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Photolysis of chlorpyrifos-methyl, chlorpyrifos-methyl oxon, and 3,5,6-trichloro-2-pyridinol

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Abstract

The photodegradation of chlorpyrifos-methyl (**1**), and two of its photodegradation products, chlorpyrifos-methyl oxon (**2**), and 3,5,6-trichloro-2-pyridinol (**3**) was studied using low pressure Hg lamps irradiating at 254 nm either in pure acetonitrile (ACN) or in 10% ACN/H_2O. Experiments conducted in pure ACN allowed us to identify the photoproducts in the photolysis of **1**, **2**, and **3** both, in air saturated samples and in the absence of oxygen as analyzed by gas chromatography–mass spectrometry (GC-MS), high resolution mass spectrometry (HRMS), and phosphorus-31 nuclear magnetic resonance (^{31}P NMR).

Since **2** and **3** are products in the photodegradation of **1**, their degradations in 10% ACN/H_2O were independently measured, and it was determined that **1** and **2** degrade at comparable rates. Instead, **3** does not interfere in the measurement since it degrades much faster, and their products do not absorb in the region of **1**.

Our results indicate that short wave photolysis could become a plausible detoxification mechanism.

KEYWORDS

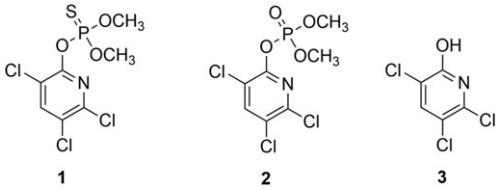
3,5,6-trichloro-2-pyridinol, chlorpyrifos-methyl, chlorpyrifos-methyl oxon, photodegradation

1 | INTRODUCTION

Agrochemicals are intensely used as part of current integrated pest management in order to protect crops and vegetables.[1] International statistics indicate that pests take off 42% of the total potential production of foodstuff even with the use of agrochemicals; nevertheless, without them, the loss would rise to 70%.[2] On the other hand, when pesticides are applied in the field, they can contaminate the soil, water, and atmosphere producing an important environmental impact.[3]

Organophosphorus pesticides are extensively used in different applications and have replaced the use of organochlorine pesticides since the second half of last century because they are less persistent in the environment.[4] The toxicity of organophosphorus insecticides results from the inhibition of acetylcholinesterase (AChE). Thiophosphate insecticides are transformed to the corresponding phosphate in the target organism by the action of cytochrome P450 resulting in a toxic bioactivation.[4] Because of the environmental impact of agrochemicals and their global use, it is necessary to find efficient ways to minimize their negative impacts. The ideal result would be the complete mineralization, obtaining nontoxic simple compounds. Conventional methodologies as adsorption of pesticides, biodegradation, ozonation, and chlorination were used in natural environmental media, although the results were rather discouraging. Methods based on the utilization of light radiation as the source of energy were used as an alternative to conventional methods. They are based on the use of natural solar light or an external ultraviolet (UV) light, like Xe or Hg lamps. These methods include direct and indirect photolysis as well as other more complex treatments like photolysis combined oxidants, photo-Fenton processes, photo-catalysis, photosensitized oxidation, and photoelectrocatalytic oxidation.[5]

The most used insecticide in Argentina is chlorpyrifos (*O,*O-diethyl *O*-(3,5,6-trichloro-2-pyridinil)-phosphorothioate),[6] an organophosphorus compound classified as moderately hazardous (class II) by the World Health Organization.[7] Chlorpyrifos-methyl (*O,O*-dimethyl *O*-(3,5,6-trichloro-2-pyridinil)-phosphorothioate), **1** (Scheme 1), with similar molecular structure but higher water solubility and vapor pressure than chlorpyrifos,[8] is one of the most widely used insecticides in the world.[3] It is classified as class III, slightly hazardous,[7] and registered in Argentina for use in the control of insects on stored grains and complementary treatments of storage and transport facilities.[9]



SCHEME 1 Structures of chlorpyrifos-methyl (**1**), chlorpyrifos-methyl oxon (**2**), and 3,5,6-trichloro-2-pyridinol (**3**)

In an attempt to find an efficient method of degrading organophosphorus insecticides, we have previously studied the reactivity of **1** with hydroxyl and perhydroxyl ions as well as the effect of cyclodextrins on these reactions.[10] Besides, the hydrolysis of chlorpyrifos-methyl oxon was studied through the use of high performance liquid chromatography (HPLC)-MS/MS methods, and its degradation products were also determined.[11] We are presenting now our results on the photodegradation of **1** and the two direct products Chlorpyrifos-methyl oxon **2** and 3,5,6-trichloro-2-pyridinol **3** (Scheme 1), using low pressure Hg lamps as light source for a detoxification process.

