

Direct and induced phototransformation of mecoprop [2-(4-chloro-2-methylphenoxy)-propionic acid] in aqueous solution

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Abstract: Mecoprop was irradiated under various conditions of pH, oxygenation and wavelengths in order to study the reactions involved in the phototransformation. Four main photoproducts were identified: 2-(4-hydroxy-2-methylphenoxy)propionic acid (I), *o*-cresol (II), 2-(5-chloro-2-hydroxy-3-methylphenyl)propionic acid (III) and 4-chloro-*o*-cresol (IV). When the anionic form of mecoprop was irradiated between 254 nm and 310 nm (UV-C or UV-B), I was the main photoproduct. At 254 nm its formation initially accounted for more than 80% of the transformation. It has not previously been reported in the literature. The reaction results from a heterolytic photohydrolysis. Product II accounted for only a low percentage of the transformation. The stoichiometry was different with the molecular form: the main photoproduct, III, resulted from a rearrangement after a homolytic scission. Products I, II and IV were also formed as minor photoproducts. Some other minor photoproducts were also identified. In contrast, IV was the main photoproduct under sunlight irradiation or when solutions were irradiated in near-UV light (UV-A). This wavelength effect is attributed to the involvement of an induced phototransformation; IV is also the main photoproduct when the phototransformation is induced by Fe(III) perchlorate or nitrite ions. In usual environmental conditions the excitation of the molecular form is negligible and the phototransformation is mainly due to induced photoreactions.

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Keywords: mecoprop; photolysis; photohydrolysis; photorearrangement; wavelength effect; induced phototransformation

1 INTRODUCTION

Mecoprop [(±)-2-(4-chloro-2-methylphenoxy)propionic acid] is a selective systemic herbicide developed in the 1950s which is absorbed by leaves with translocation to roots. It is used for the post-emergence control of broad-leaved weeds in many cultivations. It is relatively soluble in water (734 mg litre⁻¹) and may be found in surface waters.¹ Mecoprop absorbs UV light of up to 310 nm wavelength, so that the overlap with sunlight is sufficient to induce its photodegradation, mainly in summer. This is experimentally proved in the present work. Its pK_a is 3.78¹ and, consequently, in natural waters more than 99% exists in the anionic form. Nevertheless the photochemical behaviour of the molecular form should be studied for comparison with other chloro-aromatic pesticides and for a better understanding of the mechanisms involved. Both molecular and anionic forms have similar UV spectra, but not necessarily the same photochemical behaviour. In plants mecoprop is hydroxylated on the methyl group, but in soil the main

reaction induced by micro-organisms is a transformation into 4-chloro-2-methylphenol followed by ring hydroxylation at the 6-position and ring opening.¹

Only a few publications have been devoted to the photochemical behaviour of mecoprop, and some photoproducts have been identified. Le Brun *et al*² reported the formation of 2-methylphenol (*o*-cresol), 2-methylcyclohexadi-2,5-ene-1,4-dione (methylbenzoquinone), 2-methyl-1-methoxybenzene, 2-methyl-1,4-dihydroxybenzene (methylhydroquinone) and 4-chloro-2-methylphenol (4-chloro-*o*-cresol), identified by gas chromatography-mass spectrometry coupling (GC-MS) from a solution irradiated at 254 nm or in polychromatic light (200–600 nm). Romero *et al*³ concluded that photochemical transformation plays an important role in the degradation of mecoprop on dry or moist soil, but photoproducts were not identified. It has also been reported that mecoprop can be photocatalytically transformed very efficiently on TiO₂ and completely mineralised.^{4,5} The formation of several intermediates such as α -ketopropionic acid, α -

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hydroxypropionic acid and acetic acid was indicated by nuclear magnetic resonance (NMR).

The aim of the present work was a kinetic and analytical study of the phototransformation of mecoprop in various conditions of pH (molecular or anionic form), oxygenation, irradiation wavelength and sensitization, in order to understand the mechanisms involved and to compare them with those from other chloroaromatic pesticides. From this basic study in laboratory conditions the main photochemical pathways involved in environmental conditions can be deduced and also what products may be formed if artificial UV light is used for decontamination of polluted waters.

2 MATERIALS AND METHODS

2.1 Reactants

Mecoprop (96% purity) was obtained from Župa Kruševac (Yugoslavia). The commercial product, which was slightly coloured, was purified by recrystallisation from water + ethanol (1 + 1 by volume) and obtained as colourless needles. Its purity was confirmed by NMR and high performance liquid chromatography (HPLC) analyses.

4-Chloro-*o*-cresol (97%) and *o*-cresol (puriss), used as analytical references, were obtained from Aldrich and Fluka respectively. *o*-Cresol was sublimated before use to eliminate traces of oxidation products.

Sodium nitrite RP Normapur and Fe^{III} perchlorate nonahydrate (>97%) used as photo-inducers were purchased from Prolabo and Fluka respectively.

Water used for solutions was purified with a Milli-Q device (Millipore). Its purity was controlled by measurement of the resistivity (>18 MΩ cm). In unbuffered solutions both forms of mecoprop (molecular and anionic) are generally present. To compare the photochemical behaviour of both forms, solutions were irradiated either at pH 2.15 (in the presence of hydrochloric acid) or at pH 5.5 (phosphate buffer).

