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# Photochemical behaviour of 4-chloro-2-methylphenoxyacetic acid Influence of pH and irradiation wavelength

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## Abstract

The kinetics of phototransformation of MCPA is studied under various irradiation conditions. The photocatalytic transformation on $TiO_2$ in aqueous suspension is almost specific and leads to 4-chloro-2-methylphenol ($P_7$) as the main photoproduct. The same product is obtained when MCPA is irradiated on silica in the absence of water. The direct phototransformation is more complex: the reaction is not influenced by oxygen but it depends on the pH of the solution and on the irradiation wavelength. With the anionic form irradiated between 254 and 350 nm, photohydrolysis of C–Cl bond is almost quantitative (yield > 86%). It leads to the hydroxylated photoproduct $P_2$. With the molecular form the main product $P_5$ results from a photochemical rearrangement of the molecule. With both forms, some other photoproducts are also identified and quantified, particularly methylhydroquinone ($P_1$) and $P_7$. 2-Methylphenol ($P_6$) is only obtained with the anionic form as a minor product. However, irradiation of solutions in sunlight or with lamps emitting mainly at 365 nm (about 2 and 6% of the light is emitted at 334 and 313 nm, respectively) yields $P_7$ as the main photoproduct. Its formation is self-accelerated. This wavelength effect is attributed to reactions induced by quinonic compounds formed as intermediates since the disappearance of MCPA is more efficient in presence of quinonic products. $P_7$ is also the major photoproduct when phototransformation is induced by nitrite ions or Fe(III) perchlorate. Besides, it appears from Microtox® test that photoproducts formed at wavelength shorter than 350 nm are more toxic to the marine bacterium *Vibrio fischeri* than the initial compound. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* MCPA; Photolysis; Photocatalysis; Photorearrangement; Wavelength effect; Induced phototransformation; Toxicity

## 1. Introduction

MCPA (4-chloro-2-methylphenoxyacetic acid) is a quite soluble herbicide ($734 \, mg \, l^{-1}$) commonly used in combination with other herbicides for the post-emergence control of broad-leaved weeds [1]. In natural waters, it is mainly in the anionic form ($pK_a$ 3.07). Its photodegradation was previously studied by Soley et al. [2] and Clapés et al. [3]. The main photoproducts initially formed when an aqueous solution is irradiated at 290 nm are 4-chloro-2-methylphenol ($P_7$) and 4-chloro-2-methylphenylformate ($P_8$), but they does not accumulate and they are photolysed in a second stage into methylhydroquinone ($P_1$) which is the main product identified, methylbenzoquinone ($P_3$) and 2-methylphenol ($P_6$). The sensitisation by riboflavin increases the rate of degradation and the major photoproduct obtained is $P_7$, but a minor formation of $P_8$ is also observed. However, the photocatalytic transformation of MCPA and its methylated homo-logous mecoprop (2-(4-chloro-2-methylphenoxy)-propionic acid) was the subject of recent publications [4,5]. The complete mineralisation of both substrates was obtained, but it is not the purpose of the present work which is focused on the initial stages of phototransformation. The main product initially formed is $P_7$. Trillas et al. [6] showed that 2,4-dichlorophenol (2,4-DCP) and hydroxyhydroquinone are the main photoproducts in the photocatalytic degradation of 2,4-dichlorophenoxyacetic acid (2,4-D) using $TiO_2$ under different experimental conditions. 4-Chlorophenoxyacetic acid (4-CPA) belongs to the group of chlorophenoxyacetic derivatives. Photolysis of this compound in the presence of hydrogen peroxide or Fe(III) salts leads to the formation of 4-chlorophenol (4-CP) as a major photoproduct [7].

The main photoproducts resulting from the irradiation of MCPA in different conditions have been identified in a preliminary study [8] but the observed wavelength effect was not explained. In a recent study devoted to the photochemical behaviour of mecoprop, Meunier and Boule [9] have also reported and confirmed this phenomenon, which is

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attributed to the involvement of the induced phototransformation by quinonic products formed as intermediates.

The main objective of this work is a kinetic and analytic study of the phototransformation of MCPA in aqueous solution irradiated at 254 nm and in the range of solar light ($\lambda > 300$ nm) in several pH conditions. It is also to compare with the photochemical transformation in other conditions, namely direct photolysis on silica in the absence of water and photo-induced transformation. Actually when a pesticide is spread in the environment, its direct or induced photolysis may occur in water, but also at the surface of soil in the absence of water. Silica (Fontainebleau sand) was used as a simple and well-defined support representative of the soil. The study of the photocatalytic behaviour is also useful since this technique was often proposed for the decontamination of polluted waters. Results obtained in photocatalysis and irradiation on sand are presented first since the reaction is more specific than direct photolysis.

## 2. Experimental

### 2.1. Chemicals and reagents

MCPA (98%) was purchased from Chem Service. Its purity was controlled by GC–MS. 2,4-D (98%) was supplied by Aldrich. Benzoquinone (99%, Merck), $P_3$ (Prolabo), hydroquinone (Prolabo), $P_6$ (puriss, Fluka), $P_1$ (99%, Aldrich) and $P_7$ (97%, Aldrich) were sublimated before use. 2,4-DCP ($\approx$95% HPLC) was from Fluka.

$P_8$ was synthesised in University of Novi Sad, Yugoslavia, from $P_7$ and formic acetic in the presence of diphosphorus pentoxide (see Acknowledgements). Its purity was controlled by $^1$H NMR.

Fe(III) perchlorate nonahydrate (97%) and sodium nitrite RP Normapur were purchased from Fluka and Prolabo, respectively. Titanium dioxide (Degussa P25) was predominately anatase (70–80% anatase and 30–20% rutile) with a surface area of $55 \, m^2 \, g^{-1}$.

Fontainebleau sand was provided by Prolabo (granulometry: 120–150 $\mu$m). It is almost pure silica as confirmed by the energy-dispersive X-ray analysis (EDX) (98.8% Si, 0.6% K and 0.5% Ca). Organic substances were removed before use by calcination during several hours at $500°$C.

All solvents used were Carlo Erba, HPLC grade (99.9% purity), and all inorganic reagents were laboratory grade. Solutions were prepared with water purified using a Milli-Q system.

### 2.2. Photoreactors and light sources

MCPA was irradiated in various conditions: in the presence of $TiO_2$ in aqueous suspension, on silica in the absence of water and in aqueous solution at different wavelengths.

Aqueous suspensions of $TiO_2$ ($1 \, l^{-1}$) were irradiated by fluorescent lamp (Philips TLAD 15 W/05) emitting in the range 300–450 nm with a maximum emission at 365 mm. The irradiation device has been previously described [8]. $TiO_2$ was maintained in suspension before and during irradiation by magnetic stirring. They were equilibrated during half an hour before starting irradiation.

For irradiation on sand the following procedure was used: 5 mg of MCPA was dispersed on 100 g of Fontainebleau sand using diethylether. After evaporation and drying, sand was irradiated with four lamps Duke GL 20 W (maximum emission near 310 nm) through a round-bottom flask (4 l) in Pyrex glass rotating around a horizontal axis and equipped with internal spikes to favour mixing. The absorption of the flask limits the irradiation wavelengths to $\lambda > 290$ nm. After irradiation, reactant and photoproducts were extracted with methanol for analysis.

In order to compare the photochemical behaviour of the two forms (molecular and anionic) of MCPA in aqueous solution, buffered solutions were irradiated with different devices at various wavelengths:

- 254 nm, using a low-pressure mercury lamp (germicidal lamps) located on one axis of an elliptical cylindrical mirror, the quartz cylindrical reactor (2 cm i.d.) being located along the other axis.