Previous reports on the photodegradation of **1** are limited. Photodegradation of **1** as well as of chlorpyrifos in virgin olive oil using UV lamps[12,13] emitting at 200 to 280 nm, studies on the atmospheric degradation,[3,14] and quantum yield measurements in aqueous solution at 254 nm for **1** and chlorpyrifos of 0.013 and 0.016, respectively, have been reported.[15] The latter results came after the work by Dilling et al[16] who had measured the quantum yield for chlorpyrifos and for **3** at 313 nm in aqueous solutions.

Kamiya had studied the effect of humic substances on the photodegradation of chlorpyrifos[17] and the effect of cyclodextrins[18] and metal ions[19] on that reaction. Ukpebor et al[20] studied the degradation of chlorpyrifos exposed to direct sunlight in aqueous solutions at different pHs. Finally, also degradation of chlorpyrifos has been recently studied by photoreactive TiO_2 nanoparticles.[21] None of these papers investigated the photoproducts. Bavcon Kralj et al[22] found chlorpyrifos oxon and **3** as photodegradation products when an aqueous-ethanol solution of chlorpyrifos was irradiated with a 125 W xenon parabolic lamp. The same photoproducts, among others, were found by irradiation at 254 nm of a solution of chlorpyrifos in methanol.[23] There are also some reports on the photocatalytic degradation of chlorpyrifos.[21,24,25] Shemer et al[26] had measured the degradation rate and quantum yield of **3** in aqueous solution without analyzing the products. Feng et al[27] had investigated **3** by photolytic and microbial degradation at 254 nm in phosphate buffer (pH 7). They had proposed a mechanism of degradation of **3** that ends up in ammonium, carbon dioxide, and water after having formed different aromatic products. In addition, Devi et al[24] proposed that **3**, formed in the photocatalytic degradation of

chlorpyrifos, ends in ammonium hydroxide, carbon dioxide, and water. In contrast, Žabar et al[28] found by irradiation at 315 nm in an aqueous solution of **3**, different products such as a substituted pyrrol structure with carboxylic groups and 5,6-dichloro-2,3-dihydroxypyridine.

The results that we present here include the identification of photoproducts of the photolysis of **1**, **2**, and **3**, as well as the lifetimes associated whit their photodegradation in aqueous solution.

2 | MATERIALS AND METHODS

2.1 | Materials

Chlorpyrifos-methyl PESTANAL (**1**) (FLUKA) and chlorpyrifos-methyl oxon (**2**) (Supelco) were characterized by ^{1}H, ^{13}C, and phosphorus-31 nuclear magnetic resonance (^{31}P NMR), ultraviolet-visible (UV-Vis) spectrophotometry, gas chromatography–mass spectrometry (GC-MS) and high resolution mass spectrometry (HRMS). 3,5,6-Trichloro-2-pyridinol (**3**) (Sigma-Aldrich) was characterized by ^{1}H and ^{13}C NMR, UV-Vis spectrophotometry, GC-MS and HRMS. Acetonitrile (ACN) (Baker, HPLC grade) and chemicals were used as received. Water was purified with a Millipore Milli-Q apparatus.

2.2 | Irradiation methods

Irradiation was conducted using four low pressure mercury lamps (Philips G6T5, 6W) emitting at 254 nm, placed inside a metal box. The temperature inside the box when all the lamps were on was 36°C. A 1-cm path length quartz cuvette or a round-bottom quartz flask (250 mL) sealed with Teflon caps were used for the different experiments.

For the kinetics measurements, solutions of **1**, **2**, and **3** (2×10^{-5} M) in 10% ACN/H_2O were poured separately in the 1-cm quartz cuvette and irradiated at 254 nm. The relative changes of absorbance vs time data were fitted with a simple exponential function.

For product analysis, air equilibrated solutions of **1** (51.7×10^{-3} M), **2** (3.7×10^{-3} M), or **3** (52.4×10^{-3} M) were poured separately in the 1-cm quartz cuvette and irradiated at 254 nm using pure ACN because of solubility issues. In the case of **1** and **2**, the irradiation time was 235 minutes while only 30 minutes were needed for **3**. In the absence of oxygen (N_2 bubbled solutions), solutions of **1** (53.8×10^{-3} M) or **2** (15.0×10^{3} M) in ACN were irradiated at 254 nm for 240 minutes. The resultant solutions were analyzed by GC-MS and HRMS. Additionally, rather dilute solutions of **1** (1.04×10^{-3} M) and **2** (7.47×10^{-4} M) in a round-bottom quartz flask of 250 mL were irradiated, and samples were taken at different times to be analyzed by ^{31}P NMR. See Data S1 for more details.

