series of experiments was undertaken to determine whether BXN photodebromination was a homolytic or a heterolytic reaction. For this, we added muconic acid ($C_6H_6O_4$) to the acetonitrile solution of BXN+Synperonic® (10% in weight). Our hope was that this dienic molecule would be able to trap bromine radicals yielding to the corresponding bromo derivative. The deposit and the dishes irradiation were reproduced identically as for BXN+Synperonic® alone. The solution was irradiated until a BXN conversion extent of 40 ± 2% as measured by HPLC and then analyzed by LC-HRMS in negative mode. We detected a peak at m/z= 220.8870 and 222.8840 corresponding to $[C_6BrH_6O_4]^-$, the deprotonated form of the adduct $C_6H_6O_4$ + HBr. This confirms the addition of HBr on the probe molecule and thus the release of a part of Br as bromine radicals during the photolysis of BXN. In the LC-HRMS chromatogram, the double peak of Br^- at m/z = 78.92 and 80.92 was present. However, the integration of this peak gave an area 10-fold lower than that obtained by irradiation of BXN in water after the same conversion extent. This low yield in Br^- on wax is consistent with the trapping of bromine radicals by muconic acid.

The mechanism of BXN photolysis on wax and the strong accelerating effect of Synperonic® on the reaction can be described according to Scheme 2. The homolytic cleavage of the C-Br bond can take place yielding to the formation of a phenyl radical and a bromine radical. In the absence of H-donor molecule the fast radical recombination would regenerate BXN, while reduction of the phenyl radical by H-donor ethoxylated constituents of Synperonic® would produce MBr and HBr. The accelerating effect of Synperonic® on the rates of BXN phototransformation can be also due to a direct H atom transfer from the H-donor ethoxylated constituents of Synperonic® to the excited BXN to form the reduced radical of BXN and bromide radical and the same final photoproducts as described above. Photoreduction of halogenoaromatics in H-donor organic solvents was reported in the literature [12].

BXN was also irradiated in acetonitrile. BXN disappeared very slowly confirming a poor photoreactivity in the absence of water or H-donor additive. BXN was also irradiated in acetonitrile containing 2-propanol (0.5%). In this case, it was phototransformed into MBr, accumulation of which reached 20% (Figure SI-1). This chemical yield is higher than on wax in the presence of Synperonic®. It shows that 2-propanol is a better H-donor molecule than ethoxylated constituents of Synperonic® and demonstrates that the amount of MBr formation on leaves may strongly depend on the H-donor properties of the surrounding molecules.

The involvement of surfactants as H-donor molecule implies their oxidation. The chemical formula of Synperonic® molecules is CH_3-$(CH_2)_y$-$(OCH_2$-$CH_2)_x$-OH and the H atoms of the methylenes linked to the ether oxygen are the most easily extractable (13). A lot of oxidation products can be generated including peroxides, esters and aldehydes after bond scissions. Due to the numerous Synperonic® constituents and H-atom abstraction possibilities, we were not able to detect photoproducts from surfactants. This type of reaction would deserve a special focus.

3.2 Irradiations in water

Considering that MBr as BXN might be susceptible to reach surface waters, we investigated their photolysis in water. The occurrence of MBr in surface water is likely considering that BXN was reported to yield MBr when it was irradiated in the presence of natural water constituents such as chloride anions, carbonates or natural organic matter [5-7]. The phototransformation of BXN in water under irradiation with polychromatic light (300-450 nm) is shown in Figure 3A. The consumption was measured at pH 2 when BXN is in neutral form (Figure 3A, curve 1) and in neutral solution when it is in anionic form (Figure 3A, curve 2). The decay was much faster for the anionic form than for the neutral one, in accordance with a higher absorptivity of the former at $\lambda > 300$ nm (Figure 1B). Like BXN, MBr is an ionisable compound and investigations started by measuring its pKa value. This was achieved by monitoring the changes of absorbance at 277 nm with pH. A value of 5.8 ± 0.1 was found (Figure SI-2). This higher value compared to that of BXN is explained by the presence of only one electroattracting Br atom instead of 2. The kinetic of MBr photolysis was measured for the neutral form (Figure 3B, curve 1) and for the anionic form at pH = 7 (Figure 3B, curve 2). In anionic form, the rate of MBr was faster than that of BXN ($t_{1/2}$ = 1 h instead of 2.5 h). In agreement, the quantum yield of MBr photolysis measured at 313 nm upon irradiation in parallel beam was equal to 0.12 in deoxygenated aqueous solution at pH=4 and to 0.16 at pH=8.3, i.e little higher than for BXN as reported in the literature [1-4]. The addition of oxygen did not change these values.