  For preparative purposes, solutions were irradiated at this wavelength using a cylindrical device equipped with six germicidal lamps.
- In the range 275–350 nm, with six lamps Duke GL 20 surrounded by cylindrical mirror were used. Actually, these lamps also emit on mercury lines at 365, 405, 436 and 546 nm but these lines are not active in the direct phototransformation of MCPA. The quartz reactor was placed along the symmetry axis.
- 365 nm, in a water-cooled Pyrex reactor using three medium pressure mercury lamps "black light" (HPW 125, Philips) surrounded by cylindrical mirror. These lamps are fitted with a black bulb to get the selected line at 365 nm (about 85% of radiant energy and a few percents at 334 and 313 nm).
- In natural sunlight using Pyrex reactor. Experiments were carried out in Clermont–Ferrand (latitude 46°N, altitude 420 m) in April and May.
- 280 nm, using a monochromator Schoeffel equipped with a 1600 W xenon lamp for the determination of quantum yield in monochromatic parallel beam. With this device, the bandwidth at mid-height was about 10 nm. The reactor was a square quartz cuvette, with a 1 cm pathlength. The incident light intensity at this wavelength was evaluated at $2.17 \times 10^{14}$ photons $s^{-1} \, cm^{-2}$ by potassium ferrioxalate actinometry.

In order to study the influence of oxygen, some solutions were irradiated after deoxygenation by argon bubbling during 30 min. The pH of solutions was adjusted at 1.5 or 5.9 with hydrochloric acid and phosphates, respectively, in order to compare the photochemical behaviour of neutral and anionic forms.

### 2.3. Toxicity evaluation

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* previously called *Photobacterium phosphoreum*. The emission is measured after various exposure times, usually 5, 15 or 30 min [10–12]. This rapid and reproducible ecotoxicological test is based on the disturbance of the electron flux of the respiratory chain and consequently the metabolic activity of the bacterium by the toxic substance.

### 2.4. Analyses

Electronic absorption spectra were recorded on a Cary 3 (Varian) spectrophotometer. Irradiated solutions and products extracted after irradiation in different conditions were analysed by HPLC with a chromatograph Waters 510 equipped with a photodiode array detector. Separations were obtained on a 25 cm × 4.6 mm Kromasil 100 Å column (reverse phase $C_{18}$, 5 μm), using a flow rate of 1.5 ml min$^{-1}$, with detection wavelength at 280 nm. The eluent was usually a mixture acetonitrile/water + 0.1% acetic acid, 45:55 v/v (water was acidified to prevent from ionisation of MCPA and products).

Most of photoproducts were separated by using HPLC or extracted from the irradiated solutions with ether. In experiments on sand, reactants and products were extracted with methanol. Products $P_1$, $P_3$, $P_6$ and $P_7$ were identified by comparison of retention times and UV spectra with those of commercial standards, $P_8$ by comparison with an authentic sample provided by the University of Novi Sad. It may be noted that it is hydrolysed into $P_7$ in a few hours (see Section 5.1).
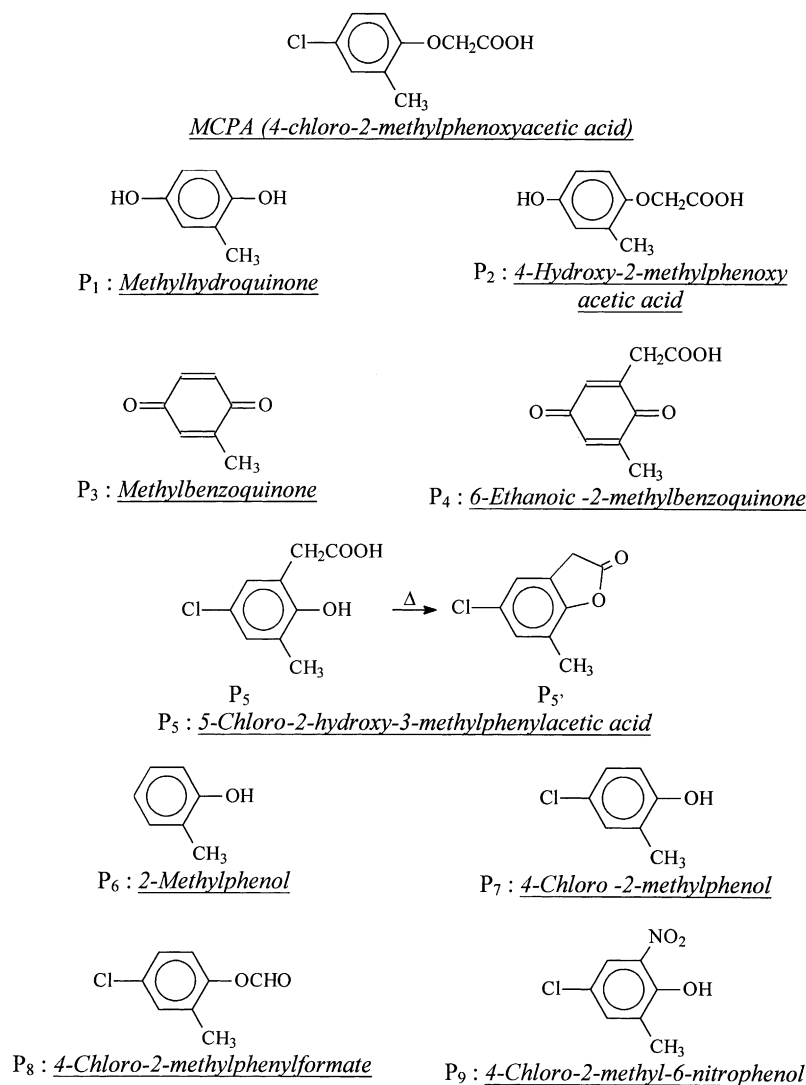


Fig. 1. Structures of MCPA and main photoproducts.

The structure of photoproducts $P_2$, $P_5$ and $P_9$ was deduced from mass spectra and $^1$H NMR spectra recorded on a Bruker AC 400 MHz spectrometer, using solution in hexadeuteroacetone after isolation by HPLC. Data for $P_2$ and $P_5$ are given elsewhere [8]. Actually $P_5$ was transformed into lactone $P_5$ on drying and results of MS and $^1$H NMR analyses correspond to $P_5$ (Fig. 1). For $P_9$:

*m/z*: 188 (monochlorinated), fragments at 170–172, 143–145, 107;

$\delta_{ppm}$ (ref. acetone $D_6$ at 2.04): 10.72 (H, s); 7.96 (H, m); 7.62 (H, m); 2.32 (3H, s), where s stands for singlet and m for multiplet.

Identifications of $P_2$, $P_5$ and $P_7$ were confirmed by using gas chromatography/mass spectrometry coupling (GC–MS). Mass spectrometers were Hewlett-Packard type 5840A and 5985. Capillary column was OPTIMA 5 Machery–Nagel (25 m × 0.25 mm) coated with siloxanes.