2.2 Irradiation

Several devices were used for the irradiation of solutions. For the determination of quantum yields, solutions were irradiated at 280 nm with a xenon lamp (1600 W) equipped with a Schoeffel monochromator providing a parallel beam. Band width at mid-height was about 10 nm. The photon flow was evaluated at 3.7×10^{14} photons cm⁻² s⁻¹ with potassium ferrioxalate.⁶

Solutions were irradiated at 254 nm in a device consisting of a cylindrical mirror with an elliptic base, a low-pressure mercury lamp ('Germicide Lamp') located along one of the focal axes and a quartz cylindrical reactor (2 cm ID) located along the other focal axis. The average photon flow received in 30 ml was evaluated as 2.1×10^{17} photons s⁻¹, using uranyl oxalate as the chemical actinometer.⁶ In order to isolate photoproducts, a solution (100 ml) was irradiated with six low pressure mercury lamps surrounded by a

cylindrical mirror. The photon flow in 100 ml was evaluated at 2.8×10^{18} photons s⁻¹ with uranyl oxalate.

Two other devices were used to study the influence of irradiation wavelength. One consisted of six fluorescent lamps (Duke GL 20W) emitting at wavelengths longer than 275 nm with a maximum near 310 nm. Mercury lines at 365, 405 and 436 nm were also emitted, but were not involved in the direct phototransformation of mecoprop. The quartz reactor was placed along the symmetry axis. The photon flow received in 21.5 ml was evaluated at 9.9×10^{16} photons s⁻¹; this value is lower than the total photon flow emitted by the lamp, since the actinometer absorbs only a low percentage of the energy emitted on lines 405 nm and 436 nm, but slightly higher than the photon flow really absorbed by the solution of mecoprop.

In the other device, solutions were irradiated with lamps (Philips HPW 125) and maintained at room temperature with a cooling jacket. These lamps were medium pressure mercury lamps fitted with a black bulb in order to select the line at 365 nm. About 85, 6 and 2% of the light was emitted at 365 nm, 334 nm and 313 nm respectively. With this device the photon flow was evaluated at 2.4×10^{17} photons s⁻¹ in 20 ml using the chemical actinometer Aberchrome 540.⁷ Potassium ferrioxalate is too sensitive in these conditions and uranyl oxalate is not sufficiently absorbing at 365 nm.

Solutions were also exposed in natural sunlight in a 'Pyrex' vessel. Experiments were carried out in Clermont-Ferrand (latitude 46° N, altitude 420 m) in September.

2.3 Deoxygenation

In order to study the influence of oxygen, solutions were deoxygenated by argon bubbling for 50 min. The reactor was closed with a septum and samples were collected with a syringe at different stages of the photochemical transformation.

2.4 Analyses

UV spectra were recorded on Varian Cary 3 spectrophotometer.

HPLC analyses of irradiated solutions were carried out on a Waters Chromatograph equipped with a photodiode array detector 996 and an auto-sampler 717. Column: C₁₈ (5 μm) 250 mm × 4 mm. Eluent: acetonitrile + water (35 + 65 by volume). Water was acidified with acetic acid (1 g litre⁻¹) to prevent the dissociation of mecoprop and products.

For identification, the main photoproducts, except *o*-cresol and 4-chloro-*o*-cresol, were isolated from irradiated solutions with a HPLC Gilson instrument equipped with a C₁₈ column, 50 mm × 21 mm.

In order to confirm the formation of *o*-cresol, solutions were extracted by nitrogen bubbling, vapours being trapped at 77 K. Using this procedure it was possible to isolate *o*-cresol from irradiated solutions as

an aqueous solution. *o*-Cresol was identified by means of UV and fluorescence spectrophotometry. An authentic sample of known concentration was then injected into HPLC to confirm the identification by comparison of retention times and to quantify the formation of *o*-cresol.

The products **I** and **III** were identified by GC-MS on Hewlett-Packard 5985 chromatograph (column Machery-Nagel Optima 5; 25 m × 0.25 mm ID) and by ¹H NMR in hexadeuteroacetone on a Bruker AC 400 instrument.

3 RESULTS

3.1 UV absorption

Molecular and anionic forms of mecoprop have similar UV spectra. They absorb at wavelengths shorter than 310 nm as shown in Fig 1. The maximum of absorption of both forms is located at 280 nm, but the molar absorption coefficient is slightly higher for the anionic form ($\epsilon=1604\text{M}^{-1}\text{cm}^{-1}$) than for the molecular form ($\epsilon=1390\text{M}^{-1}\text{cm}^{-1}$). The absorption spectrum of mecoprop overlaps with that of sunlight in summer, since the wavelength of sunlight starts at about 295 nm at sea level.⁸ The overlap is smaller, but not negligible, in winter. It is shown experimentally that mecoprop may be phototransformed in September. However, in environmental conditions some induced photoreactions may also be involved.

3.2 Irradiation of the anionic form

A solution $4.94 \times 10^{-4}\text{M}$ mecoprop buffered at pH 5.5 was irradiated at 254 nm in the presence and in the absence of oxygen. Similar UV spectra were observed in both cases. The absorption increases and a weak absorption band appears between 300 and 400 nm (Fig 1). In both cases two photoproducts appear on the HPLC chromatogram (Fig 2).

The same photoproducts are formed when solutions are irradiated between 275 and 350 nm in the presence or in the absence of oxygen. Thus the formation of

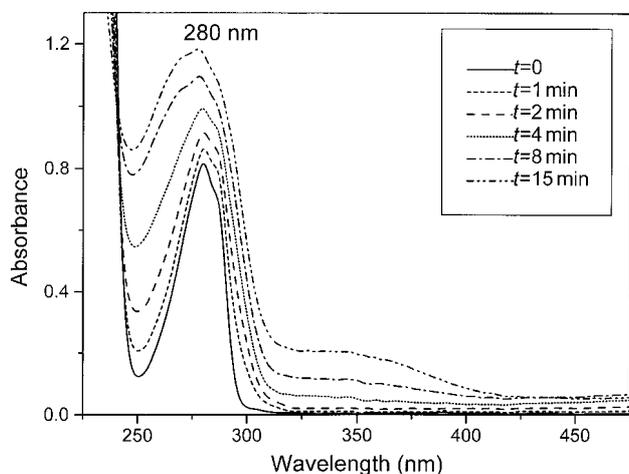


Figure 1. Evolution of the UV spectrum of an air-saturated solution of mecoprop (concentration= $4.94 \times 10^{-4}\text{M}$; pH 5.5) irradiated at 254 nm.

