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Phototransformation of Linuron and Chlorbromuron in Aqueous Solution

Valérie Faure & Pierre Boule

Laboratoire de Photochimie Moléculaire et Macromoléculaire (URA CNRS 433) Université Blaise Pascal (Clermont-Ferrand) F-63177 Aubière Cedex, France

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Abstract: The main photoproducts initially formed in the phototransformation of linuron and chlorbromuron in aqueous solution result from photohydrolysis, i.e. hydroxylation with release of halide ion, and from elimination of a methoxy group. Reductive debromination was also observed with chlorbromuron. The transformation is less specific than with diuron. The orientation of the reaction depends on the wavelength: short wavelengths (254 nm) favour demethoxylation and photohydrolysis in the *meta* position whereas, with 'black light', i.e. wavelengths longer than 330 nm, photohydrolysis in the *para* position is the main reaction observed.

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1 INTRODUCTION

Halophenylureas have been used for about 45 years as herbicides. The most studied are monuron [3-(4-chlorophenyl)-1,1-dimethylurea] and diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea]. Linuron [Fig. 1, 3-(3,4-dichlorophenyl)-1-methyl-1-methoxyurea] and chlorbromuron [3-(4-bromo-3-chlorophenyl)-1-methyl-1-methoxyurea] were introduced later, in 1962 and in 1966, respectively. Their elimination from the environment may involve chemical reactions (mainly hydrolysis and oxidation), biotransformation and photolysis, so it is important to know the relative importance of these different ways and to identify the products formed. These products may have completely different properties and might be more toxic than the initial compound.

Monuron and diuron are stable in neutral water. Their photochemical properties have been the subject of several publications. The main products formed in the photolysis of monuron result from substitution of Cl by OH,[1,2] oxidation or elimination of methyl groups,[3] formation of oligomers and biphenyl derivatives.[1,4] The formation of 4-chloroaniline, 4-chloroformanilide and 4,4′-dichlorocarbanilide has also been reported.[3] The presence of non-ionic surfactants eliminates ring hydroxylation and enhances reductive dechlorination.[5] The same effect was observed when methanol was added to the solution.[2]

The main photoproducts identified by Tanaka *et al.*[6] in the photolysis of diuron in aqueous solution resulted from the substitution of Cl by OH, and elimination or oxidation of the methyl group. Reductive dechlorination in the *para* position was also observed. Photoreduction in the *meta* position, reported by Durand *et al.*,[7] may be related to the presence of a small amount of methanol in the solution. From results published

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* To whom correspondence should be addressed.

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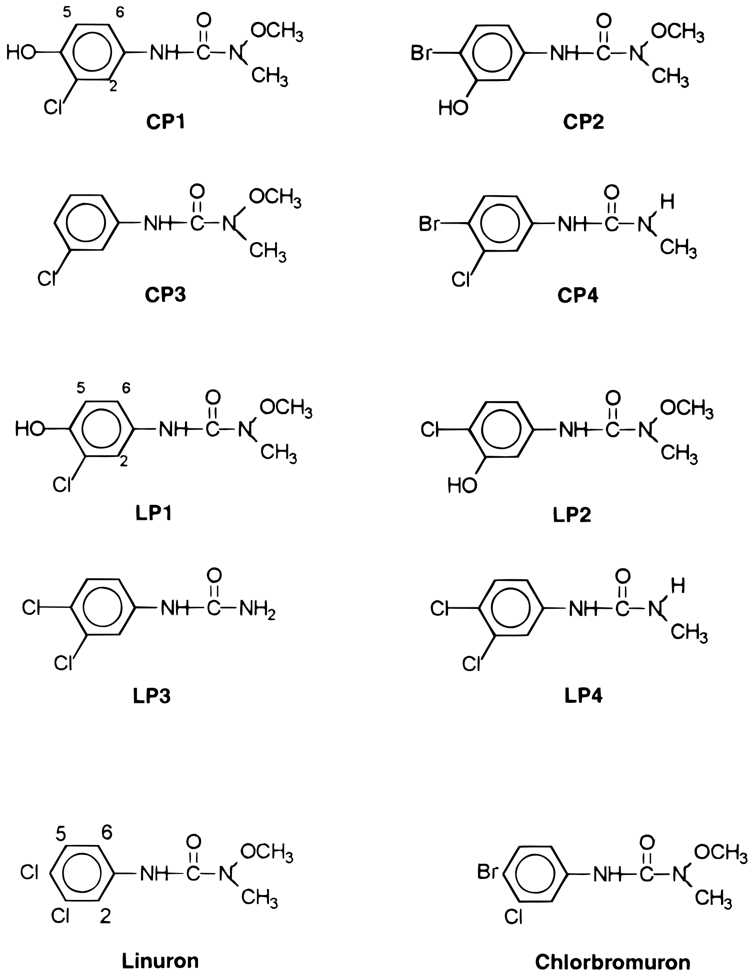