## 3. Results

### 3.1. Photocatalytic transformation

In this study, experiments have been carried out on MCPA $4.41 \times 10^{-4}$ M at natural pH (3.45) in the presence of TiO$_2$ ($1 \, g \, l^{-1}$) or in the absence of photocatalyst. Solutions and suspensions were irradiated in the range 300–450 nm. An aliquot was taken every 10 min for analysis. As shown in Fig. 2, only a very slow decrease in MCPA concentration was observed when solutions were irradiated in the absence of TiO$_2$. In contrast, 17% of initial MCPA disappeared when solutions were stirred in the presence of TiO$_2$ and MCPA was rapidly transformed under irradiation. The pH value of solution decreased as the reaction proceeded, due to the formation of HCl. The transformation was almost specific
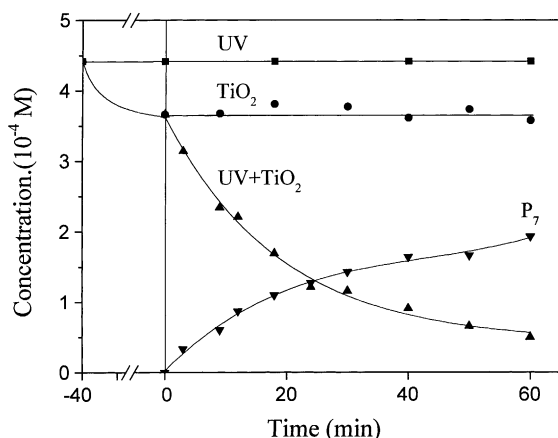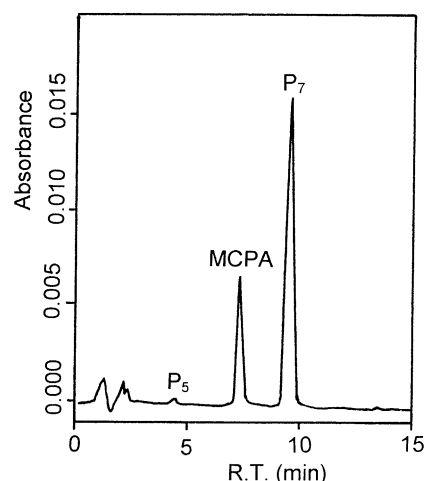
Fig. 3. HPLC chromatogram of photocatalytic transformation of an unbuffered aqueous suspension solution (MCPA $4.41 \times 10^{-4}$ M and TiO$_2$ $1 \, g \, l^{-1}$) irradiated 50 min (conversion 85%) at the room temperature at $\lambda = 290$–450 nm. Flow rate: $1.5 \, ml \, min^{-1}$; detection wavelength: 280 nm; eluent: acetonitrile/water + 0.1% acetic acid; 45:55 v/v.

as shown on the chromatogram (Fig. 3). The major primary product was previously identified as $P_7$ by comparison of the retention time and UV spectrum with those of an authentic sample. Two other minor photoproducts, $P_5$ and $P_8$, were also identified but they did not accumulate in the solution.

### 3.2. Phototransformation on sand

Disappearance of MCPA and formation of photoproducts were monitored by HPLC after extraction with methanol. The transformation was very slow. The yield of photodegradation was 87% after 9 days ($t_{1/2}$ ca. 3 days). The main product was $P_7$ as it is in the photocatalytic transformation. It did not accumulate for two possible reasons: (i) its further photodegradation since it absorbs in the same range than MCPA, and (ii) it transfers to the gas phase since its vapour pressure is not negligible. The highest yield (about 23%) was observed after 3 days. Two other minor products were detected on the HPLC chromatogram (Fig. 4). One of them was identified as $P_8$ by comparison with an authentic sample, the other ($P_5$) was isolated from irradiated acidic solution and identified by MS and $^1$H NMR.

### 3.3. Irradiation in aqueous solution

The UV spectrum of MCPA in the anionic form is given in Fig. 5. The maximum of absorption is located at 279 nm with a molecular extinction coefficient equal to $1550 \, M^{-1} \, cm^{-1}$. The molecular form has a very similar UV spectrum $\lambda_{max} = 277$ nm, $\varepsilon_M = 1395 \, M^{-1} \, cm^{-1}$. It plays a minor role under environmental conditions since the p$K_a$ is 3.07, but its photoreactivity was studied to compare the mechanism involved with that of the anionic form.

Fig. 2. Kinetics of photocatalytic transformation of MCPA ($4.41 \times 10^{-4}$ M) and formation of $P_7$ in the absence and the presence of TiO$_2$ ($1 \, g \, l^{-1}$), irradiated in the range 300–450 nm. Suspensions were equilibrated 40 min before starting irradiation.
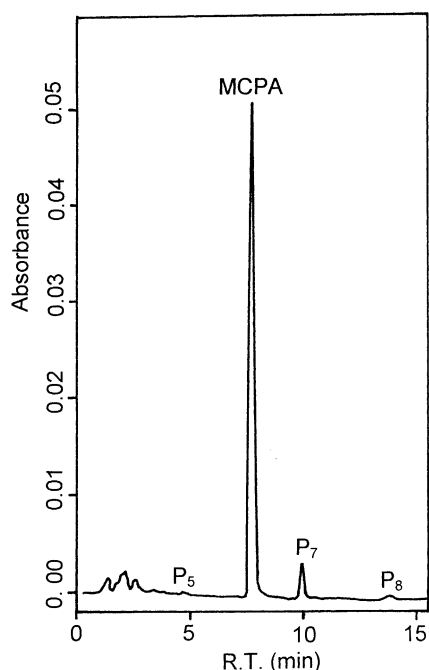
Fig. 4. HPLC chromatogram of the photolysis of MCPA irradiated 1 day, on Fontainebleau sand (4 mg/100 g) (conversion about 22%), between 290 and 365 nm at the room temperature.

### 3.3.1. Irradiation at 254 and 290–310 nm range

Air-saturated and deoxygenated solutions of MCPA $5.25 \times 10^{-4}$ or $5.50 \times 10^{-4}$ M were irradiated at pH 1.5 and 5.9, respectively, in order to compare the photochemical behaviour of the molecular form and anionic form. In both cases, many photoproducts appear on the HPLC chromatogram (Fig. 6). Kinetics presented in Fig. 7a and b show that MCPA is rapidly degraded. Only 20 min is required to reduce the concentration to $1.5 \times 10^{-4}$ M at pH 1.5 and to $0.7 \times 10^{-4}$ M at pH 5.9. MCPA is completely transformed after about 40 min with anionic form and 60 min with molecular form. In both cases, irradiation leads to an increase of absorbance and to the apparition of a weak band between 300 and 400 nm (Fig. 5).
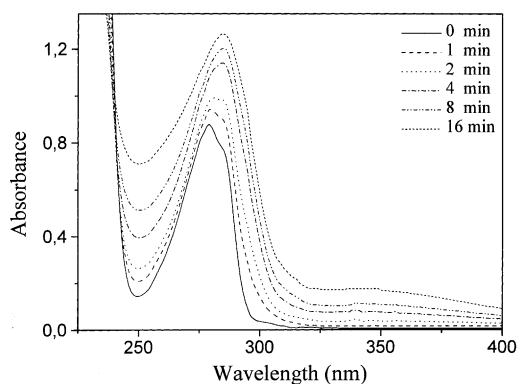


