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Main pathways in the photochemical transformation of 3-(4-bromophenyl)-1-methoxy-1-methylurea (metobromuron) in aqueous solution

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Abstract

Metobromuron (MB) in aqueous solution has a complex photochemical behaviour due to the involvement of two main different routes: demethoxylation of urea moiety and reactions (hydroxylation, oxidation, formation of adducts) resulting from the initial formation of a carbene. Both pathways occur in approximately equal proportions in the case of MB. Comparison with other halogenophenylureas indicates that the position of the halogen atom on the ring and the nature of the substituent on the urea moiety play an important role in the relative importance of these two pathways: the carbene pathway is related to the presence of a halogen atom in *para*-position on the ring and *N*-demethoxylation is much easier than *N*-demethylation. Hydroxylation of the ring without debromination was also observed. The photocatalytic degradation also leads to the formation of several products resulting from hydroxylation of the ring and demethoxylation.

Keywords: Metobromuron; Halogenophenylurea; Phototransformation; Carbene; Demethoxylation; Benzoquinone mono-imine

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1. Introduction

Halogenophenylureas form an important group of herbicides. They are chemically stable but they absorb the short wavelengths of sunlight (up to about 300 nm) and their direct photolysis may play a role in their elimination from natural waters. Many of them were the subject of photochemical studies in aqueous solution in particular 3-(3-chloro-4-methylphenyl)-1,1-dimethylurea (chlorotoluron) [1] and 3-(3-chloro-4-methoxyphenyl)-1,1-dimethylurea (metoxuron) [2]. Both these compounds undergo an almost quantitative photohydrolysis of C–Cl bond. Monuron [3-(4-chlorophenyl)-1,1-dimethylurea] has a more complex behaviour. Rosen et al. [3] reported that the substitution of Cl by OH is the main pathway, whereas Crosby and Tang [4] identified several photoproducts resulting from the oxidation or elimination of methyl groups. Hydroxylation of the ring without dechlorination and formation of 4,4′-dichlorocarbanilide were also reported. With linuron and chlorbromuron, which are 3,4-dihalogenophenyl-1-methoxy-1-methylureas, several reactions compete, mainly photohydrolysis of carbon halogen bond, demethoxylation, and reductive elimination of Br (in the case of chlorbromuron) [5,6]. The photolysis of metobromuron (MB) was reported in two publications [5,7].

The major product found by Rosen and Strusz is 3-(4-hydroxyphenyl)-1-methoxy-1-methylurea. Minor products include 3-(4-bromophenyl)-1-methylurea and 4-bromophenylurea. Mass spectral data suggested that a substituted biphenyl is formed by elimination of HBr, but this product was not identified. No mechanism was suggested for the formation of the identified photoproducts [7]. More recently, Nick and Schöler [5] reported that the main photoreactions of *N*-methoxylated phenylureas result from the cleavage of *N*-methoxy bond with the formation of formaldehyde and, in the case of halogenated compounds, from the replacement of halogen by OH and reductive elimination of the halogen especially in the presence of H donors like methanol or at high concentrations of substrate. The quantum yield of disappearance was evaluated at 0.13.

The aim of the present work is to improve the analytic study by means of HPLC, ^{1}H NMR and MS techniques, to determine what are the main initial pathways involved in the

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phototransformation using nanosecond laser flash photolysis and to compare direct photolysis with photocatalytic transformation, which is of interest for the treatment of water.

2. Experimental

2.1. Reactants

MB 99% was purchased from Riedel-deHaën. Photocatalyst was TiO_2 Degussa P25 generally used as a slurry ($1\,g\,l^{-1}$). Water used for solutions was purified by Milli-Q (Millipore) system and the purity monitored by measuring its resistivity (higher than $18\,M\Omega\,cm$).

2.2. Irradiations

Several devices were used for continuous irradiation. Solutions ca $10^{-4}\,mol\,l^{-1}$ were irradiated at 254 nm with a low pressure mercury lamp (“germicidal lamp”) 15 W located along one of the focal axes of a cylindrical mirror with an elliptic base, a quartz reactor (i.d. 2 cm) being located on the other focal axis.

In order to study the influence of wavelength on quantum yield, some solutions were irradiated at 266 nm in parallel beam with a xenon lamp associated with a monochromator Schoeffel. The band width at mid-height is ca 10 nm. Solutions were also irradiated in the range 290–350 nm with six fluorescent lamps (Duke Sunlamp GL 20) surrounded by a cylindrical mirror. These lamps emit between 275 and 350 nm, but also on mercury lines at 365, 405 and 436 nm. Wavelengths shorter than 290 nm are cut off using an air-cooled Pyrex reactor and mercury lines at $\lambda \geq 365$ nm are not active on the substrate. Thus excitation is mainly produced by wavelengths near 300 nm. However, this device is not appropriate for the determination of quantum yield since the optical path is not well defined.