Fig. 1. Structures of linuron, chlorbromuron and photoproducts.

recently it appears that photohydrolysis (i.e. hydroxylation with release of chloride ion) is initially almost quantitative in dilute solution, but a wavelength effect was observed.[8] *Para* hydroxylation is a minor pathway at 254 nm but is enhanced by increasing wavelength.[8] Linuron and chlorbromuron have been much less studied from the photochemical point of view. The main photoproducts identified by Rosen *et al.*[9] in an aqueous solution of linuron exposed to sunlight were 3-(3-chloro-4-hydroxyphenyl)-1-methoxy-1-methylurea (13%), 3,4-dichlorophenylurea (10%) and 3-(3,4-dichlorophenyl)-1-methylurea (2%). More recently Nick and Schöler[2] irradiated linuron and chlorbromuron at 254 nm. Several photoproducts were identified. The main one resulted from the cleavage of the N-methoxy linkage with the formation of formaldehyde, but the replacement of Cl by OH was also observed. In the presence of an H donor like methanol or phenylurea itself at high concentration these reactions compete with the replacement of halogen atoms by hydrogen.

The aim of the present work was to analyse photoproducts formed in the photolysis of linuron and chlorbromuron at different wavelengths in order to establish if the irradiation at 254 nm is representative of the phototransformation in sunlight. The influence of substituents on the photoreactivity was examined by comparison with results previously obtained with diuron.

2 MATERIALS AND METHODS

Linuron and chlorbromuron were provided by Chem. Service. Dichloroaniline (>97%) was supplied by Fluka.

3-(3,4-Dichlorophenyl)-1-methylurea was synthesized from 3,4-dichlorophenylisocyanate and methylamine in dry tetrahydrofuran.

The other photoproducts were identified from their [^{1}H]NMR spectra recorded at 400 MHz on a Bruker AC 400 and their mass spectra obtained on a VG MS 305 (Centre Regional de Mesures Physiques) or on an E. B. Fison, 70E type (Service Central d'Analyses of CNRS).

Water used for solutions was purified by a Milli Q system.

Solutions were irradiated at 254 nm with a low-pressure mercury lamp (germicide lamp) surrounded by a cylindrical mirror with an elliptical base, the reactor in quartz and the lamp being located on both focus axes.

For irradiations between 300 and 350 nm, fluorescent lamps type Duke GL 20E (maximum emission near 310 nm) were used. Solutions were also irradiated with 'black light' lamps emitting about 85% of photons at 365 nm (mercury line) and about 7% at 334 nm. A reactor in Pyrex was used for wavelengths longer than 300 nm.

Irradiated solutions were analysed by HPLC on a 125 × 4 mm C_{18} column using methanol + water (usually 60 + 40 by volume) as eluent, associated to a Waters chromatograph with photodiode array detector.

3 RESULTS

The UV spectra of linuron and chlorbromuron are similar, as shown in Fig. 2. The absorption is very low at wavelengths longer than 300 nm.

It was observed that solutions of linuron and chlorbromuron are not as stable as solutions of diuron. Formation of dihalogenoaniline can be observed after several weeks. This evolution is enhanced by increasing pH.

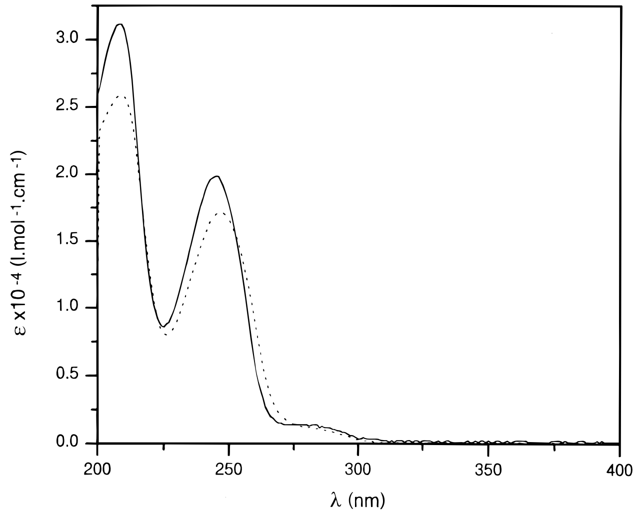

Fig. 2. UV spectra of (———) linuron and (– – – –) chlorbromuron.