Fig. 5. Evolution of the UV spectrum of an air-saturated solution of MCPA (initial concentration $5.50 \times 10^{-4}$ M, pH 5.9) irradiated at 254 nm.
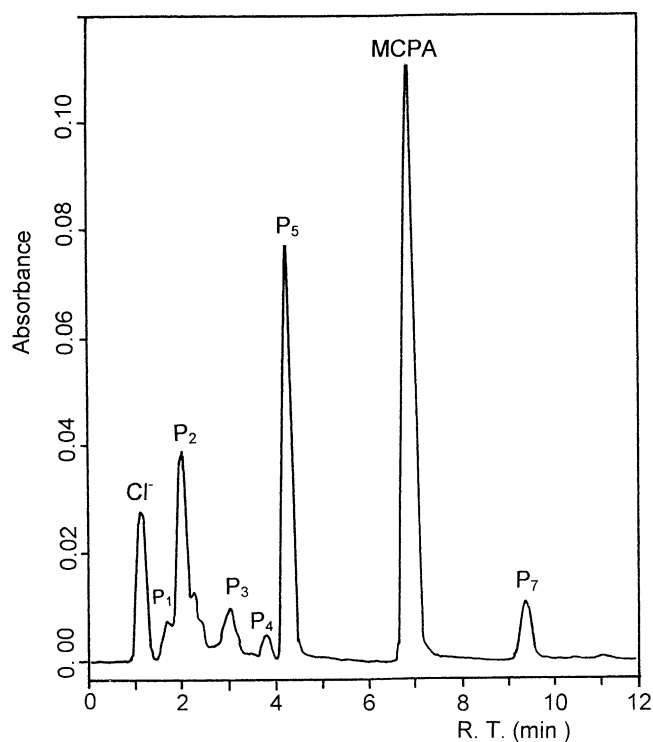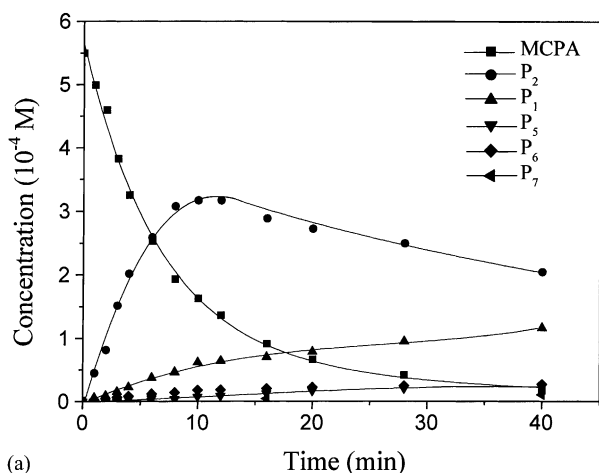


Fig. 6. HPLC chromatogram of an air-saturated solution of MCPA (initial concentration $5.25 \times 10^{-4}$ M, pH 1.5) irradiated 8 min at 254 nm (conversion about 47%.).
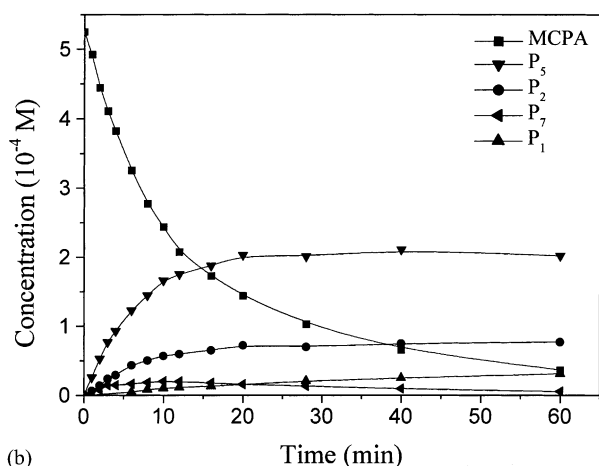
After 8 min irradiation at pH 5.9 (anionic form), $P_2$ accounts for 86% of MCPA transformed. It was identified as 4-hydroxy-2-methylphenoxyacetic acid by MS and $^1$H NMR after isolation from an irradiated solution. The yield of $P_1$ which is the main minor product is ca. 13%. Three other minor products, $P_6$, $P_3$, and $P_5$, were also quantified. They account for only a few percents of the conversion.

The main photoproduct resulting from the irradiation of molecular form is $P_5$ (51% of MCPA converted after 8 min irradiation). It was identified by MS and $^1$H NMR after isolation as the lactone $P_{5'}$, but it may be assumed from its short HPLC retention time that the product has the open configuration in solution (5-chloro-2-hydroxy-3-methylphenylacetic acid). Some other products were also identified and quantified, namely $P_2$ and $P_7$ (21 and 7%, respectively, after 8 min irradiation). $P_1$, $P_3$ and $P_4$ also appear but they do not accumulate much in the solution. $P_1$, $P_3$ and $P_7$ were identified by comparison with commercial compounds. It was experimentally proved that $P_4$ may be obtained by photo-oxidation of $P_5$ isolated and irradiated in aqueous solution. A quinonic structure can be assumed from its UV spectrum and a tentative identification as 6-ethanoic-2-methylbenzoquinone may be proposed.

It is noteworthy that most products formed in the photolysis of the molecular form are also formed in the photolysis of the anionic form, which is the main form of MCPA in
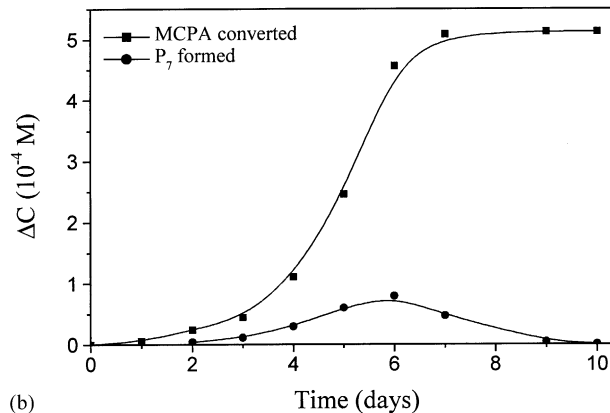
The quantum yield of disappearance of MCPA in air-saturated solutions was measured at 280 nm. This wavelength was chosen because 254 nm is quite different from sunlight and absorption is too low at $\lambda > 290$ nm for a good evaluation of absorbed light. The results obtained were evaluated at 0.59 and 0.35 for anionic and molecular forms, respectively. These values are consistent with those reported for mecoprop (0.75 and 0.34 for the anionic and the neutral form, respectively) [9]. The relatively high quantum yield of transformation of the anionic form can be related to the good formation yield of the hydroxylated product.

### 3.3.2. Irradiation in sunlight and in near-UV light

The wavelength 254 nm is not representative of sunlight but it is sometimes used for the decontamination of polluted waters. In order to compare the photochemical behaviour at short wavelengths and in natural sunlight, MCPA $5.13 \times 10^{-4}$ M solutions were exposed outdoors in April and May. The same pH were used: pH 1.5 and 5.9. It is noteworthy that the neutral form photodegradates faster than the anionic form. The half-lives were evaluated at 5 and 45 days, respectively (Fig. 8), that was unexpected since the quan-



Fig. 7. Kinetics of MCPA disappearance and formation of products in an air-saturated solution irradiated at 254 nm: (a) pH 5.9, initial concentration $5.50 \times 10^{-4}$ M; (b) pH 1.5, initial concentration $5.25 \times 10^{-4}$ M.

natural waters, but proportions are drastically different with both forms. In particular, the formation of $P_2$ is almost specific with the anionic form.

When solutions of MCPA, both forms, are irradiated in the absence of oxygen, the same photoproducts are formed with the same proportions except for $P_1$ which better accumulates in deoxygenated solutions and for quinonic $P_4$ which was only observed in irradiated air-saturated solutions of the molecular form.

Similar results were obtained in air-saturated and deoxygenated solutions irradiated between 290 and 365 nm. The same products are formed, but kinetics is a slower due to the fact that solutions absorb a lower percentage of incident light. Thus, the photochemical reaction of MCPA is affected neither by oxygen nor by the irradiation wavelength between 254 and 365 nm (the absorption is negligible at wavelength longer than 310 nm). These results are in good agreement with those reported by Meunier and Boule [9] with the mecoprop.



Fig. 8. Kinetics of MCPA disappearance and formation of $P_7$ in air-saturated solutions (concentration $5.13 \times 10^{-4}$ M) exposed to sunlight in April and May: (a) anionic form; (b) molecular form.

tum yield of neutral form is lower than that of anionic form. It may be deduced that probably a different mechanism is involved. At both pH, $P_7$ is the main photoproduct and the disappearance is self-accelerated as well as the formation of $P_7$. This self-acceleration is more significant at pH 1.5 than at pH 5.9 as it can be seen in Fig. 8.