Although we were not able to achieve the complete isolation of the photoproducts via preparative chromatography, the analysis of the different fractions obtained, either by NMR, GC-MS, or HRMS allowed us to arrive at conclusive identifications without mishaps.

2.3 | Experimental analyses

UV-Vis spectra were recorded on a Multispec-1800 Shimadzu using a quartz cell of 1-cm path length. Kinetics experiments were followed with the same apparatus. ^{1}H, ^{13}C, and ^{31}P NMR spectra were obtained in $CDCl_3$ at 400, 101, and 121 MHz, respectively, with a Bruker Avance II 400 spectrometer. The identification of the photoproducts was conducted with GC-MS analyses performed on a Varian Saturn 2200 GC/MS equipment. The column was a nonpolar phase HP5-MS from Agilent (95% dimethylpolysiloxane-5% phenyl), 30 m long, and with an internal diameter of 0.25 mm. The elution gas was Helium with a flux of 1 mL min^{-1}. The injector and ion trap temperatures were 250°C and 200°C, respectively, the oven heating ramp was 15°C min^{-1} from 80°C up to 280°C, and the interface temperature was 250°C. The pressure in the MS instrument was 10^{-5} Torr, precluding ion-molecule reactions from taking place, and MS recordings were made in the electron ionization mode (EI) at 70 eV with an emission current of 10 μA and a maximum ionization time of 25 000 μs. The mass interval swept ranged from 40 to 650 m/z. HRMS were recorded with a Bruker, Micro TOF Q II equipment, operated with an ESI source in (positive/negative) mode, with use of nitrogen as nebulizing and drying gas and sodium formate (10×10^{-3} M) for internal calibration.

3 | RESULTS AND DISCUSSION

3.1 | Photoproducts analyses

Natural environmental degradation, as well as bulk detoxification processes generally occur in water bodies. In this medium, the solubility of the studied compounds is rather low. For this reason, in laboratory assays, pure ACN was used. In order to identify the photoproducts, **1** and **2** were photolized both, in air saturated samples and in the absence of oxygen. In the case of **3**, it was studied only in air saturated samples. The crude of the reactions were analyzed by GC-MS, HRMS, and ^{31}P NMR. From the results obtained, that we describe below, we

propose the photodegradation pathways depicted in Scheme 2.

3.1.1 | Analysis in air saturated samples

The analytical techniques used allowed us to get an almost complete scan of the products of degradation. Through ^{31}P NMR, the photolysis of **1** yielded **2** and dimethyl phosphate (**4**), the latter also detected in the degradation of **2**. Using HRMS, we found compounds **2**, **3**, **4**, *O*,*O*-dimethyl phosphoro thioate (**5**), *O*,*O*-dimethyl *O*-(dichloro-2-pyridinil)-phosphoro thioate (**6**) and *O*,*O*-dimethyl *O*-(dichloro-2-pyridinil)-phosphate (**7**) in the photolysis of **1**; compounds **3**, **4**, **7**, and *O*,*O*-dimethyl *O*-(chloro-2-pyridinil)-phosphate (**8**) in the photolysis of **2**; but no degradation products were observed for compound **3** by this technique, which could be taken as an indication that mineralization could be occurring. Should this happen, the products would not be detected because the mass interval of the spectrometer starts above 50 m/z.

The analysis of the products by GC-MS showed interesting features since we were able to detect the presence of the three possible isomers of *O*,*O*-dimethyl *O*-(chloro-2-pyridinil)-phosphoro thioate (**9**), the three possible isomers of **8**, and two of the three possible isomers of dichloro-2-pyridinol (**10**), in photolyzed solutions of **1**, **2**, and **3**, respectively. Besides, in the case of **1**, the presence of **3** and **6** was also observed, and in the case of **2**, we could identify **3** and **7**.

3.1.2 | Analysis in the absence of oxygen

By HRMS we found compounds **2**, **3**, and **6** in the photolysis of **1**, and compounds **3** and **7** in the photolysis of **2**.

