Phototransformation of three herbicides: chlorbufam, isoproturon, and chlorotoluron. Influence of irradiation on toxicity

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ABSTRACT. The direct phototransformations in aqueous solution of chlorbufam (I), chlorotoluron (II), and isoproturon (III) are compared.
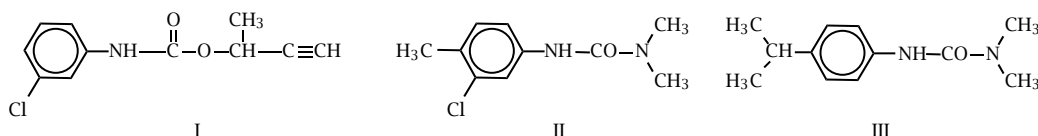
With I and II photohydrolysis (substitution of chlorine atom with formation of the corresponding hydroxylated derivative) is initially almost quantitative. It does not depend on irradiation wavelength in the range 250–300 nm. In contrast with III the main reaction is a free radical rearrangement, the reaction being more efficient at 254 nm than at wavelengths longer than 270 nm.

Compounds II and III were also irradiated on sand in the absence of water. Several photoproducts were identified, they result from elimination or oxidation of methyl groups of urea moiety.

The toxicity of photoproducts was determined using the standard Microtox® test (toxicity on the bacterium *Vibrio fischeri*). Photohydrolysis of I and II does not change much the toxicity of solutions whereas the oxidation, or at a lower scale the elimination of methyl group on the urea moiety, dramatically increases the toxicity.

1. INTRODUCTION

Chlorbufam (I), chlorotoluron (II), and isoproturon (III) are three selective herbicides acting by inhibition of photosynthesis [1]. I is a chlorinated phenylcarbamate, II and III are two substituted phenylureas, chlorinated and unchlorinated respectively. These compounds are spread in the environment where they are submitted to bio- and photodegradation. Their solubilities in water reported in the Pesticide Manual are $540\,mg \cdot L^{-1}$, $74\,mg \cdot L^{-1}$, and $65\,mg \cdot L^{-1}$ for I, II, and III respectively [1] (in the present work the solubility of chlorbufam was evaluated at about $150\,mg \cdot L^{-1}$). They are sufficient to allow the draining of these herbicides from soil to surface waters [2] where the photodegradation is a possible pathway for their elimination. As photoproducts can also be involved in the environmental pollution it is important to identify them. Indeed these degradation products may be less or more toxic than the parent compound (see Scheme 1).

To our knowledge no photochemical study has been carried out on chlorbufam. However this herbicide is similar to chlorpropham [1-methylethyl-(3-chlorophenyl) carbamate] and with the latter photohydrolysis of C−Cl bond accounts for more than 70%

of the transformation [3].

Patria *et al.* and Millet *et al.* studied the phototransformation of chlorotoluron in aqueous solution. The former observed the formation of a main unidentified photoproduct [4]. Millet *et al.* identified this product as 3-(3-hydroxy-4-methylphenyl)-1,1-dimethylurea in solutions irradiated in polychromatic light (xenon lamp). A low percentage of acetonitrile (0.5–2%) has been added to increase the solubility. The half-life of chlorotoluron was evaluated at one month in summer and more than one year in winter conditions [5].

Several studies have dealt with the phototransformation of isoproturon. Dureja *et al.* identified 11 photoproducts in an aqueous solution irradiated between 254 and 360 nm. Products were isolated by preparative layer chromatography plates and analysed by GC-MS. These products result from hydroxylation of the ring in *ortho* position, or from oxidation or elimination of methyl groups on the urea moiety. The formation of 4-isopropylaniline and azobenzene derivatives was also observed [6]. Some of these photoproducts were obtained by irradiation in alcoholic solution or on soil [7]. Results of Magnard-Billard de Saint-Laumer [8, 9] are in good agreement with previous ones. It was also reported that the photodegradation rate of isoproturon alone in methanol is higher than that of formulated