To confirm this wavelength effect air-saturated solutions $1.10 \times 10^{-3}$ M were irradiated in near-UV light using "black light" lamp, i.e. lamp with a main emission at 365 nm and minor lines at 313 and 334 nm. Solutions were adjusted at pH 1.5 and 5.9 as previously. The anionic form disappearance was very slow, since only 11% of MCPA was transformed after 24 h. With the molecular form, the phototransformation is more efficient: only 35 h ($t_{1/2}$) was necessary to eliminate 50% of the initial MCPA concentration. In both cases, the phototransformation was clearly self-accelerated as well as the formation of the main photoproduct $P_7$. It accumulates much better than when solutions are irradiated at shorter wavelength. From these results, it may be deduced that irradiation wavelength has a considerable effect on the orientation of the reaction.

### 3.3.3. Influence of quinonic derivatives

In spite of the fact that MCPA does not absorb radiation above 310 nm, its phototransformation was observed in sunlight and in near-UV light irradiations. In both cases, products $P_3$ and $P_4$ were formed. These products absorb between 300 and 400 nm. Compounds with quinonic or carbonyl group such as benzoquinone, $P_3$, acetone, and riboflavine were reported to have photosensitising or inducing properties in the phototransformation of xenobiotic compounds [3,9,13]. In order to confirm the influence of quinonic derivatives in the phototransformation of MCPA irradiated in near-UV light, irradiation were carried out in the presence of the methylbenzoquinone (MBQ), benzoquinone (BQ) or product $P_4$. A solution of $P_4$ was obtained as it follows: an air-saturated solution of product $P_5$ ($3.70 \times 10^{-4}$ M), isolated from an acidic solution of MCPA irradiated at 254 nm, was irradiated between 290 and 365 nm. The formation of $P_4$ was controlled by HPLC. After 2 h irradiation, this solution was added to solution of MCPA ($1.16 \times 10^{-4}$ M, pH 1.5) in the proportion of 25% and irradiated in "black light". The rates of the phototransformation of MCPA and formation of $P_7$ were then compared with another solution of MCPA irradiated in the same conditions but in the absence of $P_4$. As it can be seen in Fig. 9 that the rate of disappearance of MCPA was four times higher in presence of $P_4$ than in its absence after 3 h of irradiation. The influence of $P_4$ was also observed on the formation rate of $P_7$; it was noted that the formation of $P_7$ was about $10^{-5}$ M in presence of $P_4$, while $P_7$ was not formed in the absence of $P_4$ after 3 h of irradiation.

Similar results were obtained with the MBQ and BQ with this difference that the rate of MCPA phototransformation and the formation of the major photoproduct $P_7$ were
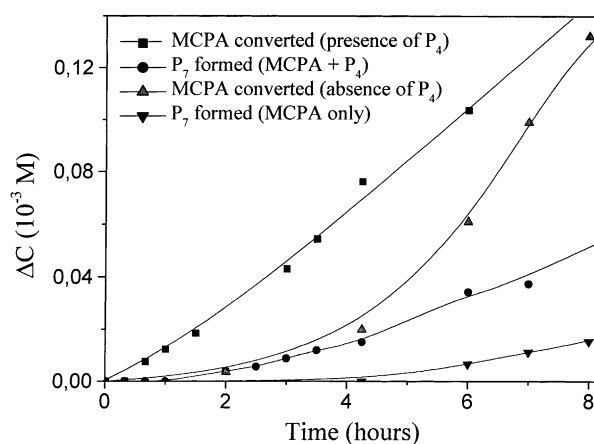


Fig. 9. Kinetics of disappearance of MCPA and formation of product $P_7$ in an air-saturated solution (initial concentration $1.16 \times 10^{-4}$ M, pH 1.5) irradiated at 365 nm in the presence of product $P_4$.

much slower. The formation of $P_7$ was observed in both cases, but it was clearly more efficient in the presence of BQ.

In order to confirm this induced phototransformation, an air-saturated solution of 2,4-D ($10^{-3}$ M), another chlorophenoxyacetic herbicide, was irradiated at 365 nm in the presence of BQ ($5 \times 10^{-4}$ M) and in its absence in the same conditions. In the presence of BQ, the transformation rate of 2,4-D and the formation rate of 2,4-dichlorophenol (2,4-DCP) are 4–5 times higher than in its absence.

From these results, it can be deduced that quinonic compounds induce the phototransformation of MCPA and other chlorophenoxyacetic herbicides (2,4-D and mecoprop, for example). Consequently, a small amount of quinonic compounds in surface waters may significantly accelerate the photodecomposition of these herbicides.

### 3.3.4. Reactions induced by nitrites and iron[III]

Oxidation processes involving $^\bullet$OH radicals, also called advanced oxidation processes (AOPs), are used for the elimination of xenobiotic compounds [14–18]. Since inorganic compounds are often present in natural waters, their influence as photo-inducers has to be taken into account. In this work, we study the photodegradation of MCPA induced by Fe(III) and nitrite ions in aqueous solution since these inorganic species are frequently present in natural waters and may induce the formation of hydroxyl radicals. Actually, nitrite ions are in very low concentration. They mainly result from the photolysis of nitrate ions. They absorb at longer wavelength than nitrate ions and they can be excited selectively in the presence of MCPA. Results are compared with those of direct irradiation.

In spite of the importance in the environmental, nitrate ions were not chosen to study the photo-induced transformation of MCPA, since they absorb only at $\lambda < 340$ nm with a very low molecular absorption coefficient $\varepsilon$. The band of lowest energy has a maximum at 302 nm with
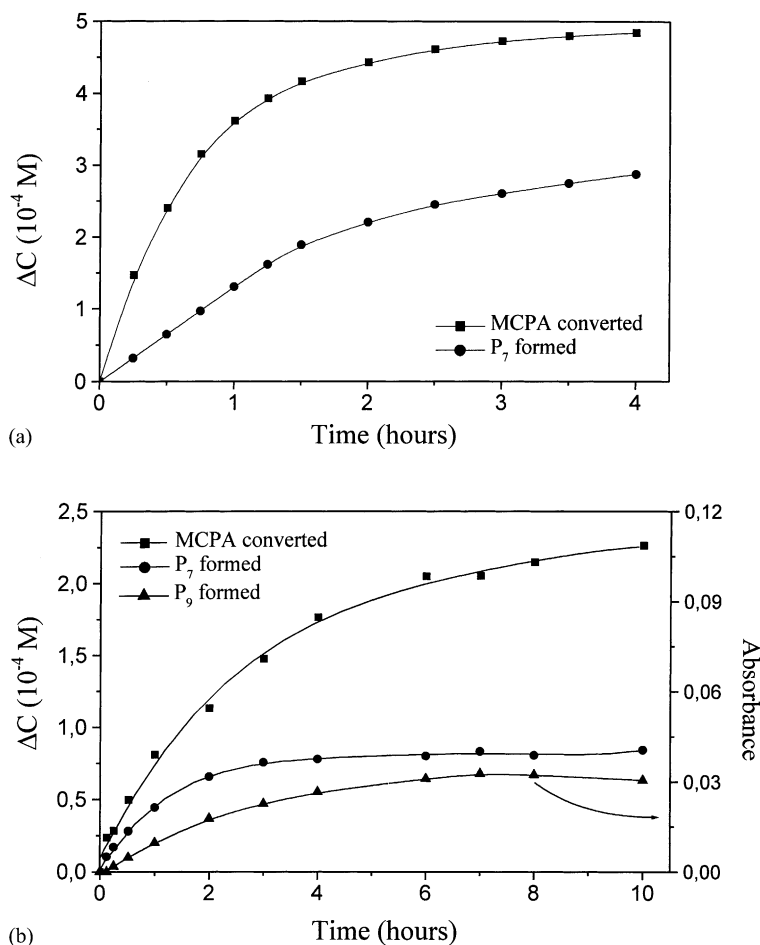
Fig. 10. Phototransformation of MCPA ($5.02 \times 10^{-4}$ M; pH 1.09) induced at 365 nm by excitation of: (a) Fe(III) perchlorate ($10^{-3}$ M), and (b) nitrite ions ($5 \times 10^{-4}$ M).