A typical HPLC chromatogram of an irradiated solution of MBr is shown in Figure 4. The list of photoproducts of BXN and MBr detected by HRMS analyses are listed in Table 1. I, II, III, HBZ and MBr were already described in the literature as photoproducts of BXN. I was the main photoproduct of BXN until a conversion extent of ~30%. It was also formed upon prolonged irradiation of MBr, but in this case, it was produced by oxidation and not photohydrolysis. II arose from I through the replacement of the second Br atom by OH. At higher conversion extent of BXN, MBr and HBZ were formed and photoproducts in C_{13}-C_{14} were also detected. For BXN, two peaks at m/z = 239.0456 and 251.0460 were found at a conversion extent of 70%. The corresponding neutral molecules are $C_{13}H_8O_3N_2$ and $C_{14}H_8O_3N_2$. MS-MS analyses revealed that $C_{13}H_8O_3N_2$ loose CO_2 and contains likely a carboxylic acid fonction. For MBr, prolonged irradiations yielded a lot of compounds, in particular $C_{13}H_8O_3N_2$ and $C_{14}H_8O_3N_2$ again along with $C_{13}H_{10}O_2N_2$, $C_{13}H_{10}O_3N_2$, $C_{14}H_8O_2N_2$, $C_{14}H_6O_2N_2$, $C_{14}H_8O_3N_2$. $C_{13}H_{10}O_3N_2$, $C_{13}H_{10}O_2N_2$ and $C_{14}H_8O_2N_2$ loose H_2O. All these adducts are debrominated confirming that the C-Br bond is the most photoreactive moiety of the molecule. $C_{14}H_8O_2N_2$ corresponds to the coupling of 2 HBZ molecules (C_7H_5NO+C_7H_5NO-2H) while $C_{14}H_8O_3N_2$ with the coupling of HBZ and III, the oxidized derivative of $C_{14}H_8O_2N_2$ (C_7H_5NO+$C_7H_5NO_2$-2H). The detection of molecules with 13 C atoms shows that a C carbon can be lost. This suggests more complex mechanisms involving oxidation, CO_2 elimination and/or ring opening [14].

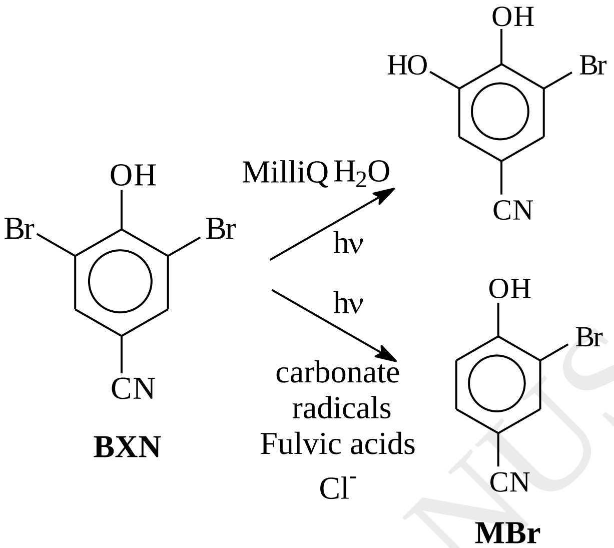
The primary photoproducts generated from BXN and MBr are in line with the heterolytic cleavage of the C-Br bond to yield hydroxylated derivatives as it previously shown for BXN [1,2,4]. At high conversion extent, the reactions become complex. Photoreduction of BXN yielding to MBr and of MBr to HBZ occurs. These processes likely involve the hydroxylated compounds, intermediary formed such as II and III, as H-donor chemicals. In addition, photooxidation takes place along with dimerization and likely ring opening. A lot of molecules are expected to be generated as previously found for halogenosalicylic acids [14].

4. Conclusion

The mechanism of BXN photolysis strongly depends on the medium. As reported in the literature, our study shows that heterolytic release of the Br atoms takes place in water. It also shows that homolytic cleavage occurs in acetonitrile and on paraffinic wax films, a solid support mimicking the surface of leaves. The photoreactivity of BXN is thus strongly affected by the medium and it is drastically enhanced by the presence of ethoxylated surfactants that play the role of H-donor molecules. The release of bromine radicals could be demonstrated using muconic acid as a trapping agent. MBr, the main photoproduct of BXN on apolar wax films that could reach surface waters by leaching, shows an aqueous photoreactivity similar as that of BXN with formation of various adducts more or less oxidized. This work demonstrates that surfactants must be taken into consideration in the studies dealing with photochemical reactivities of pesticides. The reason for that is the capacity of surfactants to serve as a hydrogen atom source and promote photoreductions just after the pesticides spraying.