Solutions in Pyrex vessel were also exposed to sunlight in Clermont-Ferrand (latitude 46°N, altitude 420 m) in late February and March.

Laser flash photolysis was performed using a frequency-quadrupled Nd:YAG laser (Quanta Ray GCR 130, pulse duration 9 ns, $\lambda_{exc} = 266$ nm). In some cases, solutions were deoxygenated by argon bubbling during 30 min.

Photocatalytic transformation was studied using TiO_2 Degussa P25 slurries ($1\,g\,l^{-1}$). Irradiations were carried out in an elliptical device (as for irradiation at 254 nm) equipped with a fluorescent lamp Philips TLD 15 W emitting between 300 and 450 nm. TiO_2 was maintained suspended by magnetic stirring in a glass reactor (window-pane glass; this glass cuts off light below 300–310 nm and prevents MB from direct photolysis).

2.3. Analyses

UV spectra were recorded on Cary 3 (Varian). HPLC analyses were carried out on a Waters chromatograph equipped with a photodiode array detector and a column C_{18} 250 mm × 4 mm. Eluent was methanol + water (55 + 45 by volume). The main photoproducts were isolated from a solution $2 \times 10^{-4}\,mol\,l^{-1}$ irradiated at 254 nm until about 40% conversion. The solution (1l) was evaporated and the crude solid extract was dissolved in about 1 ml methanol + 1 ml water. After elimination of the precipitate (mainly unreacted MB) by filtration, the clear solution was injected in a Beckman HPLC chromatograph equipped with a C_{18} column. About 40 injections were necessary to obtain sufficient amounts of products for NMR and MS analyses. Hewlett-Packard 5989 B with direct introduction and chemical ionisation (CH_4) was used for MS analysis. With this method, values of $M^+ + 1$ and $M^+ + 29$ are generally obtained. ^1H NMR in acetone D_6 were carried out on Bruker AC400. Minor photoproducts were tentatively identified by mass spectrometry. The crude mixture of products resulting from the solution evaporation was analysed by direct introduction in the spectrometer.

Formaldehyde produced during the reaction was quantified by a spectrophotometric method after complexation by chromotropic acid [8]. Capillary electrophoresis was used to show the formation of bromide ions.

3. Results

3.1. Physico-chemical properties

The solubility of MB was evaluated at $425\,mg\,l^{-1}$ ($1.64\,mol\,l^{-1}$) from the UV absorption of a saturated solution. It is a little higher than the value given in literature ($330\,mg\,l^{-1}$ at 20°C) [9].

In aqueous solution, the UV spectrum presents one absorption band with a maximum located at 245 nm, where the molar absorption coefficient was evaluated at $18600 \pm 300\,mol^{-1}\,l\,cm^{-1}$ (Fig. 1). The absorption is negligibly small at wavelengths longer than 300 nm.

When the solution is irradiated in the presence or absence of oxygen, the absorption decreases between ca 230 and

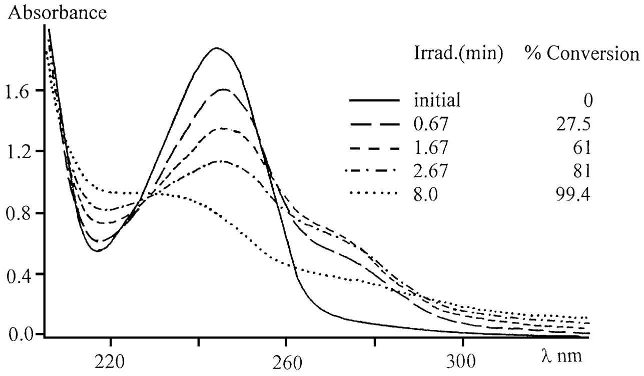


Fig. 1. Evolution of the UV spectrum of a deoxygenated solution of MB $9.6 \times 10^{-5}\,mol\,l^{-1}$ irradiated at 254 nm.

260 nm, whereas it increases at shorter and longer wavelengths (Fig. 1).

3.2. Quantum yields

In the experimental device used for irradiation at 254 nm, a solution 10^{-4} mol l^{-1} is completely transformed in 8 min and a solution 10^{-3} mol l^{-1} in approximately 90 min.

The quantum yield of disappearance of MB was evaluated in air-saturated solutions at two different wavelengths. In both cases, the drop in concentration was measured by HPLC. At 254 nm, the photon flow was evaluated at 8×10^{15} photon s^{-1} cm^{-3}. With an initial concentration of 10^{-4} mol l^{-1}, it can be assumed that all incident light is absorbed by the solution. In these conditions, the value obtained for the quantum yield is $\phi_{254} = 0.10$.

The quantum yield was also measured at 266 nm in parallel beam experiments. The incident photon flow was evaluated at 2×10^{13} photon s^{-1} cm^{-2} and the effective intensity absorbed by the solution deduced from the measurement of absorbance. The quantum yield at this wavelength was $\phi_{266} = 0.11$. The difference between the two values of ϕ is in the range of experimental error since they were obtained with different devices and calculated from different actinometries. Then the average value $\phi = 0.105 \pm 0.01$ was adopted for air-saturated solutions.