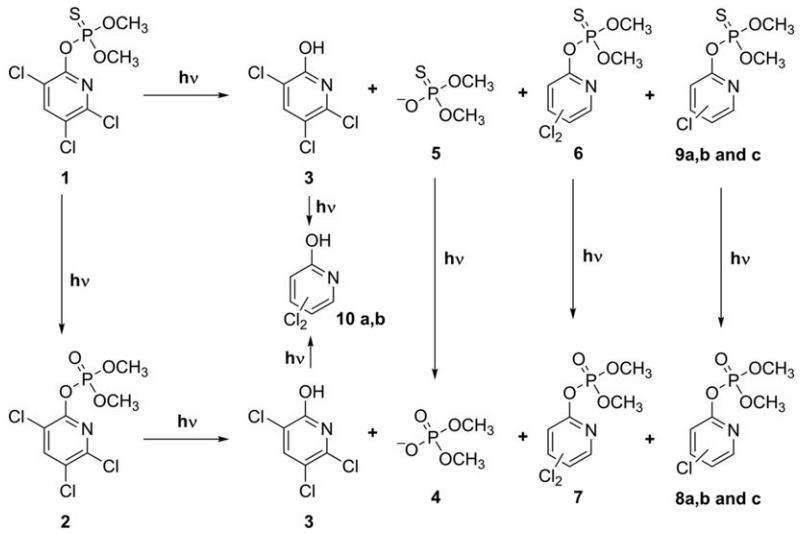
GC-MS showed the presence of **2**, **6**, and one of the three possible isomers of **9** coming from degradation of **1**; in the case of **2**, we observed the presence of **7** and two of the three possible isomers of **8**.

Given these results, it seems that there is no special involvement of dissolved molecular oxygen in the mechanism of degradation, that is, there seems to be no participation of reactive oxygen species (ROS) in the mechanism of degradation. There is still, of course, oxygen available for the P=S to P=O interchange reaction that takes place when no dissolved oxygen is present. This supply is believed to come from the water content of the solvent. It is nevertheless worth to be known that no special reactions are to be expected because of the ubiquitous presence of oxygen in the environment.

3.2 | Irradiation with UV light

In order to assess whether the reaction observed only depends on the absorption of light, one experiment was run in the dark at 36°C, the temperature inside the box when the lamps are irradiating. No reaction was observed by UV-Vis spectrometry up to 900 minutes indicating that there are no thermal contributions.

A solution of **1** (2×10^{-5} M) in 10% ACN/H_2O in the quartz cuvette of 1 cm path length placed inside the metal box was irradiated at 254 nm for a total of 350 minutes. The UV-Vis spectrum of the solution was taken before irradiation and at different irradiation times. The insecticide has two absorption bands at 229 and 289 nm. Upon irradiation, both bands decreased indicating its consumption (Figure 1A). When a rather concentrated solution of **1** (9.5×10^{-5} M) in pure ACN was irradiated during 100 minutes, the two absorption bands disappeared (attributed to the consumption of **1**), and one new band



SCHEME 2 Proposed photodegradation pathways of **1**

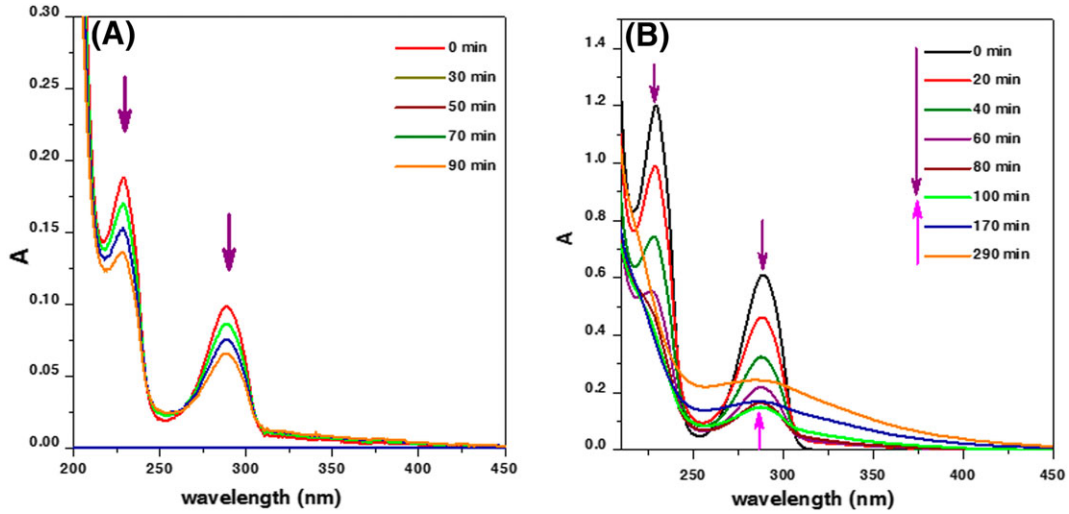


FIGURE 1 Spectra of **1** at different irradiation times. A, in 10% acetonitrile (ACN)/H_2O, $[\mathbf{1}]_0 = 2 \times 10^{-5}$ M, optical path = 1 cm; B, in acetonitrile (ACN), $[\mathbf{1}]_0 = 9.5 \times 10^{-5}$ M, optical path = 5 cm

was observed at 288 nm that later grew with continued irradiation for 290 minutes (attributed to the formation of **2**) (Figure 1B). For these reasons, in order to calculate the decay for the photodegradation of **1** in 10% ACN/H_2O, only the first points were taken into account, and the lifetimes we arrived at were 2.59 and 2.27 hours for 229 and 289 nm, respectively.