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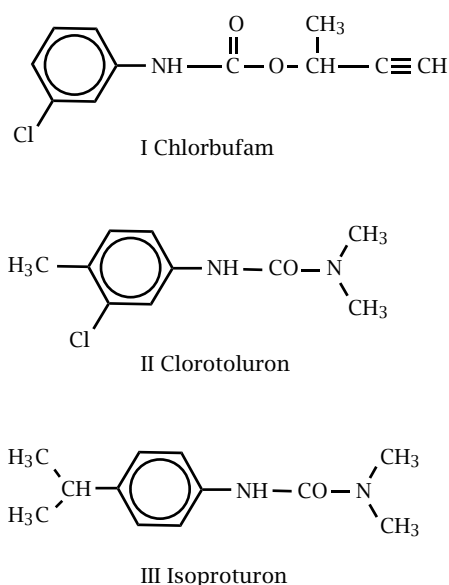
Scheme 1 I: *1-methyl-2-propynyl-(3-chlorophenyl) carbamate, II: 3-(3-chloro-4-methylphenyl)-1,1-dimethylurea, III: 3-(4-isopropylphenyl)-1,1-dimethylurea.*

one in water. Patria *et al.* reported that isoproturon is rapidly phototransformed at 253.7 nm but the three photoproducts detected were not identified [4]. The photochemical half-life was evaluated at more than one year even in summer conditions [5]. The photodegradation is then relatively difficult in environmental conditions.

The aim of the present work is to study the initial reaction involved in the phototransformation of chlorbufam, chlorotoluron, and isoproturon irradiated at various wavelengths in aqueous solution. The attention is focused on the analysis of the main photoproducts initially formed in order to improve the understanding of mechanisms involved and to study the influence of the photoproducts on the toxicity of solutions. With compounds II and III the photodegradation in the absence of water is compared with phototransformation in aqueous solution.

2. MATERIALS AND METHODS

2.1. Reactants. Chlorbufam 99% and chlorotoluron 98% were purchased from Chem Service and Ciba Geigy respectively. Isoproturon of high purity was provided by Rhône-Poulenc Agrochimie. No significant impurity was detected in it by HPLC.

Sand Fontainebleau from OSI used for dispersion of herbicides was washed with water and maintained several hours at temperature higher than 500 °C to eliminate all organic substances. Water was purified on Milli-Q (Millipore) device. Methanol and acetonitrile (HPLC grade) used for HPLC were from Carlo-Erba.

Several chemicals purchased from Aldrich were used for the synthesis of reference compounds: N-methylformamide, 3-hydroxy-4-methylaniline, 4-

isopropylaniline, dimethyl-carbamyl chloride, dimethylamine, and thionyl chloride.

2.2. Synthesis of photoproducts.
Ct_1: *3-(3-hydroxy-4-methylphenyl)-1,1-dimethylurea*.

This compound was synthesized according to a method adapted from the work of Crosby and Tang [10]. It consists in the reaction between 5-amino-*o*-cresol and dimethylcarbamyl chloride (in excess) in anhydrous THF (Yield 70%).

NMR ^{1}H (400.1 MHz, acetone D_6) δ ppm: 2.10 (s, 3H); 2.97 (s, 6H); 6.72 (dd, 1H, $J = 2.1$ Hz and 8.1 Hz); 6.88 (d, 1H, $J = 8.1$ Hz); 7.52 (s, NH); 7.87 (d, 1H, $J = 2.1$ Hz); 8.15 (s, OH).

NMR ^{13}C (100.6 MHz, acetone D_6) δ ppm: 35.7 ((N($\underline{C}H_3$)$_2$); 106.7 (C_2); 110.5 (C_6); 117.5 (C_4); 129.9 (C_5); 139.5 (C_1); 155.2 (C_3); 155.9 (CO).

MS: 194 (M$^{+\cdot}$); 149 (M-NH(CH$_3$)$_2$); 122 (M-CON(CH$_3$)$_2$); 72(CON(CH$_3$)$_2$).

I_1: *2 amino-5-isopropyl-N,N-dimethylbenzamide*.

The first step consists in synthesizing 2-amino-5-isopropyl benzoic acid as described by Tilley *et al.* [11]. In a second step the acid chloride is prepared and let to react with dimethylamine. (Yield 15%).

NMR ^{1}H (400.1 MHz, CDCl$_3$) δ ppm: 1.20 (d, 6H, $J = 6.9$ Hz, CH($\underline{C}H_3$)$_2$); 2.80 (m, $\underline{C}H$(CH$_3$)$_2$); 3.20 (s, 6H, N(CH$_3$)$_2$); 4.15 (s, 2H, NH$_2$); 6.67 (d, 1H, $J = 8.3$ Hz); 6.96 (d, 1H, $J = 2.0$ Hz); 7.03 (dd, 1H, $J = 2.0$ Hz and $J = 8.3$ Hz).