In the presence of isopropanol, the main product results from the reduction of C–Br bond as it appears in Section 3.7. The quantum yield of formation of this product at 266 nm in deaerated solutions containing 1% (v/v) isopropanol was evaluated at 0.06 ± 0.01. In the same conditions, the quantum yield of disappearance of MB is 0.133. This result will be discussed later. For comparison, the quantum yield of disappearance was also evaluated for monuron [3-(4-chlorophenyl)-1,1-dimethylurea] 10^{-4} mol l^{-1} irradiated at 266 nm in the presence of isopropanol 1% (v/v). The same value was obtained in air-saturated and in deoxygenated solutions $\phi_{\mathrm{D}}^{\mathrm{m}} = 0.068$. The quantum yield of photoreduction (formation of fenuron) evaluated in the same experiment is $\phi_{\mathrm{R}}^{\mathrm{m}} = 0.047$.

3.3. Analytical study

Five photoproducts MB_1–MB_5 appear in the HPLC chromatogram of an air-saturated solution of MB 10^{-4} mol l^{-1} irradiated up to 27% transformation (Fig. 2). Products MB_2–MB_4 were isolated by HPLC as detailed in Section 2.3 and analysed by mass spectrometry and ^{1}H NMR. Results are presented in Table 1.

MB_4 is unambiguously identified as 3-(4-bromophenyl)-1-methylurea resulting from the elimination of methoxy group. MB_3 is identified as a product of hydroxylation of the ring 3-(4-bromo-2-hydroxyphenyl)-1-methoxy-1-methylurea. The fact that the observed influence of OH on the shift of aromatic protons is different from the expected influence let us deduce that hydroxylation occurs in position 2 and that hydroxyl group interacts with carbonyl group.

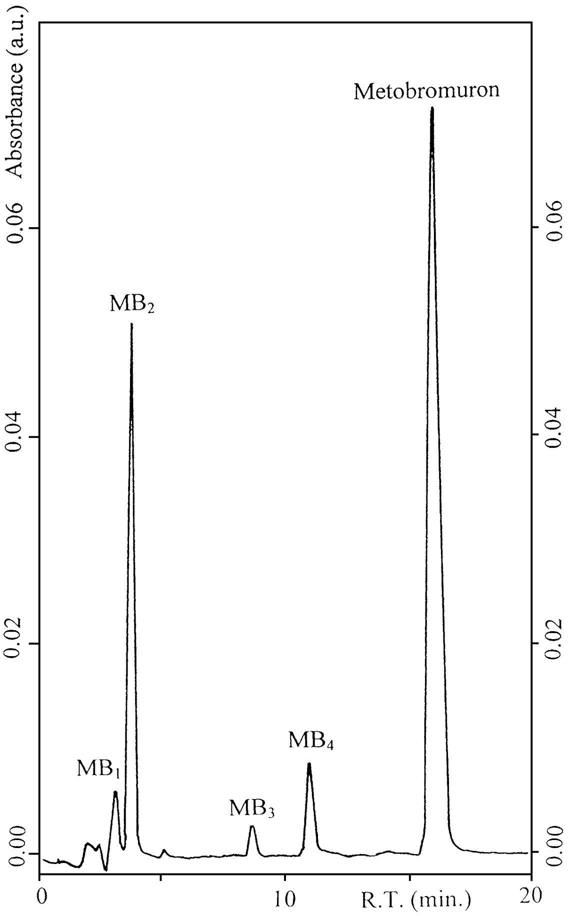


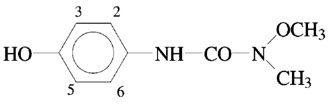
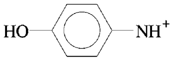
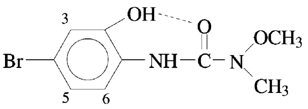
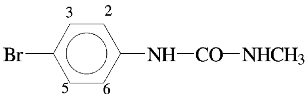
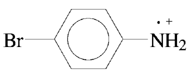
Fig. 2. HPLC chromatogram of a solution of MB irradiated at 254 nm in an air-saturated solution, conversion extent 27%. HPLC conditions: column C_{18}; eluent methanol–water 55/45 by volume; detection 260 nm.

MB_2 is identified as the product of photohydrolysis, 3-(4-hydroxyphenyl)-1-methoxy-1-methylurea. In spite of the fact that the NMR and mass spectra of MB_2 indicates an almost pure compound, experimental evidence shows that it consists of a mixture of several photoproducts, probably four. As it can be seen in Fig. 3a, this peak can be split by using a mixture methanol–water 30/70 (v/v) (instead of 55/45, v/v) as the eluent in HPLC. The product of shortest retention time in this group MB_2^1 was easily identified as *p*-benzoquinone using the commercial compound as standard (exactly same retention times and UV spectra).