Acknowledgments: Zelikha Bououden thanks the Seddik Benyahia University for having granted her for two stays in The ICCF laboratory.

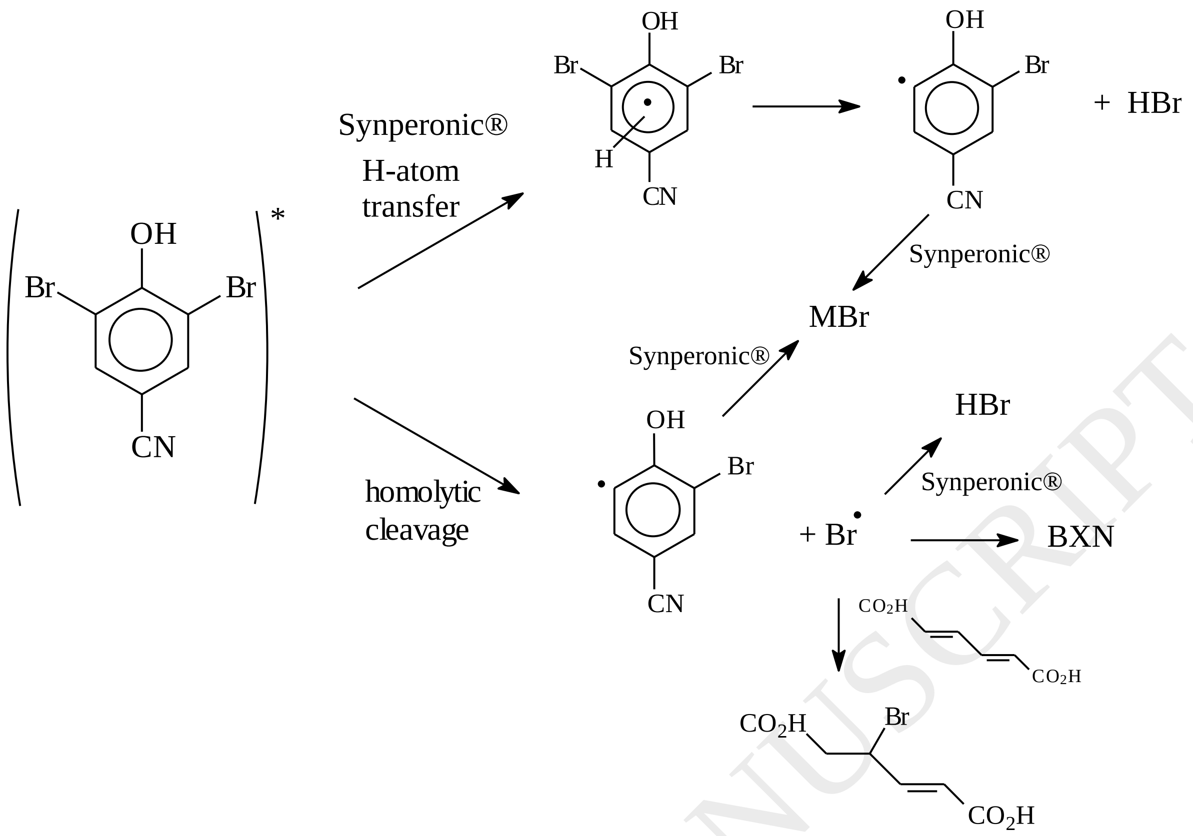
Schemes



BXN

MBr

Scheme 1: Photolysis of BXN in water, as reported in the literature [1-7]