$\varepsilon = 7.2 \, \text{M}^{-1} \, \text{cm}^{-1}$ and it is not possible to selectively excite nitrate ions in the presence of MCPA. Nitrite ions have the advantage to absorb at longer wavelengths ($\lambda_{\text{max}} = 352$ nm, $\varepsilon_{\text{max}} = 22 \, \text{M}^{-1} \, \text{cm}^{-1}$) and to have higher quantum yield of photolysis [19,20]. In acidic solution, they are protonated into nitrous acid ($pK_a = 3.37$) and it was shown that the latter is a more efficient photo-inducer than the anionic form since its quantum yield of photolysis was evaluated at 0.45 [19]. It is the reason why nitrous acid obtained by acidification of sodium nitrite at pH 1.09 was used to photo-induce the transformation of MCPA. It was previously controlled that no reaction occurs in the absence of light. However, $NO_2^-$ and $HNO_2$ are good ${}^{\bullet}OH$ quenchers [21]:

$${}^{\bullet}OH + NO_2^- \rightarrow OH^- + NO_2{}^{\bullet}$$
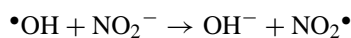
The rate constant range between $9 \times 10^9$ and $1.1 \times 10^{10} \, \text{M}^{-1} \, \text{s}^{-1}$ in basic or acidic medium. Consequently, high concentrations of $NO_2^-$ are unfavourable to the oxidation of organic substances. Concentration $5.02 \times 10^{-4}$ M was chosen.

Fe(III) perchlorate $10^{-3}$ M at pH 1.09 was also used as a photo-inducer. In these conditions, MCPA shows a photodegradation faster with Fe(III) perchlorate than with nitrite ions: it is degraded in 4 h in presence of Fe(III), whereas the half-life ($t_{1/2}$) is more than 10 h in presence of the nitrite ions (Fig. 10).

When Fe(III) is irradiated in the presence of MCPA, the main identified photoproduct is $P_7$ which accumulates in the solution. The chemical yield is initially ca. 25%. The induced photodegradation by nitrite ions is more complex since the oxidation rate is less efficient than with Fe(III) and two products accumulate in the solution, $P_7$ as in the case of Fe(III) and a product of longer retention time $P_9$ (Fig. 11). This product was isolated from an irradiated solution and identified as 4-chloro-2-methyl-6-nitrophenol (Fig. 1). This identification was corroborated by the fact that $P_9$ is formed in the reaction of $P_7$ with concentrated nitric acid. In the same conditions, MCPA do not react with nitric acid. It was also observed that $P_7$ reacts with nitrous acid with formation of $P_9$, but this reaction does not occur with MCPA.
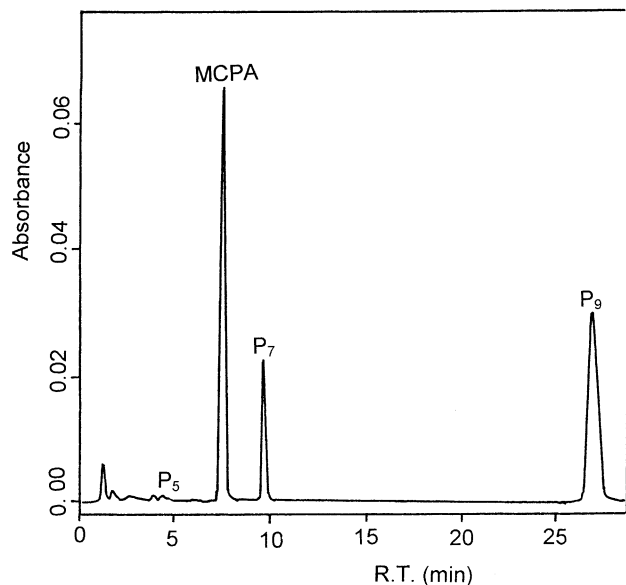
Fig. 11. HPLC chromatogram of a solution of nitrite ions ($5 \times 10^{-4}$ M) and MCPA ($5.02 \times 10^{-4}$ M) irradiated 10 h at 365 nm (conversion about 45 %) (pH 1.5).

## 4. Evaluation of toxicity

Solution $10^{-3}$ M irradiated at pH 3.45 was analysed by HPLC and the toxicity was evaluated by Microtox® test after adjustment of the pH at 7.0.

The disappearance of MCPA and $EC_{50}$ (i.e. concentration which inhibits 50% of the luminescence of the bacterium *V. fischeri*) after 5 min exposure was monitored and reported in Fig. 12. It clearly appears that the irradiation increases the toxicity on this bacterium. It may be due to the formation of the main photoproduct $P_5$, but also to quinonic compounds which directly act on oxygen transfer processes in the bacterium and are highly toxic to *V. fischeri* (the $EC_{50}$ of unsubstituted BQ is in the range 0.08–0.8 $\mu mol\,l^{-1}$ according to Kaiser and Palabrica [22]).



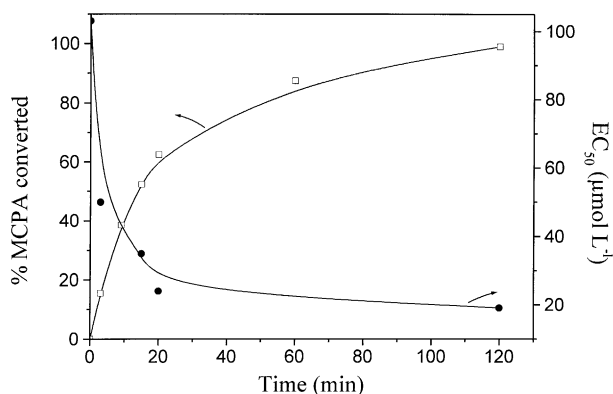Fig. 12. $EC_{50}$ evolution (5 min of exposition to *V. fischeri*) and MCPA conversion in an unbuffered solution ($9.93 \times 10^{-3}$ M) irradiated at 254 nm.

## 5. Discussion and mechanisms

### 5.1. Photocatalysis and reactions photo-induced by Fe(III) and nitrous acid

#### 5.1.1. Photocatalysis

The photocatalytic transformation of MCPA into $P_7$ surely results from an oxidation because the same product is obtained with different oxidizing species, namely Fe(III), quinonic derivatives and •OH produced with nitrite ions. In photocatalysis, two oxidizing species may be involved: hydroxyl radicals and positive holes $h^+$. With chloroaromatic derivatives hydroxyl radicals often lead to the hydroxylation of the ring with or without dechlorination. With MCPA, as well as with other chlorophenoxy compound [4,6], the main product of photocatalytic transformation results from the elimination of the side chain. It is unlikely that this reaction results from the oxidation of $CH_2$ group since the reaction rate of •OH with the aromatic ring is much easier (almost diffusion-controlled) than the oxidation of methyl or methylene group in aliphatic acid [23]. Thus, it may be assumed that the formation of $P_7$ in the photocatalytic transformation of MCPA mainly results from a substitution of the side chain by •OH (Scheme 1a). However, the oxidation of methylene group by hydroxyl radicals and the oxidation of MCPA by positive holes $h^+$ cannot be excluded. They can explain the formation of $P_8$. Positive holes are expected to be involved in a charge transfer process with the anionic form of MCPA adsorbed on $TiO_2$ surface as it was proposed by Yoneyama et al. [24] for acetic acid. $P_8$ does not accumulate since it spontaneously react with water leading to $P_7$ (Scheme 1b).