The fact that *p*-benzoquinone observed by HPLC was not detected by mass spectrometry is simply due to its elimination by evaporation during the concentration of the solution. It was checked in a side experiment that *p*-benzoquinone escapes from a solution undergoing vacuum evaporation at 40°C.

MB_2^2 was identified by MS and ^{1}H NMR as 3-(4-hydroxyphenyl)-1-methoxy-1-methylurea. Just after irradiation,

Table 1
Identification of products MB$_2$–MB$_4$ by ^{1}H NMR (in acetone D$_6$) and mass spectrometry (direct injection, chemical ionisation with methane)

Compound	*m*/*z*	^{1}H NMR (*δ*, ppm)
MB2 	196 (M$^+$) 197 (M$^+$ + 1); 225 (M$^+$ + 29) 166 (loss of methoxy) 136 (protonated isocyanate) 108  88 (CO-NCH$_3$OCH$_3$)$^+$	8.42, s broad, NH or OH 8.09, s, OH or NH 7.38, m, H$_2$ and H$_6$ 6.73, m, H$_3$ and H$_5$ 3.68, s, OCH$_3$ 3.06, s, CH$_3$
MB3 	275/277 (M$^+$ + 1) 303/305 (M$^+$ + 29)	8.58, s broad, NH 8.53, s, OH 7.86, d ($J_{3\text{-}5}$ = 2.6 Hz), H$_3$ 7.40, dd ($J_{5\text{-}3}$ = 2.6 Hz and $J_{5\text{-}6}$ = 8.8 Hz), H$_5$ 6.90, d ($J_{6\text{-}5}$ = 8.8 Hz), H$_6$ 3.70, s, OCH$_3$ 3.06, s, CH$_3$
MB4 	228/230 (M$^+$) 229/231 (M$^+$ + 1) 257/259 (M$^+$ + 29) 198/200 protonated isocyanate 171/173 	8.05, s broad, NH (ring) 7.48, m, H$_3$, H$_5$ 7.34, m, H$_2$, H$_6$ 5.68, s broad, NH (chain) 2.75, s, CH$_3$

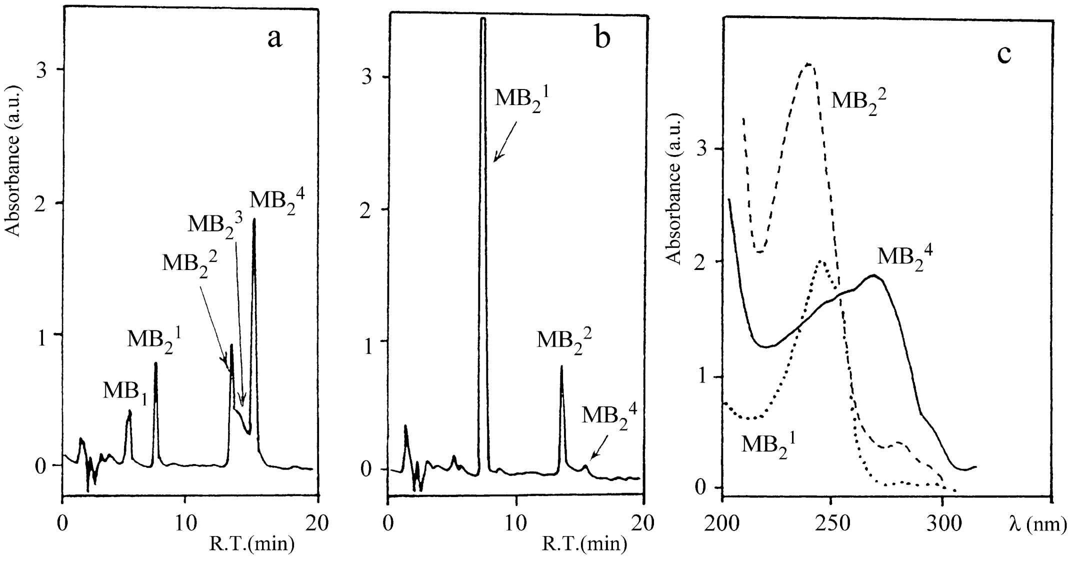
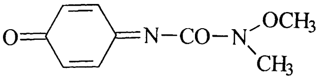
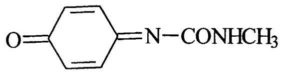


Fig. 3. Expanded first part of the HPLC chromatogram of a solution of MB 1.2 × 10^{-4} M irradiated up to 53% transformation showing the splitting of MB$_2$ peak: (a) analysed just after irradiation; (b) analysed after 8 h of standing in the dark; (c) UV spectra of photoproducts MB$_2^1$, MB$_2^2$ and unstable MB$_2^4$ obtained with photodiode array detector.