NMR ^{13}C (100.1 MHz, CDCl$_3$) δ ppm: 24.3 (CH(CH$_3$)$_2$); 33.1 (CH(CH$_3$)$_2$); 35.2 (N($\underline{C}H_3$)$_2$); 39.3 (NCH$_3$); 116.8 (C_3); 120.3 (C_1); 125.7 (C_6); 128.6 (C_4); 137.9 (C_5); 143.1 (C_2); 171.4 (CO).

MS: 206 (M$^{+\cdot}$); 191 (M-CH$_3$); 162 (M-N(CH$_3$)$_2$); 134 (M-CON(CH$_3$)$_2$); 118; 91.

The formylated compounds.

Ct_2: 3-(3-chloro-4-methylphenyl)-1-formyl-1-methyl-urea

I_2: 3-(4-isopropylphenyl)-1-formyl-1-methylurea and the demethylated products

Ct_3: 3-(3-chloro-4-methylphenyl)-1-methylurea

I_3: 3-(4-isopropylphenyl)-1-methylurea
were obtained by reaction of the corresponding phenylisocyanates with N-methylformamide or methylamine respectively.

Didemethylated photoproducts.

Ct_4: 3-chloro-4-methylphenylurea and I_4: 4-isopropyl-phenylurea
were synthesized according to the method proposed by Kulshrestha and Mukerjee [7] by reaction of the corresponding aniline with potassium cyanate.

The structure of all synthesized compounds was controlled by ^{1}H NMR and mass spectrometry (electron impact 70 eV).

The main photoproduct Cb formed by photohydrolysis of chlorbufam was identified by MS and ^{1}H NMR after isolation:

NMR ^{1}H (400 MHz, acetone D_6) δ ppm: 1.50 (d, CH$_3$); 3.00 (s, C≡H); 5.44 (qd, $J = 6.7$ and 2.15 Hz, CH); 6.51

(m, H_4); 6.99 (d, $J = 8.3$ Hz, H_6); 7.09 (t, $J = 8.3$ Hz, H_5); 7.20 (t, $J = 2.2$ Hz, H_2); 8.32 (s, OH); 8.67 (s, NH)

MS (electrospray): m/z $206(M + 1)$ and $228(M + 23)$

2.3. Irradiations. For kinetic and analytical studies solutions were irradiated at 254 nm with a low pressure mercury lamp, commonly called germicidal lamp. The lamp and the reactor in quartz were placed along both focal axes of a cylindrical mirror with an elliptic base. The photon flow received by the solution was evaluated at 7.0×10^{15} photons·s^{-1}·cm^{-3}, using potassium ferrioxalate as the chemical actinometer.

For the isolation of photoproducts a device with 6 lamps in a cylindrical mirror was used, the reactor being along the symetry axis.

To study the influence of the irradiation wavelength, solutions were irradiated with 6 fluorescent lamps Duke GL 20 emitting between 275 and 350 nm with a maximum at 310 nm and also on the mercury lines 365, 405, 436, and 546. However only wavelengths shorter than ca. 310 nm are efficient for the photodegradation of pesticides. The reactor was in quartz to prevent from the cut off effect of "Pyrex." Lamps were surrounded by a cylindrical mirror as in previous device.

Quantum yields were measured in monochromatic light at 275 nm, 276 nm, or 280 nm (band width about 10 nm at mid-hight) using a xenon lamp equipped with a monochromator Schoeffel. This device provides a parallel beam that makes possible the determination of absorbed photon flow using Beer-Lambert law.

The irradiation of chlorotoluron and isoproturon on sand was carried out with a device consisting of a round-bottom flask (3 litres) presenting internal spikes for mixing the support, and rotating around a horizontal axis. It was irradiated with 4 fluorescent lamps Duke GL20 emitting at wavelengths longer than 275 nm with a maximum near 310 nm. Wavelengths shorter than 290 nm were cut off by the flask. The herbicides were dispersed on sand using diethyl ether, the solvent being eliminated first by evaporation and then by keeping under vacuum overnight.

2.4. Analytical methods. UV spectra of solutions were recorded on CARY 3 (Varian).

Irradiated solutions were analysed by HPLC on a column C_{18} 250×4 mm. A photodiode array detector Waters was used for chlorbufam and a classical UV detection for chlorotoluron and isoproturon. The eluent was methanol/water 65:35 (for chlorbufam) and a mixture acetonitrile/water 60:40 v/v for the other herbicides.