3.1 Phototransformation of linuron

3.1.1 *Analytical study*

A typical chromatogram of a solution irradiated during 1 h at 254 nm is given in Fig. 3.

The four main photoproducts LP1–LP4 (Fig. 1) were isolated and analysed by MS and [^{1}H]NMR. They are identified from results presented in Table 1.

3.1.2 *Influence of wavelength*

The quantum yield was evaluated at 254, 277 and 296 nm. It is a little higher at 254 nm (0·05–0·06) than at 277 and 296 nm (0·02). Recently the value 0·096 was obtained by Nick and Schöler[2] at 254 nm. At wavelengths longer than 300 nm it was not possible to measure it because the absorption was too low. However it was observed that the ratio of products depended on wavelength between 254 and 365 nm as it appears in Table 2.

Long wavelengths favour *para*-hydroxylation, as was reported for diuron.[8] This effect is mainly important at the limit of the absorption band i.e. at $\lambda > 300$ nm.

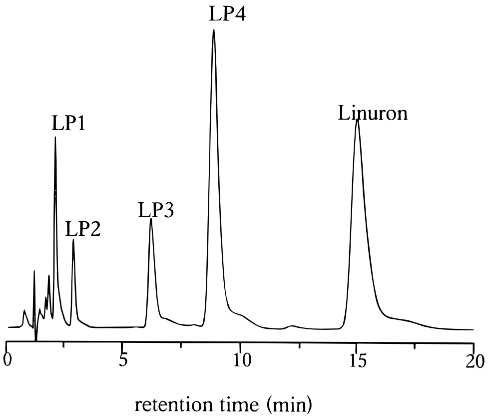

Fig. 3. HPLC chromatogram of a solution of linuron (10^{-4} M) irradiated during 1 h at 254 nm. Eluent methanol + water (52 + 48 by volume). Detection 250 nm.

TABLE 1
MS and [^{1}H]NMR Analyses of the Main Products formed by Irradiation of Linuron at 254 nm in an Air-Saturated Aqueous Solution (10^{-4} M)

	MS (e-impact 70 eV)		*[^{1}H]NMR in CD_3OD (δ ppm) (ref. CD_2HOD 3·5 ppm)*				
	m/e	*Cl number*	*H_2*	*H_5 (d)*	*H_6 (dd)*	*OCH_3 (s)*	*CH_3*
Linuron	248	2	8·01	7·59	7·64	3·93	3·35
LP1	230	1	7·66	7·04	7·36	3·90	3·35
LP2	230	1	7·43	7·35	7·06	3·95	3·30
LP3	204	2	7·92	7·55	7·41	—	—
LP4	218	2	7·91	7·54	7·40	—	2·95

TABLE 2
Influence of Wavelength on the Phototransformation of Linuron in Air-Saturated Aqueous Solution

Photoproduct λ *(nm)*	*LP1*	*LP2*	*LP3*	*LP4*
254	+	+	+	+ +
295–350	+	+	D[a]	D
'Black light' (85% 365 nm 7% 334 nm)	+ +			
Sunlight	+ +	+	D	D

[a] D = detected as a minor product.

Wavelength also influenced demethoxylation, which was induced to a greater extent by excitation in the main absorption band ($230 < \lambda < 270$ nm) than by excitation between 270 and 300 nm. Demethoxylation can be related to the formation of formaldehyde which was experimentally detected in solutions irradiated at 254 nm using its reaction with chromotropic acid.

3.2 Phototransformation of chlorbromuron

3.2.1 Analytical study

Four photoproducts CP1–CP4 (Fig. 1) were isolated by HPLC in an air-saturated solution ($1{\cdot}2 \times 10^{-4}$ M) irradiated at 254 nm. The main peak observed by detection at 250 nm corresponds to CP4. These were identified by MS and NMR and results are given in Table 3. The presence of Cl or Br is easily deduced from mass spectra.