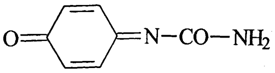
MB_2^4 presents a higher HPLC peak than MB_2^2, but it decreases and disappears after a few hours standing in the dark, whereas that of *p*-benzoquinone (MB_2^1) increases (Fig. 3b). It was also observed that the UV spectrum of MB_2^4 obtained with photodiode array detector presents a maximum at around 268 nm (Fig. 3c). This unstable product which transforms into *p*-benzoquinone in the dark was tentatively identified as the substituted *p*-benzoquinone mono-imine:

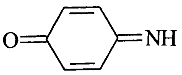


for the following reasons: it was reported by Corbett that unsubstituted *p*-benzoquinone mono-imine obtained by oxidation of 4-aminophenol has a maximum of absorption between 250 and 260 nm and that this compound is spontaneously transformed into *p*-benzoquinone in about 1 h at pH = 5.85 [10]. The minor product MB_4^3 also disappears after a few hours storage in the dark. It may be a second substituted *p*-benzoquinone imine, probably *p*-benzoquinone imine formed from the demethoxylated product MB_4:



MB_1 shows some UV characteristics similar to those of MB_2. It surely gathers together at least two photoproducts as is visible in the wide-spread chromatogram. Some of these products too are unstable and disappear on standing. Essays for identification by HPLC isolation, MS and ^{1}H NMR analyses failed. These compounds could be benzoquinone imines of the third and fourth generations:



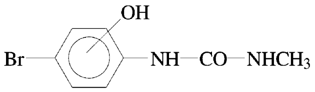
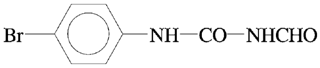
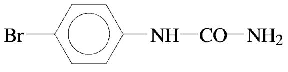
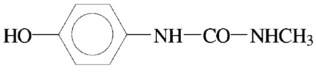
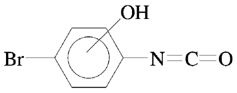
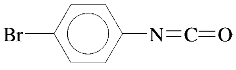
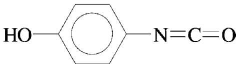
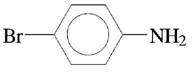
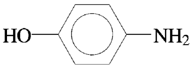


In order to identify other minor products, an air-saturated solution 2×10^{-4} M was irradiated at 254 nm until 40% transformation, treated as described in Section 2.3 and then analysed by mass spectrometry. Results are reported in Table 2. Products previously identified are not mentioned in this table.

Products result from different processes: demethoxylation, demethylation, oxidation of the ring, oxidation of methyl group, hydrolysis of C–Br bond. Their formation will be discussed in Section 4. Some other minor products were detected on the mass spectrum, but not identified. No product of the reductive elimination of Br was observed ($m/z = 180$). The mass 438 reported by Rosen and Strusz [7] was not observed in these conditions.

The detection of several phenylisocyanates is not surprising: they result from the decomposition of corresponding phenylureas in the mass spectrometer. To limit this decomposition, direct introduction was preferred to GC–MS.

Table 2
Products other than MB_2–MB_4 identified by mass spectrometry on the crude mixture of products of the photolysis of MB 2×10^{-4} mol l^{-1}[a]

Compound	*m/z*	Suggested formula
I	244/246	
II	242/244	
III	214/216	
IV	166	
Pyrolysis in MS	213/215	
Pyrolysis in MS	197/199	
Pyrolysis in MS	135	
Products of phototransformation or of pyrolysis in MS	171/173	
	109	

[a] Values of *m/z* were deduced from values of $M^+ + 1$ experimentally obtained by chemical ionisation (methane).

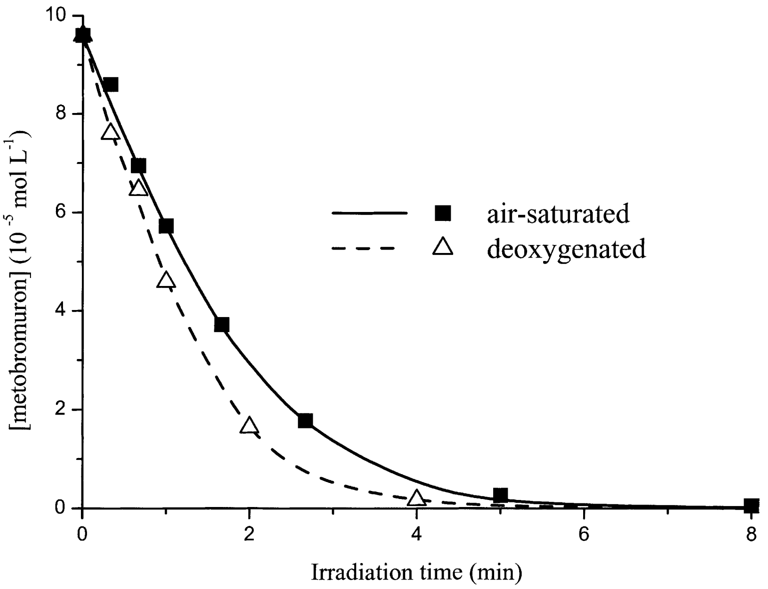


Fig. 4. Kinetics of phototransformation of MB 9.6×10^{-5} mol l^{-1} in air-saturated and deoxygenated solutions.