Isolated photoproducts were identified by ^{1}H NMR on Bruker AC 400 (400 MHz), and by mass spectrometry on Hewlett-Packard 5989 B (electronic impact 70 eV).

2.5. Test of toxicity (Microtox®). The toxicity of photoproducts or the influence of irradiation on the toxicity of solutions was determined with Microtox® test. This test consists in determining the concentration (EC_{50}) in toxic compound that inhibits 50% of the natural luminescence of a marine bacterium *Vibrio fischeri*. The emission is measured after various exposure times, usually 5, 15, or 30 min. A decrease of EC_{50} corresponds to an increase of toxicity.

Assays were carried out with a Microbics M500 analyser. All materials for analyses (test reagent, diluent, osmotic adjusting solution, reconstitution solutions) were supplied by Azur Environmental (Carlsbad, CA, USA).

3. RESULTS

3.1. UV absorption. Chlorbufam, chlorotoluron, and isoproturon have similar UV spectra. The maximum of the main absorption band is located near 240 nm as it appears in Table 1. A band of lower intensity is located near 280 nm. The absorption is very low at wavelengths longer than 300 nm. The UV spectrum of chlorbufam is given in Figure 1 as an example. The spectra of chlorotoluron and isoproturon are not significantly different.
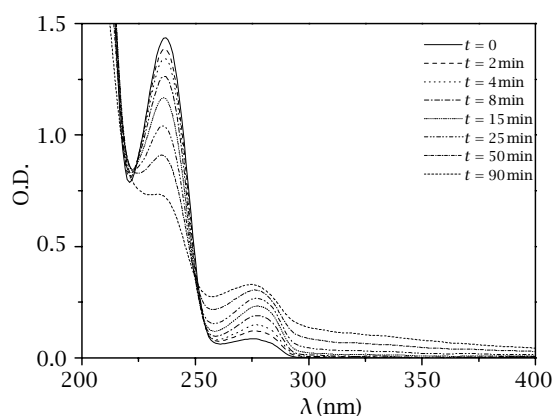

Figure 1. *Evolution of the UV spectrum of an air-saturated solution of chlorbufam* 1.02×10^{-4} *M irradiated at 254 nm*

The solubility of chlorbufam was determined by comparison of the UV absorption of a saturated solution with the UV absorption of a solution of known concentration containing a low percentage of methanol to increase the solubility. It was checked that the absorption was not modify by the percentage of methanol in the range 1–5%.

3.2. Irradiation of chlorbufam. An air-saturated solution of chlorbufam 1.02×10^{-4} M was irradiated at 254 nm. The evolution of the UV spectrum is given in Figure 1. The absorbance decreases between 224 and 250 nm and increases at longer wavelengths. The presence of two isosbestic points at 224 and 250 nm corresponds to a good accumulation of photoproducts. Several products can be detected on the HPLC chromatogram but only one (Cb) accumulates as a primary photoproduct. The same reaction was observed in the absence of oxygen. The main photoproduct was isolated as indicated below for analysis.

A saturated solution (6.7×10^{-4} M) was irradiated at 254 nm with the device with 6 lamps, till almost complete degradation of the reactant. Solution was extracted with ether. After evaporation and drying the main photoproduct was identified by MS and ^{1}H NMR

Table 1. Main characteristics of the UV absorption spectra of the three herbicides.

	λ_{max} (nm)	ε (M$^{-1}\cdot$cm^{-1})	λ_{max} (nm)	ε (M$^{-1}\cdot$cm^{-1})
Chlorbufam	238	15200 ± 200	276	910 ± 20
Chlorotoluron	241	16540 ± 200	280	1370 ± 30
Isoproturon	240	16200 ± 150	280 (shoulder)	1180 ± 30

(see Section 2.2). From NMR spectrum it was 95% pure, the main impurity being chlorbufam for about 5% (see Scheme 2).
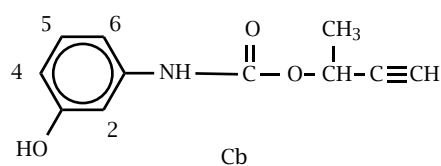
Scheme 2

The isolated photoproduct Cb was used for the calibration of HPLC. The transformation is quantitative as far as 50% transformed. It is also initially specific when solutions were irradiated in polychromatic light between 275 and 350 nm. In this case, it was proved that the specificity of the reaction is not influenced by the concentration of chlorbufam nor by the presence of oxygen as far as 40% converted.