#### 5.1.2. Reactions photo-induced by Fe(III)

The excitation of Fe(III) salts is known to induced photo-oxidations. Two pathways may be assumed:

1. Oxidation involving the intermediate formation of •OH radicals [25] (Scheme 2a). It is probably the main pathway.
2. Oxidative decarboxylation involving the formation of a complex between Fe(III) and the acidic function. By analogy with the mechanism proposed for the photo-oxidation of nitrilotriacetic acid (NTA) [26], the sequence given in Scheme 2b may be proposed. It is probably a minor pathway since MCPA has not so good complexing properties as NTA.

#### 5.1.3. Reactions photo-induced by $HNO_2$

The excitation of nitrous acid also leads to the formation of •OH radicals, but $HNO_2$ is a good •OH quencher and when the concentration of $HNO_2$ is higher than the concentration of substrate •OH radicals mainly lead to the formation of nitrogen oxides that regenerate nitrous oxide or may lead to nitrations or nitrosations:

$$HNO_2 \xrightarrow{h\nu} NO^\bullet + {}^\bullet OH$$

$$HNO_2 + {}^\bullet OH \rightarrow NO_2^\bullet + H_2O$$
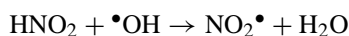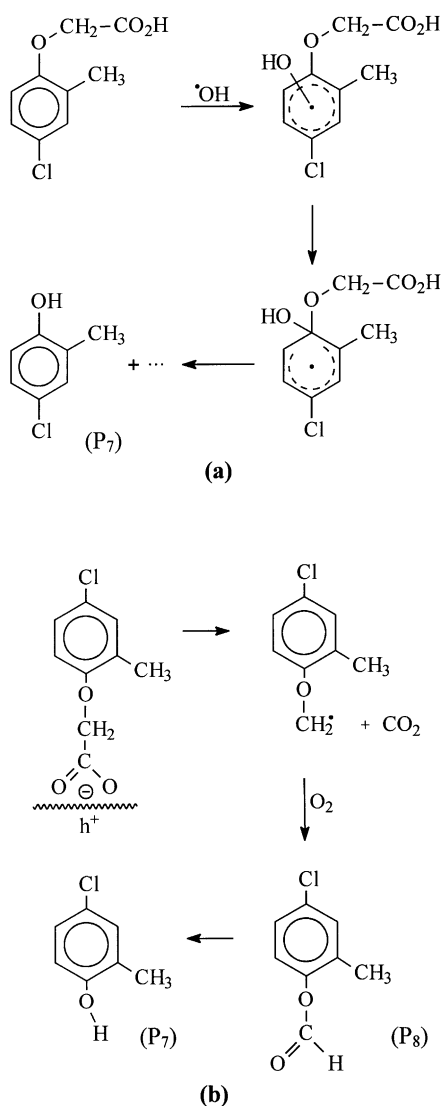
Scheme 1. Proposed pathway of photocatalytic transformation of MCPA over $TiO_2$ suspension: (a) substitution of the side chain; (b) decarboxylation and oxidation of methylene group.

The formation of $P_7$, which is unfavoured by increasing nitrite concentration, is attributed to the substitution of the side chain by hydroxyl radical as in photocatalytic reaction. $P_9$ does not result from a dark nitration of MCPA by nitrogen oxides since the yield also decreases with increasing nitrite concentration. It might be due either to the reaction of $NO_2^\bullet$ with the intermediate $^\bullet OH$ radical complex or to the nitration of $P_7$ by nitrogen oxides. The study of this reaction is presently in progress.

## 5.2. Direct photolysis

### 5.2.1. Aqueous solutions irradiated between 254 and 310 nm

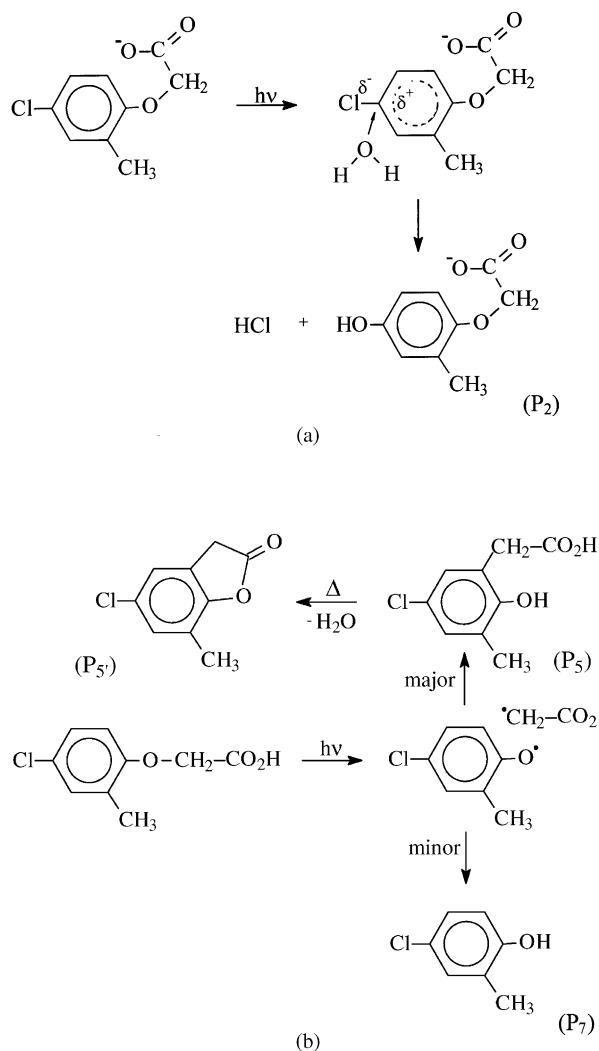Different mechanisms are involved in direct phototransformation of MCPA in aqueous solution. The reaction
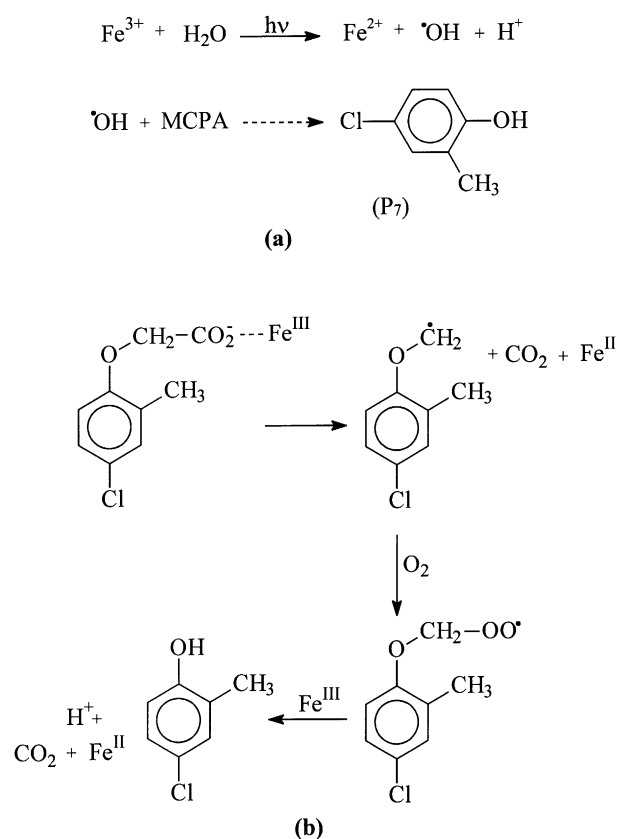


Scheme 2. Proposed reaction mechanisms of induced phototransformation of MCPA by Fe(III).

depends on the pH of solution, but it is influenced neither by oxygen nor by the irradiation wavelength between 254 and 310 nm.