3.4. *Influence of oxygen*

In an argon-flushed solution, the phototransformation of MB is about 25% faster than in an aerated solution (see Fig. 4), and the HPLC chromatogram shows some additional peaks. The shoulder on the UV spectrum of MB_2, which was attributed to *p*-benzoquinone mono-imine derivative, does not appear in deoxygenated solution.

3.5. *Formation of bromide ions and formaldehyde*

It was experimentally proved by capillary electrophoresis, on an irradiated solution of MB 10^{-3} mol l^{-1}, that bromide ions are formed in the reaction.

The formation of formaldehyde was also proved and it was quantified by complexation with chromotropic acid and spectrophotometric measurements [8]. In a solution irradiated up to a 16% MB degradation, formaldehyde accounts for ca 50% of MB converted.

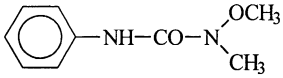
3.6. *Wavelength effect*

When MB is irradiated in the range 290–350 nm, the transformation is slower than at 254 nm due to the lower absorption of the solution. Some new products appear on the HPLC chromatogram of irradiated solutions.

The phototransformation may also be observed in sunlight, but it is relatively slow. Only 20% was transformed after 1 month in a solution 10^{-4} mol l^{-1} exposed in Clermont-Ferrand in late February and March. Photoproducts do not accumulate much, in particular MB_3 and MB_4 accumulate much less than MB_2. In the case of linuron and chlorbromuron, it was previously reported that demethoxylation is more efficient at 254 nm than in near UV [6].

3.7. *Influence of solvent*

For comparison with aqueous solutions, MB was irradiated in methanol and in water–methanol mixtures. In pure methanol, the transformation rate is about four times higher than in water and two isosbestic points appear on the UV spectra of irradiated solutions. The HPLC analysis shows the formation of a major photoproduct different from products formed in water. This product may be assumed to result from the substitution of Br by H:



In aqueous solutions containing 5% methanol, both types of reactions compete and the transformation rate is about twice as high as in pure water.

Isopropanol was used to quench the intermediate species (carbene) observed in laser flash photolysis. When solutions of MB are irradiated in the presence of isopropanol 1% in volume, the two main products formed are 3-phenyl-1-methoxy-1-methylurea (reduction product) and 3-(4-bromophenyl)-1-methylurea (demethoxylation). The formation of other photoproducts is negligible.

3.8. *Laser flash photolysis*

The photochemical behaviour of MB is much more complex than the phototransformation of *meta*-halogenated compounds. It may be related to a particular reactivity of *para*-halogenated compounds, as it was reported for *p*-halogenated phenols [11] and *p*-halogenated anilines [12].

For this reason, the formation of short-lived intermediates was studied by means of nanosecond laser flash

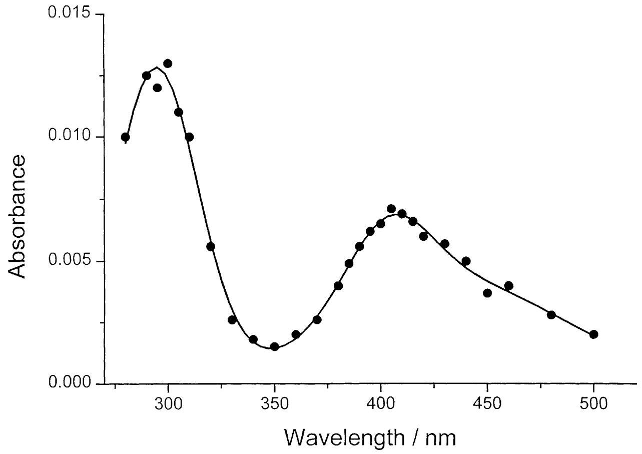
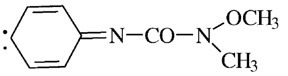


Fig. 5. UV spectrum of the first transient observed in the laser flash photolysis of MB.

photolysis and transient absorption spectroscopy on solutions 2×10^{-4} mol l^{-1}. Results were reported elsewhere [13]. The first transient observed, just after pulse end, has two absorption bands located at 300 and 405 nm (Fig. 5). It was identified as the following carbene:



In deoxygenated solution, it reacts with water yielding the *p*-hydroxylated product via the intermediate formation of another transient absorbing at 440 nm. In the presence of oxygen, an *N*-substituted iminoquinone-*O*-oxide absorbing at 300 and 460 nm is formed and leads to *N*-substituted benzoquinone mono-imine. When the solution contains isopropanol (0.17 M), the carbene is quantitatively reduced into anilino radical absorbing at 440 nm. At a higher MB concentration (10^{-3} mol l^{-1}), the carbene is expected to react with a second molecule of MB with the formation of an adduct as it was previously observed with 4-chlorophenol and 4-chloroaniline. This reaction fits well with the formation of the adduct ($m/z = 438$) reported by Rosen and Strusz [7]. The quantum yield of formation of carbene at 266 nm was evaluated at 0.060 ± 0.008 by quantification of the reduction product presumed to constitute the unique fate of carbene in the presence of isopropanol 1% (v/v). By comparing this quantum yield to the quantum yield of disappearance of MB in the same conditions ($\phi = 0.133$), it is concluded that the formation of carbene accounts for approximately 45% of the phototransformation.