3.3. Irradiation of chlorotoluron. An air-saturated solution of chlorotoluron 1.6×10^{-4} M was irradiated at 254 nm in the device with one lamp described in Section 2.3. A decrease of the optical density was observed between 230 and 256 nm whereas an increase occured at longer wavelengths. The presence of two isosbestic points at 230 nm and 256 nm let assumed that the photoproduct(s) accumulate(s) in the solution.

Actually only one peak appears on the HPLC chromatogram. In order to isolate this photoproduct Ct_1, one litre of a solution 3.3×10^{-4} M was irradiated up to 60% transformation with 6 low pressure mercury lamps. After concentration a mixture Ct_1+ chlorotoluron was extracted from the irradiated solution with ethyl acetate. Then Ct_1 was separated by column chromatography on silicagel. From ^{1}H NMR and mass spectrometry it was identified as 3-(3-hydroxy-4-methylphenyl)-1,1-dimethylurea, see Scheme 3 (see Section 2.2).

To confirm this identification, this compound was synthesized as described in Section 2.2. HPLC retention time and spectral data (NMR, MS) were identical. The synthesis of Ct_1 allowed the calibration of HPLC and the evaluation of the yield. It was deduced that the conversion is initially quantitative. When the transformation of chlorotoluron reaches 80% the formation of
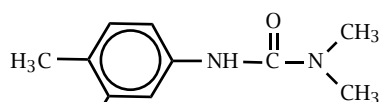
Scheme 3

Ct_1 accounts for 70–80% of chlorotoluron converted as it appears in Figure 2.

The same photoproduct was obtained when a solution was irradiated at 280 nm *i.e.,* in the other absorption band, and the quantum yield was the same taking into account the accuracy of the measurement as it is reported in Table 2.
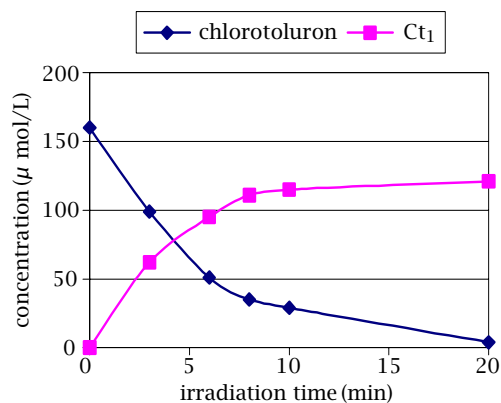

Figure 2. *Disappearance of chlorotoluron and formation of product Ct_1 in an air-saturated solution 1.6×10^{-4} M irradiated at 254 nm.*

3.4. Irradiation of isoproturon. An air-saturated solution of isoproturon 0.97×10^{-4} M was irradiated at 254 nm. The absorption decreases between 236 and 256 nm and increases at longer wavelengths. Two isosbestic points are localized at 236 and 256 nm on the UV spectra of irradiated solutions (Figure 3).

Only one photoproduct I_1 appears on the HPLC chromatogram of an irradiated solution. Its retention time is lower than the retention time of isoproturon. In order to isolate and identify this product a more concentrated solution (3.4×10^{-4} M) was irradiated in the device with 6 lamps up to 60% transformation. After concentration

Table 2. Quantum yield of phototransformation of the three herbicides in air saturated solution.

	C (10^{-4} mol·L^{-1})	λ (nm)	ϕ
Chlorbufam	6.56	254	0.047 ± 0.005
	6.84	276	0.058 ± 0.005
Chlorotoluron	1.60	254	0.031 ± 0.003
	1.79	280	0.037 ± 0.003
	0.24	xenon lamp [5]	0.055-0.095*#
Isoproturon	1.06	254	0.0020 ± 0.0005
		275	$4.5 \times 10^{-4} \pm 5 \times 10^{-5}$
	0.24	xenon lamp [5]	4×10^{-3}*

according to pH, * in the presence of CH_3CN 0.5%.
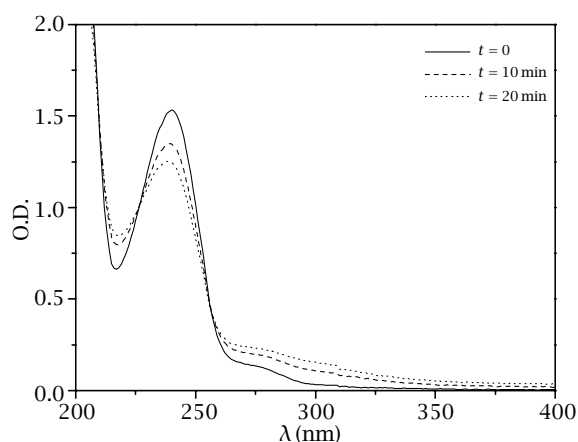
Figure 3. *Evolution of the UV spectrum of an air-saturated solution of isoproturon* 0.97×10^{-4} *M irradiated at 254 nm.*