3.2.2 Influence of wavelength

As was observed with linuron *para*-hydroxylation is the main reaction observed at long wavelengths whereas the excitation of 254 nm (main UV band) enhances demethoxylation and *meta*-hydroxylation. (Table 4). It was also noted that at 254 nm CP4 is the main photoproduct in the absence of oxygen and that deoxygenation increases the ratio CP2/CP1.

TABLE 4
Influence of Wavelength on the Phototransformation of Chlorbromuron Irradiated in Air-Saturated Aqueous Solution (10^{-4} M)

Photoproduct λ *(mm)*	*CP1*	*CP2*	*CP3*	*CP4*
254	+	+	+	+ +
275–350	+	+	+	+
'Black light'	+ +			

Results in sunlight are not available, but it can be assumed that they are intermediate between the two last lines of Table 4.

The quantum yield was evaluated at 0·05 at 254 nm in good agreement with results of Nick and Schöler.[2] It is lower at 277 nm.

4 DISCUSSION AND MECHANISMS

The *meta*-hydroxylation on the ring with dechlorination is a common reaction observed with chlorobenzenes, 3-halophenols and diuron. It results from a nucleophilic substitution involving a molecule of water (Fig. 4a) and for this reason it has been called photohydrolysis.[10–12] With linuron and chlorbromuron it is less selective than with diuron irradiated at short wavelengths.

The fact that the ratio *para*-hydroxylation/*meta*-hydroxylation increases with increasing wavelength was

TABLE 3
(a) MS and (b) [^{1}H]NMR Analyses of the Main Products formed by Irradiation of Chlorbromuron at 254 nm in an Air-Saturated Aqueous Solution (10^{-4} M)

(*a*) *MS* (*e-impact 70 eV*)	*m/e*	*Cl number*	*Br number*
CP1	*230*, 232	1	0
CP2	274, 276	0	1
CP3	*214*, 216	1	0
CP4	262, *264*, 266	1	1

(*b*) [^{1}*H*]*NMR*	*Solvent*	*NH*	H_2	H_4	H_5	H_6	OCH_3	CH_3
chlorbromuron	CD_3OD	—	8·03 (d)	—	7·79 (d)	7·58 (dd)	3·95 (s)	3·35 (s)
	$(CD_3)_2CO$	8·90 (s)	8·00 (d)	—	7·58 (d)	7·52 (dd)	3·70 (s)	3·10 (s)
CP1	CD_3OD	—	7·58 (d)	—	6·96 (d)	7·28 (dd)	3·90 (s)	3·35 (s)
CP2	$(CD_3)_2CO$	8·60 (s)	7·51 (d)	—	7·32 (d)	6·98 (dd)	3·75 (s)	3·10 (s)
CP3	$(CD_3)_2CO$	8·80 (s)	7·83 (t)	7·02 (ddd)	7·26 (t)	7·53 (td)	3·75 (s)	3·10 (s)
CP4	$(CD_3)_2CO$	8·30 (s)	7·93 (d)	—	7·49 (d)	7·25 (dd)	—	2·54 (s)