3.9. Heterogeneous photocatalysis

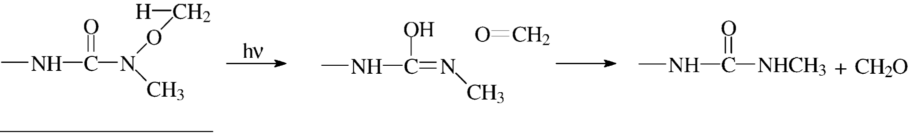
Prior to photocatalytic essays, it has been determined that the adsorption equilibrium on the TiO_2 surface (1 g l^{-1}) is reached in ca 5 min for a solution 10^{-4} mol l^{-1}. In these conditions, about 25% of MB is retained on the surface which should correspond to about 20% of the surface saturation.

Photocatalytic degradation of MB was studied by irradiating in the range 300–450 nm. It appears from the HPLC chromatogram that two products already observed in the direct photolysis are also formed in the photocatalytic transformation of MB. The main one is 3-(4-bromo-2-hydroxyphenyl)-1-methoxy-1-methyl urea (MB_3) which was a minor product in direct photolysis, the second one is 3-(4-bromophenyl)-1-methylurea (MB_4). A tentative identification of other minor photoproducts by GC–MS failed because of the instability of urea derivatives in these conditions, but three photoproducts were identified by direct introduction of the crude photoproducts mixture recovered by evaporation from the solution, namely 3-(4-hydroxyphenyl)-1-methoxy-1-methylurea (MB_2^2), 4-bromophenylurea ($m/z = 214$–216) and 3-phenyl-1-methoxy-1-methylurea ($m/z = 180$).

4. Discussion and mechanisms

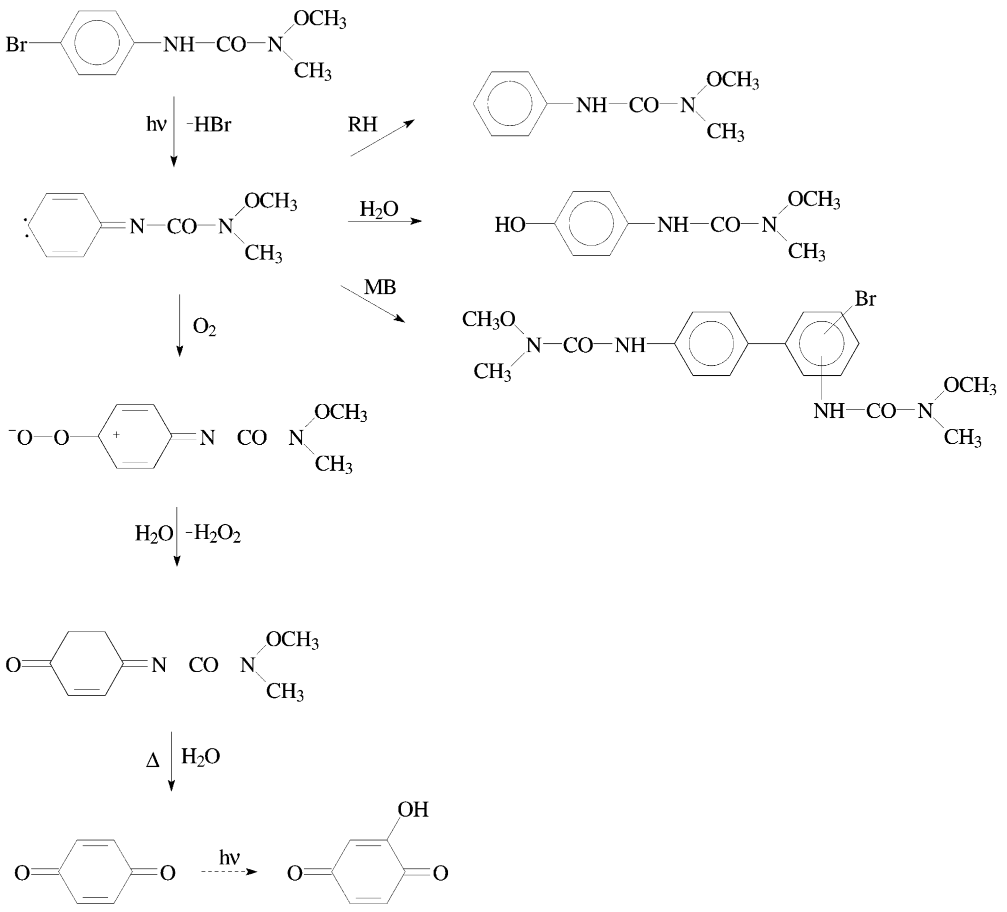
The two main pathways in the phototransformation of MB are the formation of a carbene, a short-lived species which leads to the formation of several photoproducts, and the demethoxylation of urea moiety with liberation of formaldehyde. Both pathways have similar efficiencies, since the quantum yield of formation of carbene is about 45% of the quantum yield of disappearance and that of demethoxylation around or a little more than this value.