Scheme 2 : Photolysis of BXN on wax in the presence of Synperonic®

Figures

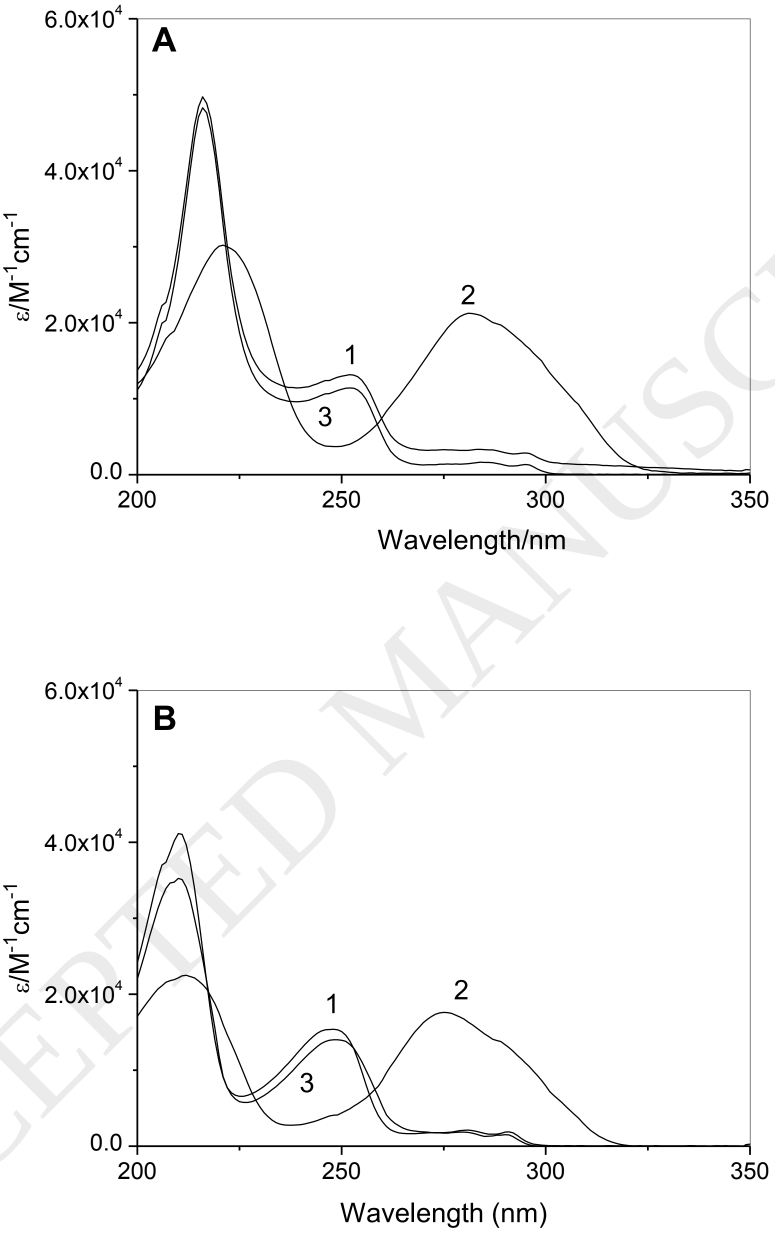


Figure 1: UV spectra of BXN (A) and MBr (B). 1: in water pH 2; 2: in water pH 8; 3: in acetonitrile

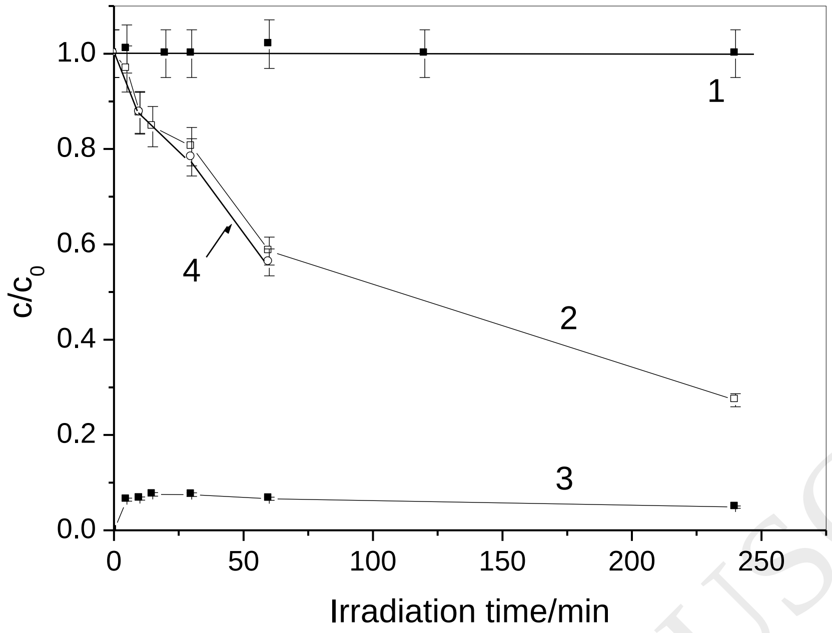


Figure 2: Consumption profile of BXN deposited on paraffinic wax films and irradiated in the solar simulator (1) alone and (2) in the presence of Synperonic® (10% in weight). Formation of MBr (3) when BXN was irradiated in the presence of Synperonic®. Consumption profile of MBr deposited on paraffinic wax films and irradiated in the solar simulator in the presence of Synperonic® (10% in weight) (4).