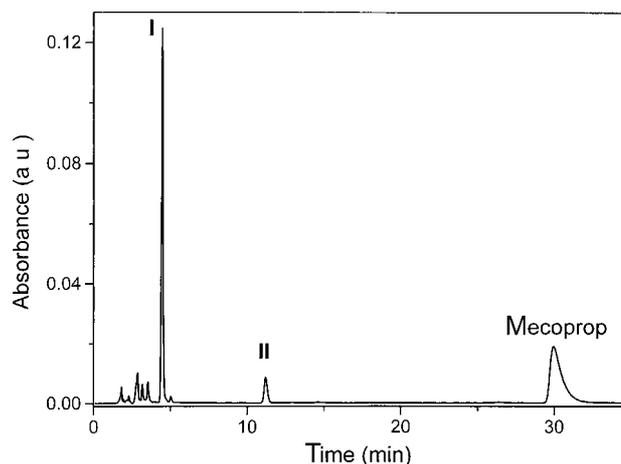


Figure 2. HPLC chromatogram of an air-saturated solution of mecoprop (concentration= $4.85 \times 10^{-4}\text{M}$; pH 5.5) irradiated 3 min at 254 nm. Conversion about 59%.

products is affected neither by oxygen nor by the irradiation wavelength between 254 nm and 350 nm. (Absorption is very low at $\lambda > 310\text{nm}$).

Product **I** is clearly the main primary photoproduct. Its UV spectrum, obtained on a photodiode array detector, is similar to the spectrum of mecoprop. It was isolated by preparative HPLC and identified by MS and ¹H NMR as 2-(4-hydroxy-2-methylphenoxy)propionic acid (Fig 3). m/z : 196M^{+}

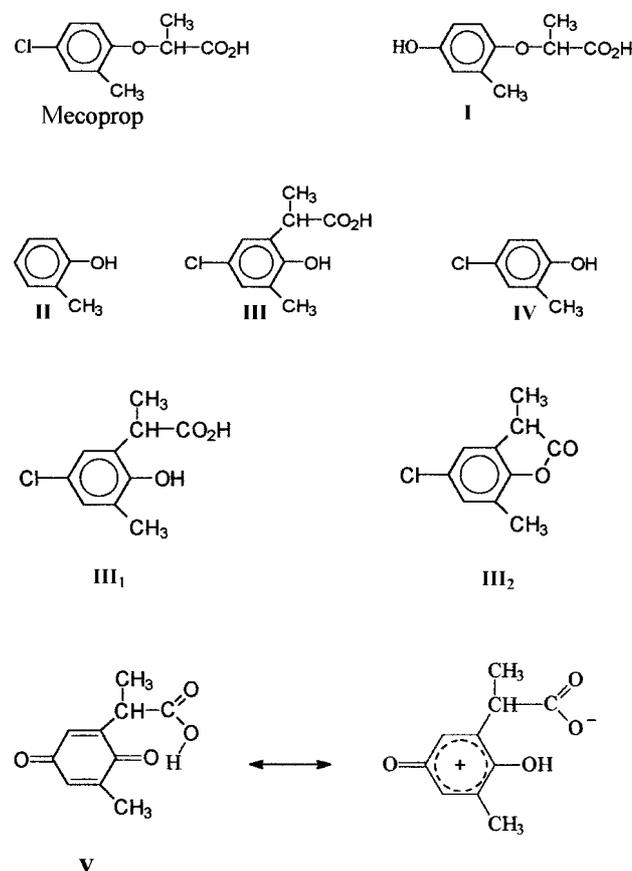


Figure 3. Structures of mecoprop and main photoproducts.

(26%); main fragments 123 (loss of $\text{CH}_3\text{-CH-CO}_2\text{H}$) (86%); 95 (loss of $\text{COCH}_3\text{-CH-CO}_2\text{H}$) (21%); 45 (CO_2H) (91%). $^1\text{H NMR}$ 400MHz (acetone D_6) δ ppm: 6.69 (H_6), d, $J=8.7\text{Hz}$; 6.64 (H_3), d, $J=3\text{Hz}$; 6.55 (H_5), dd, $J=3$ and 8.7Hz ; 4.65 (CH), q; 2.17 (CH_3 on the ring), s; 1.55 (CH_3 chain), d. (s=singlet; d=doublet; dd=double doublet; q=quadruplet). This product has not been reported in previous work.

Product **II** was extracted from the irradiated solution by nitrogen bubbling and isolated as an aqueous solution as described in Section 2.4. It was identified as *o*-cresol.

Solutions of known concentrations of products **I** and **II** were prepared from product **I** isolated by preparative HPLC and from the commercial compound, respectively. Calibration of HPLC with these solutions allowed a comparison between the kinetics of **I** and **II** formation and the disappearance of mecoprop. It appears from Fig 4 that the yield of **I** is initially about 85% when the air-saturated or deoxygenated solution is irradiated at 254nm. Product **II** is a minor product, but its formation is more efficient in the absence of oxygen, which is not really surprising since it is a reduction product. Similar results were obtained when solutions were irradiated in the range 275–350nm. The quantum yield was evaluated at 0.75 in an air-saturated and deoxygenated solutions irradiated at 280nm.