I$_1$
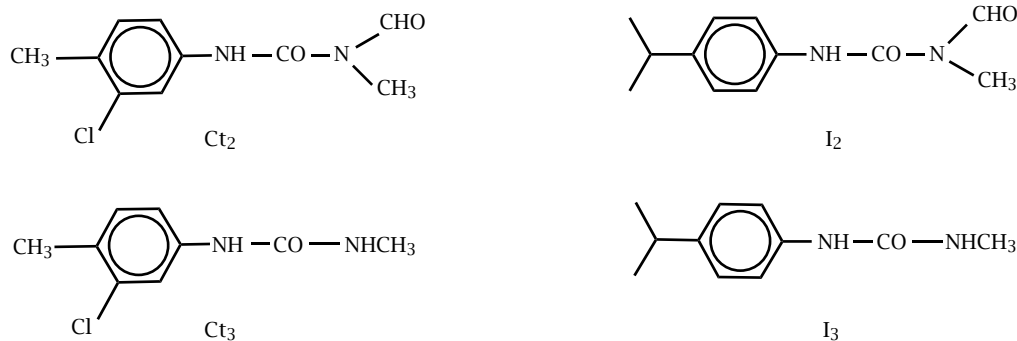
Scheme 4

280 nm using the parallel beam obtained with a xenon lamp equipped with a monochromator. Values are gathered in Table 2. However some measurements were carried out at 254 nm in conditions of almost total absorption of light in order to observe a possible wavelength effect. With chlorbufam and chlorotoluron quantum yield has the same value in both absorption bands, whereas with isoproturon it is significantly lower at 275 nm than at 254 nm.

3.6. Irradiation on sand. In order to study the influence of water on the photochemical behaviour, chlorotoluron and isoproturon were irradiated in dispersed state on sand in the absence of water. This technique was successfully used for diuron [13]. With this compound elimination or oxidation of methyl groups on the urea moiety (formation of formylated derivative) was observed. With chlorotoluron and isoproturon 5 mg were dispersed on 100 g of sand using diethylether. After elimination of ether, dispersed herbicides were irradiated at λ > 290 nm with the device shortly described in Section 2.3. Then unreacted compound and photoproducts were extracted with methanol and analysed by HPLC.

The transformation rate was much lower than in aqueous solution and it decreased with irradiation time. This phenomenon may be attributed to an adsorption of sand on the flask (diffusion of light) or to a non-uniform dispersion of substrate on the sand. (The formation of microcrystals of substrate should make difficult the complete photodegradation because of the screen effect of products formed at the surface of microcrystals).

the solution was extracted with ether and product I$_1$ was isolated and purified by chromatography on silicagel. Product I$_1$ was identified as 2-amino-5-isopropyl-N-N-dimethylbenzamide from ^{1}H NMR and mass spectrometry, see Scheme 4 (see Section 2.2).

To confirm this identification I$_1$ was synthesized as indicated in Section 2.2. Photoproduct and synthesized compound had the same HPLC retention time and spectral data (NMR, MS). The synthesized compound was used to calibrate the HPLC. It was deduced that I$_1$ accounts for about 66% of isoproturon converted in air-saturated solution. The same photoproduct was obtained in deoxygenated solution but the formation rate was about 20% higher. The chemical yield was evaluated at 71%. In contrast product I$_1$ is not observed when solutions are irradiated at wavelengths longer than 275 nm using lamps GL20. In these conditions no photoproduct was identified. It was previously reported by Kotzias and Korte that this rearrangement (in the case of monuron) is more efficient at short wavelengths [12].