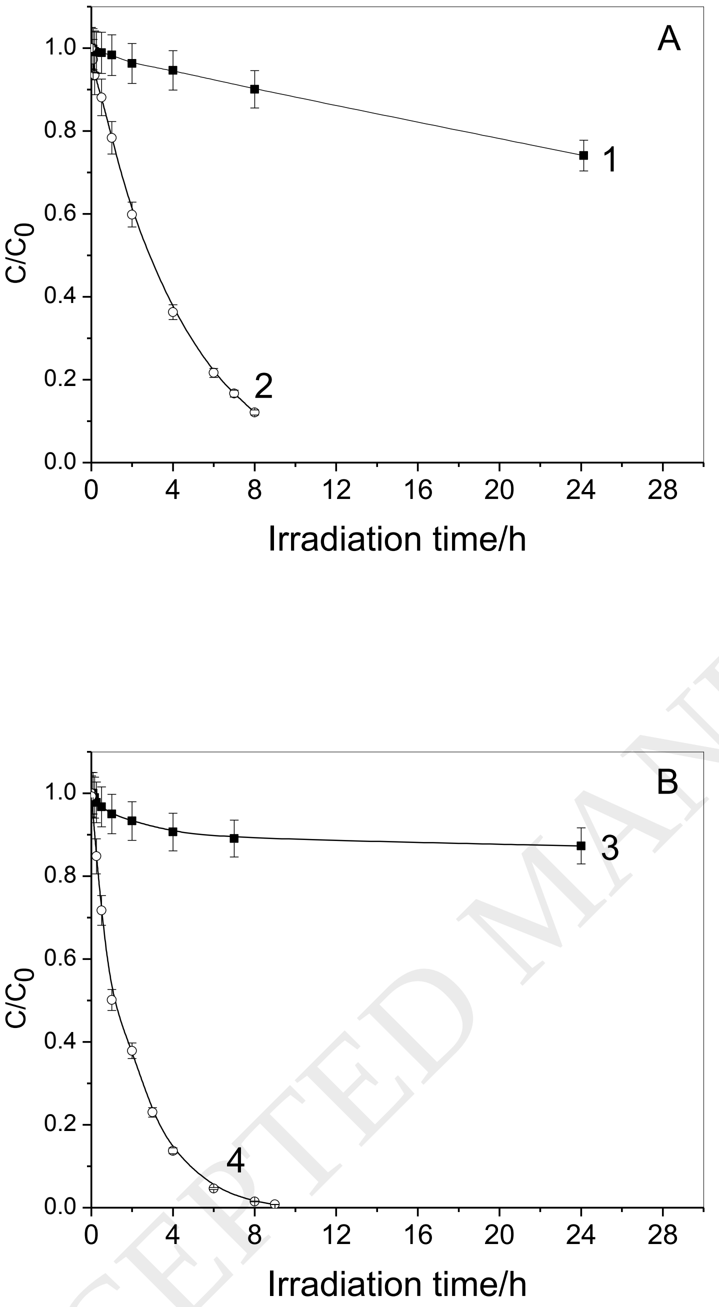


Figure 3: Consumption profiles of BXN (5×10^{-5} M) (A) upon irradiation using polychromatic light 300-450 nm in molecular form (1) and anionic form (2) and of MBr (5×10^{-5} M) (B) in molecular form (3) and anionic form (4)