3.3 Irradiation of the molecular form

Solutions of $4.80 \times 10^{-4}\text{M}$ mecoprop were irradiated at 254nm in a solution buffered at pH 2.15 in order to study the photochemical behaviour of the molecular form (pK_a 3.78). Similar results were obtained in air-saturated and in deoxygenated solutions, showing that oxygen plays a minor role in the reaction. An increase of UV absorption was observed as well as the formation of a new weak absorption band between 300 and 400nm, as was the case in the less acidic solutions.

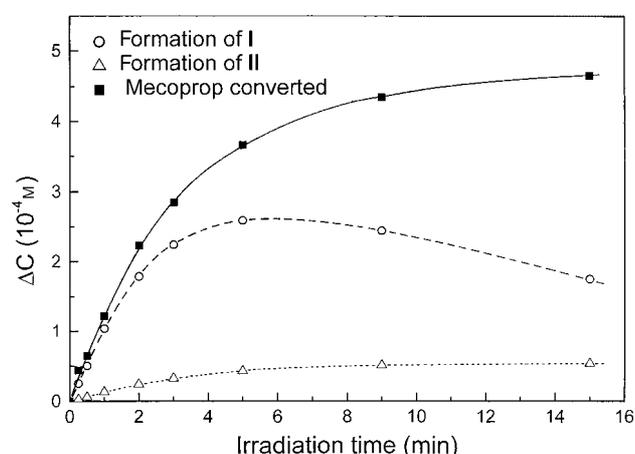


Figure 4. Kinetics of mecoprop disappearance and formation of products **I** and **II** in an air-saturated solution (concentration= $4.85 \times 10^{-4}\text{M}$; pH 5.5) irradiated at 254nm.

However, the HPLC chromatogram was more complex and at least two new photoproducts, **III** and **IV** were formed. The same photoproducts were obtained by irradiation in the range 275–350nm (Fig 5). The quantum yield was measured in monochromatic parallel beam at 280nm. It is higher in air-saturated solution ($\phi=0.34$) than in deoxygenated solution ($\phi=0.23$).

Product **IV** was identified as 4-chloro-*o*-cresol (Fig 3) by comparison of UV spectra and retention time with those of a commercial standard.

Product **III** was isolated by preparative HPLC and identified by MS and $^1\text{H NMR}$ 400MHz spectrometry. It was found to have the same molecular weight as product **I**, but was a chlorinated compound. m/z : 196, $\text{M}^{+\cdot}$ (48%); 198, $\text{M}^{+\cdot}$ (16%); 168 (loss of CO) (100%); 170 (loss of CO) (33%); 133 (loss of Cl and CO) (55%); 105 (loss of Cl and $\text{CH}_3\text{-CH-CO}$) (81%); 77 (62%); 51 (65%).

The $^1\text{H NMR}$ 400MHz spectrum of product **III** corresponds to a mixture of two compounds **III**₁ and **III**₂ (Fig 3) approximately in the ratio 3:2. **III**₁ δ ppm (acetone D_6): 7.03 (H_3 and H_5), s; 4.03 (CH), q; 2.23 (CH_3 on the ring), s; 1.45 (CH_3 - chain), d. **III**₂ δ ppm (acetone D_6): 7.25 (H), d, $J=2.4\text{Hz}$; 7.18 (H), d, $J=2.6\text{Hz}$; 6.80 (CH), q; 2.27 (CH_3 - ring), s; 1.56 (CH_3 - chain), d. It was concluded that **III**₂ resulted from the lactonisation of **III**₁ during isolation and drying. To corroborate this identification, it was shown experimentally that the proportion of **III**₂ increased as the mixture was heated to dryness.

The irradiation of an air-saturated aqueous solution of product **III** in the range 275–350nm led to the formation of a main product of slightly shorter HPLC retention time, characterised by strong absorption bands located at 261nm and 365nm. This product, which was not formed in deoxygenated solution, is most likely to be the quinonic derivative (**V**; Fig 3) since it is well known that the irradiation of 4-

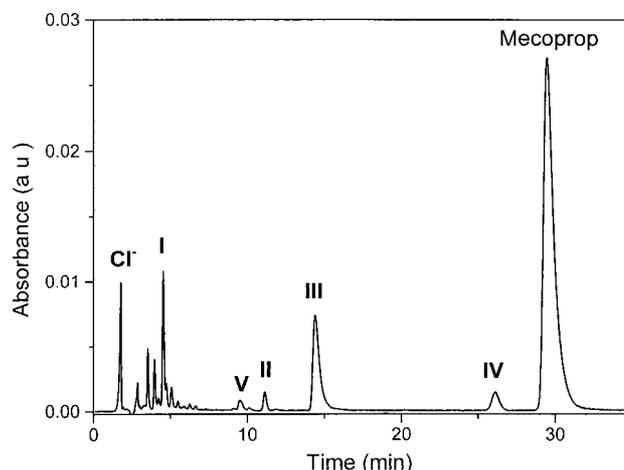


Figure 5. HPLC chromatogram of an air-saturated solution of mecoprop (concentration= $5.03 \times 10^{-4}\text{M}$; pH 2.15) irradiated 5min between 275 and 350nm. Conversion about 41%.

chlorophenol in air-saturated solution leads to the formation of *p*-benzoquinone in high yield.^{9,10} The strong absorption at 365 nm is probably due to an internal H-bond.

Product **V** was observed as a minor secondary photoproduct in irradiated air-saturated solution of mecoprop (Fig 5). Another minor secondary photoproduct was identified as methyl-*p*-benzoquinone.

3.4 Irradiation in sunlight and at 365 nm

An unbuffered 5.82×10^{-4} M solution of mecoprop was exposed to sunlight in September. The half-life of mecoprop was evaluated at 8 days. Product **IV** has the kinetics of a secondary photoproduct and it accumulates in the solution (Figs 6a and b). It can be deduced that the irradiation wavelength has a significant influence on the orientation of the reaction.