3.5. Kinetic study. The disappearance quantum yields of the three herbicides were measured at 275, 276, or
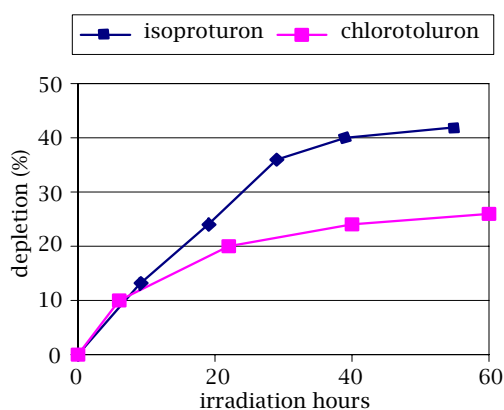
Scheme 5

Figure 4. *Phototransformation of chlorotoluron and isoproturon dispersed on sand (5 mg/100 g).*

Several photoproducts were detected on HPLC chromatogram, but the amounts were too low for isolation.

For identification, compounds resulting from oxidation (formylated derivatives Ct$_2$ and I$_2$) or elimination of one methyl group (Ct$_3$ and I$_3$), and products resulting from the elimination of both methyl groups of urea moiety (Ct$_4$ and I$_4$) were synthesized. By comparison of their HPLC retention times, the products formed after irradiation of chlorotoluron in the absence of water correspond to compounds Ct$_2$ and Ct$_3$. Similarly, I$_2$ and I$_3$ were detected during the phototransformation of isoproturon on sand. But in both cases, no quantitative evaluation was possible.(see Scheme 5)

3.7. Microtox$^{®}$ text. The toxicity of herbicides and photoproducts was tested on *Vibrio fischeri* with Microtox$^{®}$ technique as indicated in Section 2.5. Results are gathered in Table 3.

With chlorbufam the toxicity of unirradiated solution 5×10^{-4} M was compared with toxicity of solutions irradiated up to 15, 33, and 56% of transformation. No significant change was observed. It can be assumed that the total number of molecules stay unchanged. It can be deduced that the product of photohydrolysis and parent product have similar toxicities. With the two other herbicides the toxicity of each photoproduct identified and synthesized was compared with the toxicity of parent compound. It clearly appears that, except for the product of photohydrolysis of chlorotoluron, photoproducts are much more toxic for *Vibrio fischeri* than the parent herbicide. Among all the compounds tested, the products of N-didemethylation and the formylated derivatives lead to the more important biological effects observed on the bacterium.

4. MECHANISM

The formation of hydroxylated derivatives initially quantitative with chlorbufam and chlorotoluron is attributed to a photohydrolysis *i.e.,* a heterolytic substitution of chlorine involving a molecule of water. It is not influenced by the presence of oxygen. Such a reaction was previously reported for 3-chloroaniline, chlorpropham [3], dichloroanilines [14], diuron [13], *etc.* (see Scheme 6)
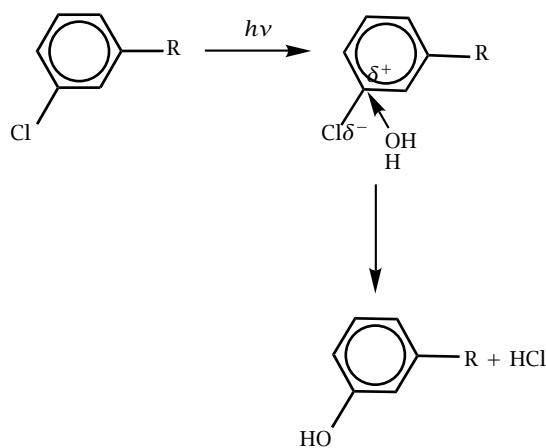
Scheme 6

The formation of product I$_1$ from isoproturon results from a radical scission and rearrangement. Such a reaction was previously reported in the case of naphthoxyacetic acid [15], fenuron [16], and monuron [12]. With the latter it was reported to be more efficient at short wavelengths (see Scheme 7).

In the absence of water the two main photoproducts initially formed with chlorotoluron and isoproturon result from the elimination or oxidation of a methyl group

Table 3. Evaluation of the toxicity of photoproducts with Microtox® test (exposure time: 5 min).