With the anionic form, the formation of photoproduct $P_2$ is almost specific in air-saturated and in deoxygenated solution. This reaction was previously reported for several halogenoaromatic derivatives [27–29]. It cannot be explained by a radical mechanism. It results from a heterolytic mechanism of photohydrolysis involving the polarisation of C–Cl bond in the excited state. This reaction is easier with the anionic form since the presence of ion charge favours the polarisation of the ring. Nevertheless, this reaction also occurs with the neutral form, but with a lower efficiency. Products $P_1$ and $P_3$ are formed in a secondary steps. The minor formation of $P_6$ is tentatively explained by the reduction of the intermediate formed after release of chloride ion. The mechanism of transformation of the anionic form is presented in Scheme 3a.

The neutral form mainly leads to $P_5$ which results from a radical rearrangement. This reaction was previously reported for mecoprop [9], dichlorprop and 2-naphtoxyacetic acid [30]. The minor formation of $P_7$ is explained by in cage oxido-reduction of intermediate radicals. The mechanism is presented in Scheme 3b.
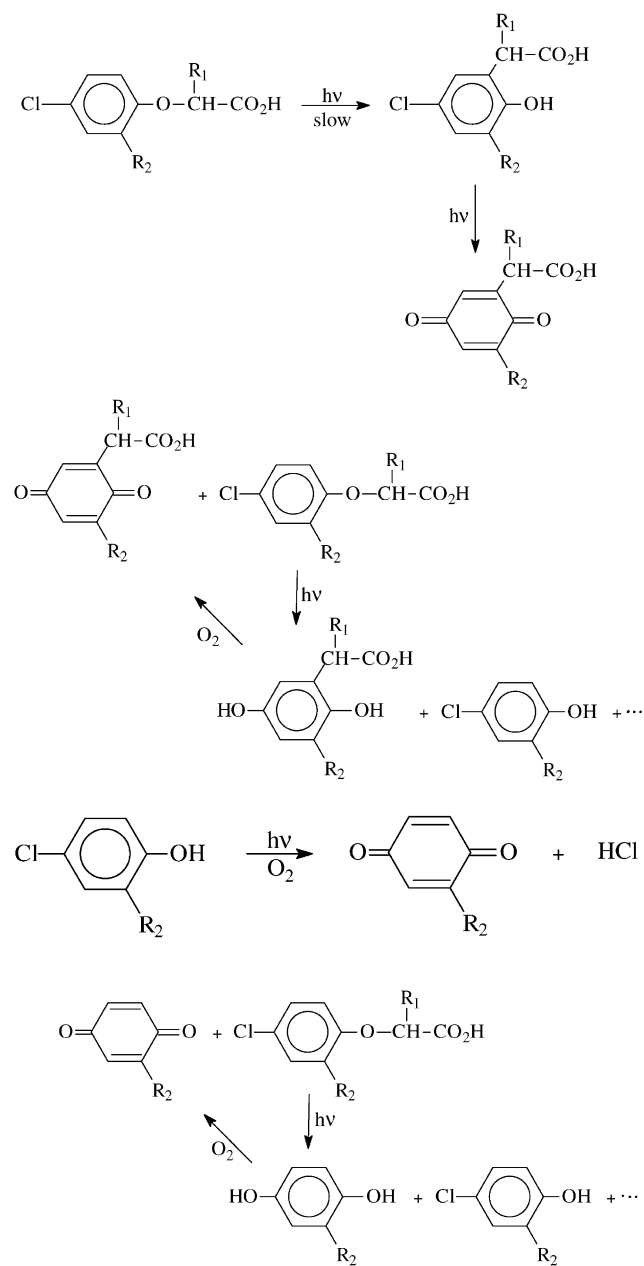
transformation of MCPA induced by excitation of Fe(III) salts or nitrous acid show that $P_7$ may result from an oxidation.

The mechanism of MCPA photolysis at wavelengths longer than 320 nm in aqueous solution is then clarified. With the molecular form (pH 1.5) product $P_5$, directly ob-

Scheme 3. Proposed mechanism of direct photolysis of MCPA in aqueous solution: (a) anionic form; (b) neutral form.

### 5.2.2. Irradiation at 365 nm or in sunlight

MCPA does not absorb at wavelengths longer than 310 nm and it was experimentally proved that the formation of $P_7$ may be induced by quinonic derivatives and particularly by product $P_4$. It is consistent with the fact that the phototransformation in near-UV light or in sunlight is self-accelerated and easier with the neutral form than with the anionic form of MCPA. The first step of the mechanism is a slow formation of quinonic derivatives ($P_3$ or $P_4$) followed by a photo-induced reaction. Two possibilities may be considered: sensitisation by energy transfer and redox reaction. The first mechanism is to be eliminated since the energy of the triplet level ($E_T$) of substituted BQ is certainly much lower than that of MCPA. According to Murov et al. [31], the $E_T$ value of BQ and 4-chloroanisole are 224 and 327 kJ mol$^{-1}$, respectively ($E_T$ of MCPA is unknown, but 4-chloroanisole have a similar chromophore and consequently a similar UV spectrum). On the other hand, the results obtained in the

| MCPA | $R_1 = CH_3$ | $R_2 = H$ |
| 2,4-D | $R_1 = H$ | $R_2 = Cl$ |
| mecoprop | $R_1 = CH_3$ | $R_2 = CH_3$ |

Scheme 4. Mechanism of phototransformation of chlorophenoxyacetic acids in near-UV light.

tained from irradiation, is easily oxidised into a quinonic compound ($P_4$) which oxidises MCPA into $P_7$. $P_5$ is transformed into a hydroquinonic derivative which is reoxidised into a quinone. Consequently, quinones contribute to the accumulation of $P_7$. The formation of MBQ can also participate in the induced reaction (Scheme 4).

With the anionic form, the formation of $P_7$ is assumed to be sensitised by MBQ, but the reaction is not so efficient. In environmental conditions, photo-induced processes play a major role in the transformation of MCPA and other chlorophenoxyacetic acids such as mecoprop and 2,4-D.

### 5.2.3. Irradiation on sand

The formation of $P_7$ as the main photoproduct is assumed to result from the decarboxylation and the oxidation of methylene group. $P_8$, which is detected as a minor product, is most probably formed as an intermediate in the phototransformation of MCPA into $P_7$.

## 6. Conclusions

Direct photolysis of MCPA on silica and the phototransformation in the presence of $TiO_2$ are almost specific. The major photoproduct is 4-chloro-2-methylphenol ($P_7$). In aqueous solution, the phototransformation of MCPA is not significantly affected by oxygen nor by the irradiation wavelength between 254 and 310 nm, but it is highly depending on the pH. At pH 5.9, the anionic form is almost quantitatively photohydrolysed with a high quantum yield (0.59). In very acidic solution pH 1.5, the main pathway is a photochemical rearrangement. In both cases, some minor photoproducts are formed: $P_1$, quinonic derivatives, $P_6$ and $P_7$. When solutions are exposed to near-UV light, the latter is the major product. This wavelength effect is due to the photoreaction induced by quinonic derivatives formed in aerated solution.

Fe(III) salts and nitrous acid induce the transformation of MCPA and lead to the formation of $P_7$ as the major photoproduct, as it is the case in the photocatalytic transformation on $TiO_2$, but with nitrous acid nitration of the ring also occurs. The irradiation of solution at 254 nm increases the toxicity to the bacterium *V. fischeri*.

## Acknowledgements

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