In order to confirm this wavelength effect, a 4.85×10^{-4} M solution of mecoprop buffered at pH 5.5 was irradiated with HPW 125 lamps emitting about 85% of photons on the mercury line 365 nm and a small percentage at 313 and 334 nm (see Section 2.2). The phototransformation was very slow, but about 13% of mecoprop was transformed after 15 days. The main photoproducts detected were **IV**, **I** and **II**. Only photoproducts **IV** and **I** were detected in a solution of mecoprop in the molecular form (5.03×10^{-4} M; pH 2.15) irradiated under the same conditions. The

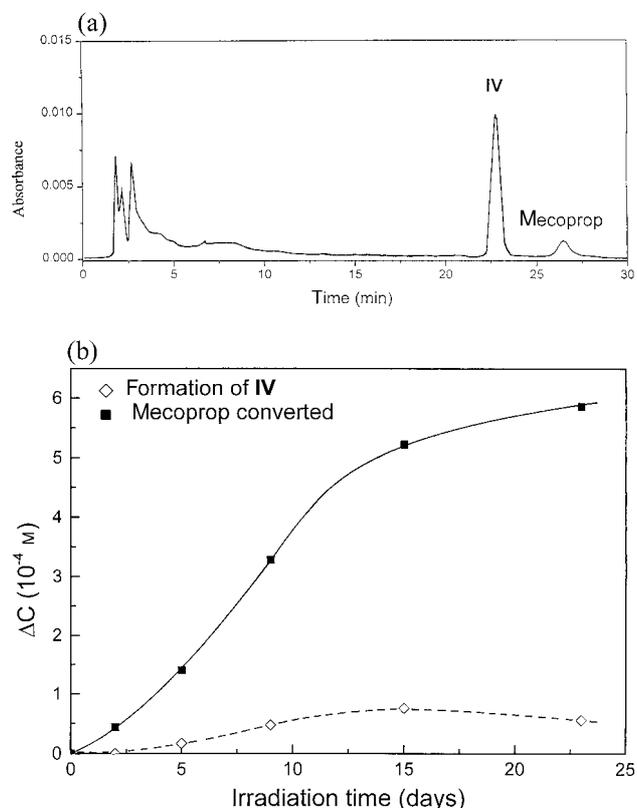


Figure 6. (a) HPLC chromatogram of an unbuffered solution of mecoprop (concentration 5.82×10^{-4} M) exposed 23 days to sunlight in September; conversion about 98%. (b) Kinetics of mecoprop disappearance and formation of 4-chloro-*o*-cresol (**IV**).

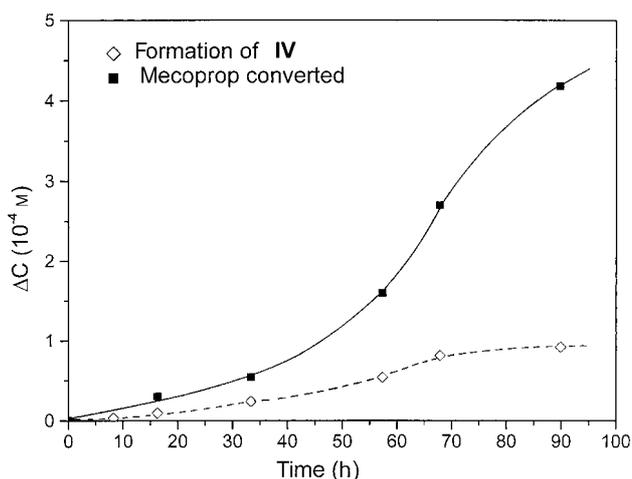


Figure 7. Kinetics of mecoprop disappearance and formation of 4-chloro-*o*-cresol (**IV**) in an air-saturated solution (concentration $=5.03 \times 10^{-4}$ M; pH 2.15) irradiated at 365 nm.

disappearance of mecoprop was clearly self-accelerated (Fig 7) and it is noteworthy that **IV** corresponded to the main peak on the chromatogram of a solution irradiated with HPW 125 lamps, whereas it was a minor photoproduct when the molecular form was irradiated at short wavelengths.

Product **V** absorbs between 300 and 400 nm and it may be assumed to play a role in the phototransformation of mecoprop at longer wavelengths. To demonstrate this, an air-saturated solution of **III** (3.2×10^{-4} M; pH 2.2) was irradiated between 275 and 350 nm. The formation of **V** was observed (Solution A). The rate of formation of **IV** was then compared between two solutions (B and C) of mecoprop (4.71×10^{-4} M) irradiated under the same conditions at 365 nm, the only difference between B and C being the presence of 25% of solution A in solution C. It was noted that the formation of **IV** was five times higher with solution C than with solution B, indicating that the presence of **V** induced the formation of **IV**. Similarly it was observed that the formation of **IV** may be induced by the addition of a small amount of methylbenzoquinone to a solution of mecoprop.

An air-saturated solution of methylbenzoquinone (1.07×10^{-4} M) was irradiated at 365 nm in the presence of mecoprop (4.75×10^{-4} M), or in its absence. The formation of methylhydroquinone was observed in both cases, but it was clearly more efficient in the presence of mecoprop, which was transformed into product **IV**. It can be deduced that methylbenzoquinone induces the transformation of mecoprop and that the formation of **IV** results from the oxidation of mecoprop. This result is in good agreement with the phototransformation of mecoprop induced by Fe^{III} . The involvement of singlet oxygen was ruled out since no formation of **IV** was observed when a 3×10^{-5} M solution of Rose Bengal was irradiated in visible light in the presence of 3.9×10^{-4} M mecoprop.

The results obtained in direct photolysis are summarised in Table 1.