Chlorbufam (irradiated solutions)		
irradiation time (min)	% transformation	EC_{50} (µ mol·L^{-1})
0	0	1530
15	15	1140
40	33	1340
70	56	2000
Chlorotoluron (toxicity of photoproducts)		
neat chlorotoluron		981*
Ct_1 (photohydrolysis on the ring)		2310*
Ct_2 R_C-NCH$_3$ CHO		19
Ct_3 R_C-NHCH$_3$		100
Ct_4 R_C-NH$_2$		88

$$\left(R_C = CH_3 - \underset{Cl}{\bigcirc} - NH - CO - \right)$$

Isoproturon (toxicity of photoproducts)		
neat isoproturon		128
I_1 (rearrangement)		63
I_2 R_i-NCH$_3$ CHO		2.2
I_3 R_i-NHCH$_3$		72
I_4 R_i-NH$_2$		9.7

$$\left(R_i = \, \rangle - \bigcirc - NH - CO - \right)$$

*extrapolated values (EC_{50} >higher than solubility).
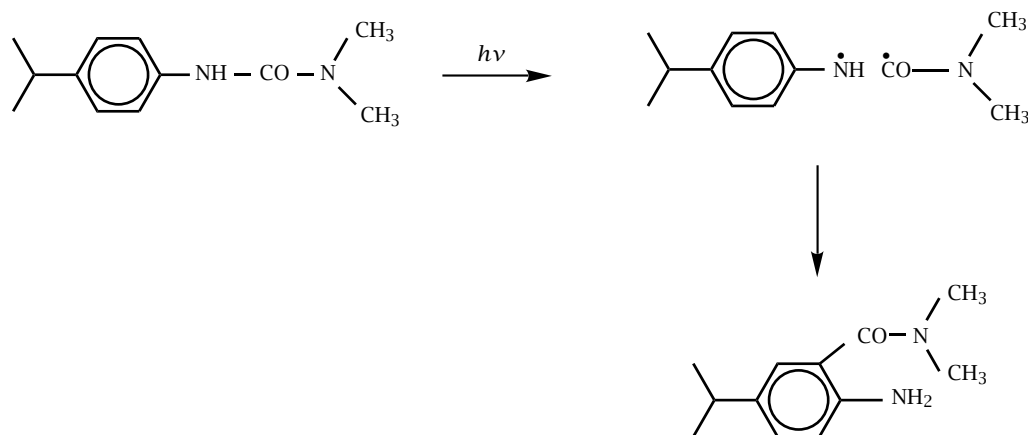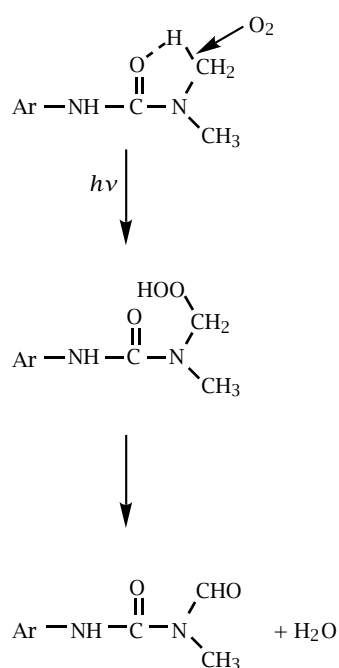

Scheme 7

on the urea moiety. The same reactions were observed with diuron [13]. With the latter it was experimentally proved that demethylated product can be formed in the absence of oxygen.

A mechanism involving the intermediate formation of a methylenolate hydrolysed during HPLC analysis was tentatively proposed. Similar mechanism can be suggested for chlorotoluron and isoproturon but not experimentally proved.

The oxidation of methyl group is assumed to involve a hydrogen bond between methyl and carbonyl groups as it was proposed in the case of diuron [13] (see Scheme 8).

Scheme 8

5. CONCLUSIONS

The presence of a halogen atom on the ring has a significant influence on the photochemical behaviour of phenylurea herbicides in aqueous solution: chlorotoluron and isoproturon have completely different reactivities.

Photohydrolysis *i.e.,* heterolytic substitution of a halogen atom by OH involving a molecule of water is the main reaction observed with *meta*-chlorinated aromatic herbicides chlorotoluron and chlorbufam.

A free radical rearrangement is the main reaction ob-

served with isoproturon irradiated at 254 nm in aqueous solution, but this reaction is not observed when isoproturon is irradiated near 300 nm.

In the absence of water the irradiation of chlorotoluron and isoproturon leads to the oxidation or the elimination of a methyl group of the urea moiety.

Photohydrolysis or photochemical rearrangement do not significantly change the toxicity of studied herbicides on *Vibrio fischeri*, whereas the elimination of a methyl group of the urea moiety and above all the formation of a formylated derivative dramatically increases the toxicity.

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