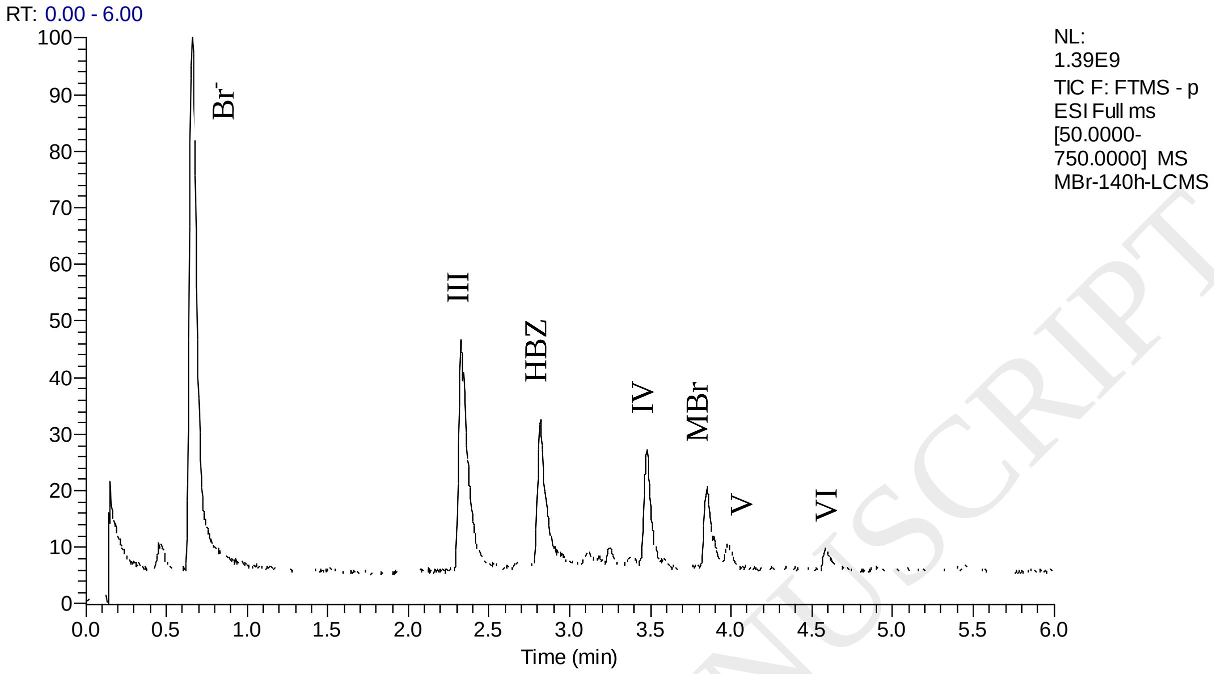


Figure 4: TIC chromatogram of a solution of MBr irradiated until almost complete MBr photodegradation

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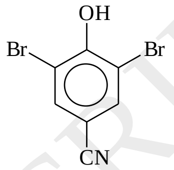
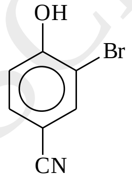
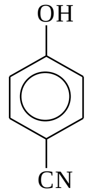
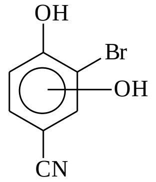
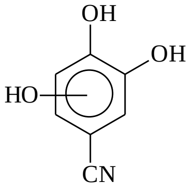
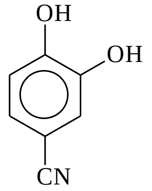
Table

Table 1: Main identified photoproductsgeneratedfrom irradiation of BXN and MBr in different conditions. Secondary photoproducts identified by the label (S).

Name	conditions of detection	Mass measured in ES^-	Δppm	Structure or formula of neutral compound
BXN		273.8511 and 275.8487 and 277.8486	0.1	
MBr	BXN/Wax + Synperonic BXN/Acetonitrile + 2-propanol BXN/Water (S)	195.9393 and 197.9371	0.1	
HBZ	BXN/Wax + Synperonic (S) BXN/Acetonitrile + 2-propanol (S) BXN/Water (S) MBr in all the previous conditions	118.0286	0.1	
I	BXN/Water MBr/Water (S)	211.9345 and 213.9323	1.0	
II	BXN/Water MBr/Water (S)	150.0185	0.1	
III	BXN/Water (S) MBr/Water	134.0234	0.1	
IV	MBr/Water (S)	225.0661	2.8	$C_{13}H_{10}O_2N_2$
V	MBr/Water (S)	235.0510	3.2	$C_{14}H_8O_2N_2$
VI	MBr/Water (S)	233.0353	3.1	$C_{14}H_6O_2N_2$
VII	BXN/Water (S) MBr/Water (S)	251.0460	3.3	$C_{14}H_8O_3N_2$
VIII	MBr/Water (S)	241.0614	3.4	$C_{13}H_{10}O_3N_2$

Minor photoproducts				
	BXN/Water (S) MBr/Water (S)	239.0459	3.2	$C_{13}H_8O_3N_2$
	MBr/Water (S)	207.0557	1.0	$C_{13}H_8ON_2$