Table 1. Comparison of initial transformation rates of mecoprop under the different conditions used

Conditions of irradiation	Photon flux ($\text{photon cm}^{-3}\text{s}^{-1}$)	Initial transformation rate (air-saturated solutions)
'Germicide' lamp, 254 nm	7.1×10^{15}	Anionic form: $1.8 \times 10^{-4}\text{M min}^{-1}$ Molecular form: $0.57 \times 10^{-4}\text{M min}^{-1}$
6 GL 20W lamps, max 310nm+mercury lines	$\approx 4.6 \times 10^{15a}$	Anionic form: $0.75 \times 10^{-4}\text{M min}^{-1}$ Molecular form: $0.43 \times 10^{-4}\text{M min}^{-1}$
3 HPK 125 lamps, max at 365 nm	1.2×10^{16}	Anionic form: $0.075 \times 10^{-4}\text{M day}^{-1}$ Molecular form: $0.18 \times 10^{-4}\text{M day}^{-1}$
Sunlight, September		Unbuffered solution: $0.21 \times 10^{-4}\text{M day}^{-1}$

^a See Section 2.2.

3.5 Induced phototransformation

Fe^{III} salts absorb in the range 300–400 nm and may induce the photooxidation of organic substrates present in the solution. Several processes may be involved, depending on the substrate.^{11–13} In the present work, Fe^{III} perchlorate (10^{-3}M) was used to induce the degradation of mecoprop in acidic solution ($5.03 \times 10^{-4}\text{M}$; pH 2.15) irradiated at 365 nm. The acidification was necessary to prevent the precipitation of Fe^{III} hydroxide. After 30 min about 83% of mecoprop was transformed, whereas direct photolysis is negligible under these conditions. It clearly appears in Fig 8 that the main product is 4-chloro-*o*-cresol (**IV**) that accumulates in the solution.

Methanol was used as a quencher of $\cdot\text{OH}$ to identify the role of these radicals in the reaction. In the presence of methanol (20ml litre^{-1} , about 0.49M) transformation is inhibited by about 80%, whereas about 99% of $\cdot\text{OH}$ is quenched. (Evaluated from the rate constant $9.7 \times 10^8\text{M}^{-1}\text{s}^{-1}$ for the reaction $\cdot\text{OH} + \text{CH}_3\text{OH}$).¹⁴ It was deduced that hydroxyl radicals contribute to the formation of **IV**, but probably another pathway is also involved.

Nitrite and nitrate ions are also photochemical

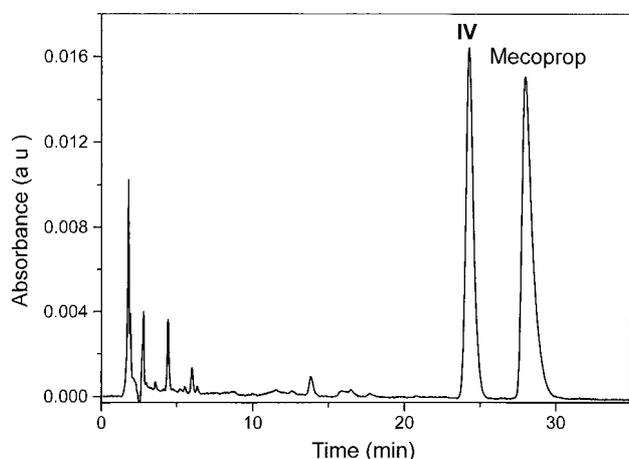
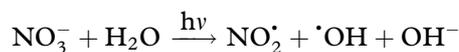
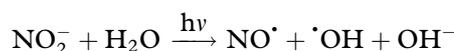


Figure 8. HPLC chromatogram of a solution of Fe^{III} perchlorate (10^{-3}M) and mecoprop (concentration = $5.03 \times 10^{-4}\text{M}$) irradiated 15 min at 365 nm. Conversion about 65%.

sources of hydroxyl radicals.^{15–17}



The quantum yield of photolysis is significantly higher with HNO_2 (about 0.45) than with NO_2^- (0.015–0.07 according to the wavelength) and NO_3^- (0.009–0.017).¹⁷ Nitrite ions were preferred to nitrate ions in the present work since they absorb at longer wavelengths (maximum at 352 nm) than nitrate ions (maximum at 302 nm) and it is possible to excite them selectively at 365 nm in the presence of mecoprop. A further advantage is that nitrite ions have a higher molar absorption coefficient and higher quantum yield, but unfortunately NO_2^- ions are good $\cdot\text{OH}$ quenchers and the production of $\cdot\text{OH}$ in a solution is only efficient at low concentrations of nitrite.

A $5.0 \times 10^{-4}\text{M}$ solution of mecoprop with $5 \times 10^{-4}\text{M}$ sodium nitrite and acidified at pH 2.15 was irradiated at 365 nm. Several photoproducts were formed but only product **IV** accumulated in the solution. The efficiency increased with increasing irradiation time, as shown in Fig 9, and it may be assumed that **IV** is not only formed as a primary photoproduct. By comparison with a solution kept in the dark it was established that this transformation did not result from a thermic reaction of HNO_2 . The rate of formation of **IV** was significantly higher at pH 2.15 than at pH 5.15, due to the fact that the photolysis of HNO_2 is more efficient than the photolysis of NO_2^- .