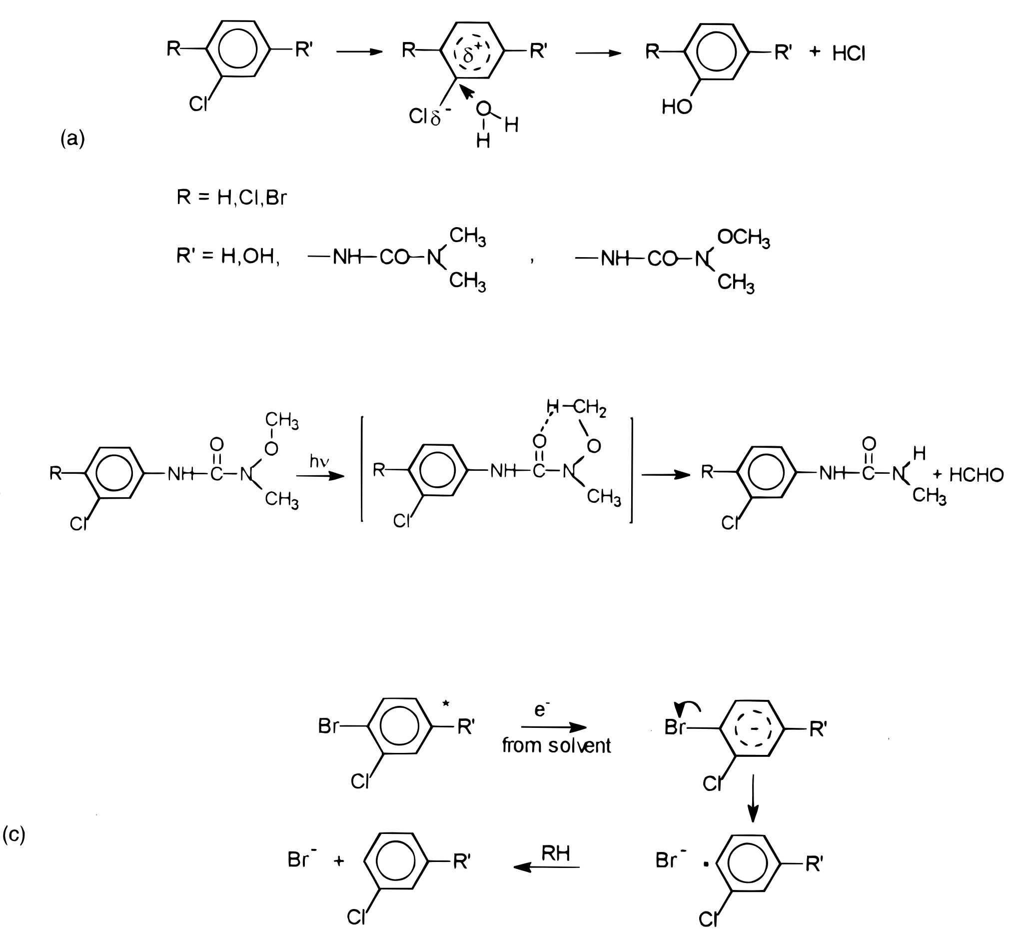

Fig. 4. Proposed mechanisms of photo-induced reactions.

tentatively explained, with diuron, by the involvement of an enolic form, since it was observed neither with 3,4-dichlorophenol nor with diuron methylated on both nitrogen atoms[8] and because the anionic form is expected to absorb at longer wavelengths. This explanation, which was not definitively proved, can be applied to linuron and chlorbromuron, but this effect is not so clear as with diuron because of the competition between photohydrolysis and the other reactions (demethoxylation and reduction).

Demethoxylation associated with formation of formaldehyde is more efficient by irradiation in the absorption band centered at 242–245 nm than by excitation in the lowest excited state. A Norrish-type II mechanism is most likely. (Fig. 4b); it was previously proposed in the case of monolinuron.[13–14] It can be noted that demethoxylation is more efficient than photohydrolysis when linuron and chlorbromuron are excited in the second absorption band centred near 245 nm, but this wavelength effect cannot be correlated with bond energies since the energy of the O–N bond is lower that the energy of the C–Cl bond.

Photoreduction of the ring was observed with chlorbromuron but not with linuron. Previously it was observed with diuron and monuron when the solution contained organic substances such as alcohol[7] or surfactants.[5] It is attributed to a substitution involving the formation of a radical after electron transfer from the solvent ($SN_2.ET.Ar^*$ substitution), more efficient with Br than with Cl (Fig. 4c).

CONCLUSION

The photoreactivity of halogenophenylureas depends on the substituents on nitrogen and on the ring, but photohydrolysis of the C-halogen bond occurs in all cases. Linuron and chlorbromuron can be photolysed at 254 nm and at wavelengths representative of sunlight, but the transformation is significantly different and irradiations at 254 nm cannot be used to study the photochemical transformations in environmental conditions. The *para*-hydroxylated derivative is the main product obtained in near-UV radiation, whereas other reactions are favoured by shorter wavelengths. The ratio *meta*/*para* hydroxylation increases with decreasing wavelength. The methoxy group is more easily eliminated than the methyl group, and the reaction is more efficient at short wavelengths, i.e. by irradiation in the main (second) absorption band. Photoreduction of the ring is easier with Br than with Cl and can be attributed to a radical mechanism. Our results on irradiation at 254 nm are in good agreement with those of Nick and Schöler.[2]

It is noteworthy that the presence of a methoxy group on nitrogen reduces the stability of the solution in the dark. With both linuron and chlorbromuron a slow hydrolysis leading to the formation of dihalogenoaniline was observed.

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