Demethoxylation may be explained by the following mechanism previously proposed for linuron and chlorbromuron [6]:

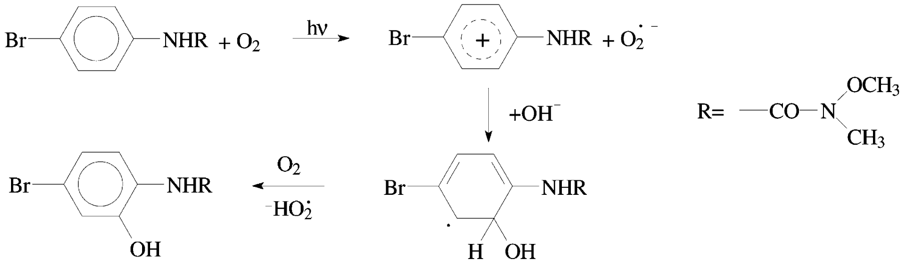


Demethylation which follows demethoxylation probably occurs by a similar mechanism.

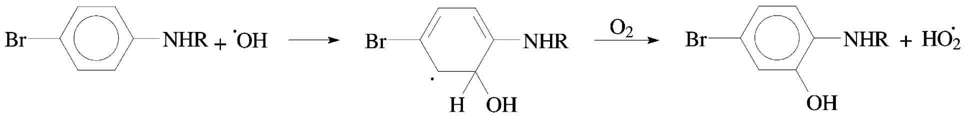
The high reactivity of the intermediate carbene explains the substitution of Br by OH (photohydrolysis) or by H (observed in reductive medium only), the formation of *p*-benzoquinone mono-imine in the presence of oxygen and the formation of the adduct ($M^+ = 438$ Da) reported by Rosen and Strusz for irradiated solutions of higher concentrations. Benzoquinone and hydroxybenzoquinone are formed in the second and third steps, respectively.



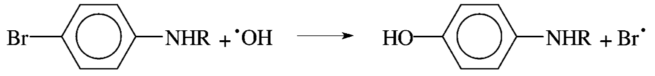
The hydroxylation observed in direct photolysis may be explained by the following sequence:



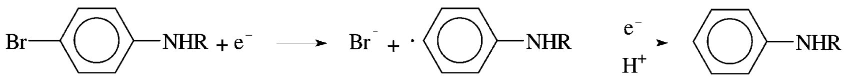
In photocatalysis, hydroxylation of the ring is the main primary reaction. It results from the oxidation by $^{\bullet}OH$ or positive holes h^+ formed on the surface of the photocatalyst.



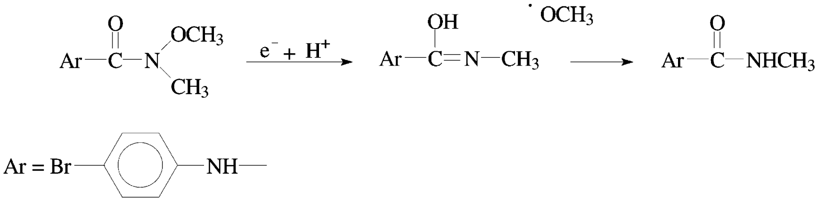
The debromination of the ring is either due to substitution of $Br^{\bullet}$ by $^{\bullet}OH$, or to reduction by electrons of the conduction band.



$Br^{\bullet} + e^- \rightarrow Br^-$



Demethoxylation is a little more difficult to explain. The involvement of an enolic form is tentatively suggested:



It can be noted that MB shows a higher quantum yield of disappearance at 266 nm in deaerated aqueous solutions of isopropanol (1%, v/v) than monuron (0.133 vs 0.068), although the two compounds have similar structures (they are both *p*-halogenated *N*-substituted phenylureas). These values may be divided into two parts: carbene formation and other transformation pathways. The formation of carbene from MB excitation seems a little more efficient than for monuron (0.060 vs 0.047), but the difference is not really meaningful. The non-carbene phototransformation routes are more significant for MB (0.073 vs 0.021). It may be then concluded that the faster transformation of MB is mainly due to the fact that *N*-demethoxylation in MB is much easier than *N*-demethylation in monuron.

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