4 DISCUSSION AND MECHANISMS

4.1 Direct excitation

The formation of **I** (hydroxylated photoproduct) is almost quantitative with the anionic form of mecoprop excited in aqueous solution. This reaction is not influenced either by oxygen or by wavelength in the range 254–310 nm. Similar photoreactions have been

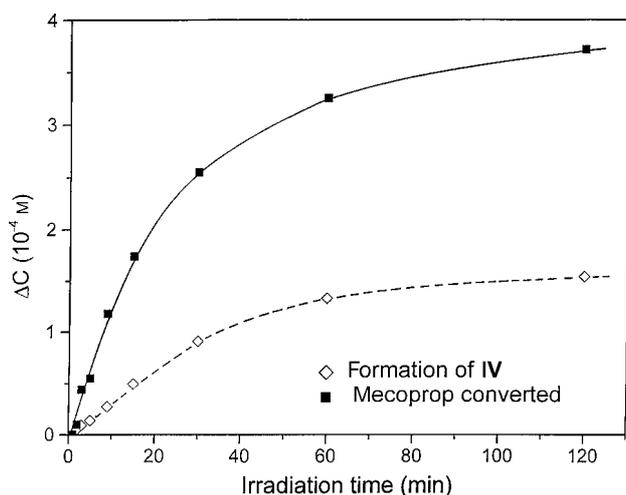


Figure 9. Phototransformation of mecoprop ($5.0 \times 10^{-4} \text{ M}$) induced by excitation of nitrite ions (concentration $5.0 \times 10^{-4} \text{ M}$) at 365 nm (pH 2.15).

reported with chlorobenzene,¹⁸ 3-chlorophenol,¹⁹ 3-chloroaniline and chlorpropham.²⁰ It results from a heterolytic photohydrolysis (Fig 10(i)). This reaction

is more efficient with the anionic form than with the molecular form.

The formation of product **III** from the molecular form of mecoprop results from a rearrangement after homolytic scission of the ether bond. A similar rearrangement was reported in the case of 2-naphthoxyacetic acid.²¹ The formation of a lactone occurs when the product is isolated and dried (Fig 10(ii)).

With the molecular form of mecoprop, product **IV** was detected as a minor photoproduct in air-saturated or deoxygenated solutions irradiated between 250 and 350 nm. Its formation is self-accelerated and more efficient in the presence of oxygen in solutions irradiated in near-UV. Both direct and induced reactions are probably involved. The direct formation of **IV** is more efficient when irradiating the molecular form, as it is for the formation of product **III**. It may be attributed to a reaction between the two radicals initially formed (Fig 10(ii)).

The induction by quinonic compounds was established experimentally. It is consistent with the influence of oxygen, the self-acceleration and the

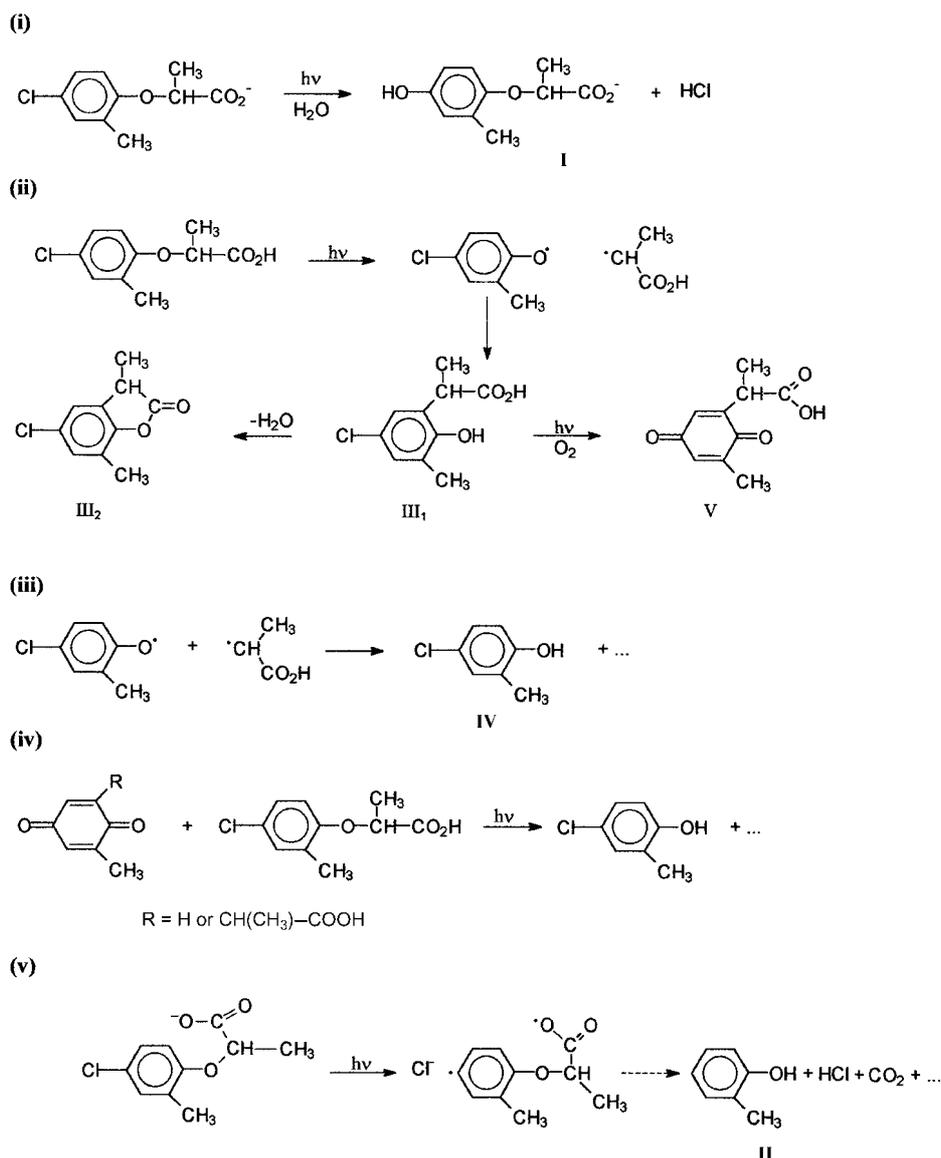


Figure 10. Mechanisms of direct phototransformations.

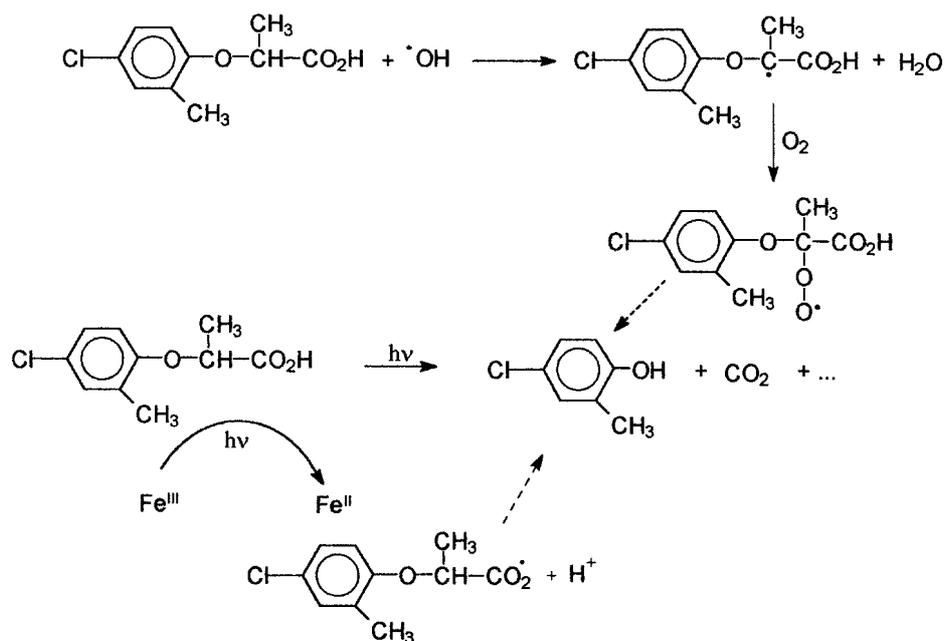


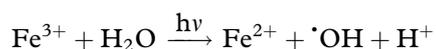
Figure 11. Mechanisms of induced phototransformations.

accumulation of product **IV** in solutions irradiated in the near-UV. (Fig 10(iv)).

The minor formation of *o*-cresol from the anionic form of mecoprop is tentatively explained by an internal charge transfer that induces the reduction of the ring (Fig 10(v)).

4.2 Induced phototransformation

The main reaction observed when Fe^{III} perchlorate is excited in the presence of mecoprop is the formation of 4-chloro-*o*-cresol (**IV**). The excitation of Fe^{III} salts induces oxidation. Two pathways may be assumed (Fig 11): oxidative decarboxylation involving the formation of a complex between Fe^{III} and substrate either in the ground state or in the excited state,¹¹ or the intermediate formation of $\cdot\text{OH}$ radicals:^{12,13}



The latter is most probably involved, since the reaction is inhibited by methanol and the formation of **IV** was also observed when the transformation was induced by nitrite ions. However it is not the only pathway, since the formation of **IV** was observed when $\cdot\text{OH}$ was 99% eliminated. In acidic solution $\cdot\text{OH}$ is assumed to react with $-\text{CH}-$.

4.3 Irradiation in the near-UV—wavelength effect

The photochemical transformation when solutions are irradiated at wavelengths longer than 300 nm was not expected. However, such a wavelength effect has previously been reported in the case of MCPA (4-chloro-2-methylphenoxyacetic acid),²² although it was not explained. From present results, the formation of 4-chloro-*o*-cresol as the main photoproduct may be explained by the excitation of quinonic photoproducts formed by oxidation of **III**. The first step of the reaction in unbuffered solution is necessarily the

formation of **I** and **III**, which is very slow in sunlight or with lamps emitting mainly at 365 nm. The formation of **I** induces a decrease of pH that favours the further formation of **III**. The latter, which is a derivative of 4-chlorophenol, is easily oxidised into a quinonic compound which plays the role of photo-inducer for the formation of **IV**. Quinonic compounds, particularly **V**, are transformed into hydroquinone derivatives. The latter is photooxidised into a quinone that consequently plays a photocatalytic role in the formation of **IV**. This mechanism explains the high accumulation of **IV** in solutions irradiated in the near-UV. The formation of methylbenzoquinone from **IV** can also participate in the induced phototransformation that is consistent with the self-accelerated formation of **IV**.

5 CONCLUSIONS

The formation of the main primary photoproducts resulting from the phototransformation of mecoprop is not influenced either by oxygen or by wavelength in the range 254–310 nm, but depends on pH (different photochemical behaviour of molecular and anionic forms): heterolytic photohydrolysis is the main reaction observed with the anionic form, whereas a photochemical rearrangement is the main pathway with the molecular form. A number of other photoproducts were identified: *o*-cresol, 4-chloro-*o*-cresol and quinonic derivatives. The photoreactivity of the molecular form is interesting for comparison with other chloroaromatic pesticides, but generally it plays a minor role under environmental conditions.

Different photochemical reactivity was observed when solutions were irradiated in sunlight or near-UV light. Under these conditions 4-chloro-*o*-cresol is formed as the main photoproduct. This phenomenon confirms the wavelength effect previously reported in

the case of 4-chloro-2-methylphenoxyacetic acid. It is attributed to reactions induced by quinonic compounds formed as intermediates.

The transformation of mecoprop can be induced by Fe^{III} salts and nitrite ions, leading to the formation of 4-chloro-2-methylphenol as the main product. An oxidation of the acetic moiety by hydroxyl radicals may be suggested.

Mecoprop does not accumulate in environmental conditions and induced reactions play a major role in the phototransformation.

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