Nevertheless, as chlorpyrifos-methyl oxon (**2**) and 3,5,6-trichloro-2-pyridinol (**3**) were found among the products, and their UV absorption bands lie in close proximity to the bands of the parent molecule, we performed independent degradation studies of these compounds under the same conditions of the photodegradation of **1**.

The UV-Vis spectrum of **2** (2×10^{-5} M) in 10% ACN/H_2O shows two absorption bands at 227 and 288 nm; these bands decreased with time as the solution was irradiated up to 1240 minutes without noticeable new bands formed (Figure 2). The lifetimes calculated at the two maxima were around 7.2 hours.

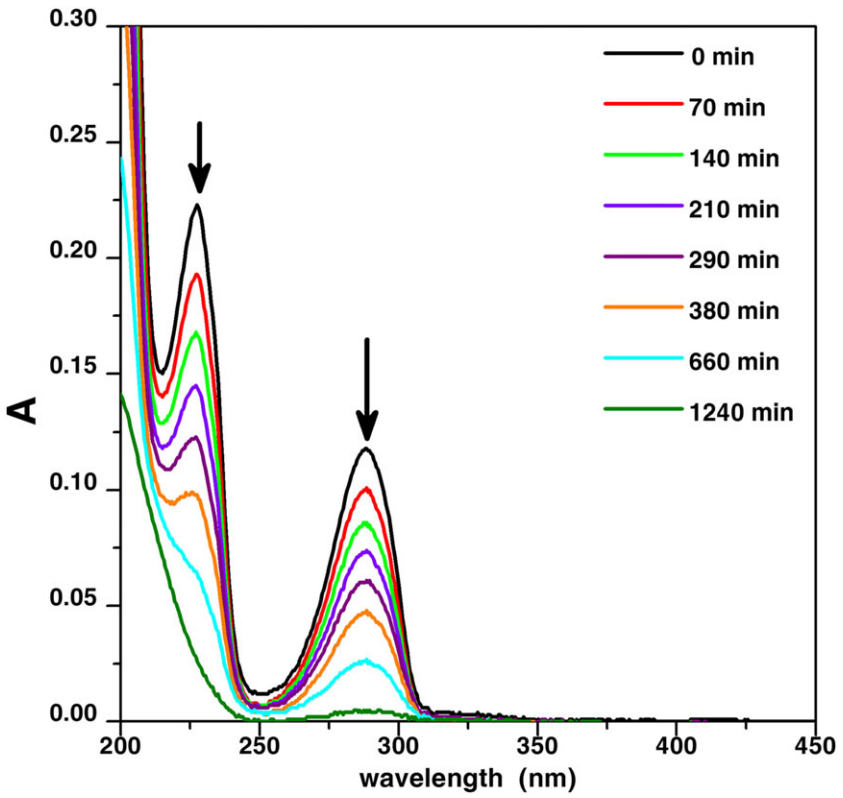


FIGURE 2 Spectra of **2** in 10% acetonitrile (ACN) at different irradiation times. $[\mathbf{2}]_0 = 2 \times 10^{-5}$ M. Optical path = 1 cm

The UV-Vis spectrum of **3** (2×10^{-5} M) in 10% ACN/H_2O shows two absorption bands at 239 and 320 nm. After 1 minute of irradiation, these two bands disappeared, and two new bands were observed at 262 and 348 nm that later decreased with continued irradiation for 16 minutes (Figure 3). From the decay in absorbance at these wavelengths, we could estimate a residence time of 5.4 minutes for the band at 262 nm that could be attributed to **10** because when exchanging a chlorine atom by a hydrogen atom in one of the three positions of the aromatic ring of **3**, the maximum wavelength should change. The residence time for the other compound resulted of the order of 1.7 minutes.

Andre et al[29] studied the photolysis of pyridine in aqueous solution with a germicidal lamp. They observed the disappearance of the band corresponding to pyridine (λ_{max} 250 nm) and the formation of the compound 5-amino-2,4-pentadienal (λ_{max} 360 nm) over time. The band observed at 348 nm in the photolysis of **3** (Figure 3) shows the same profile as that of 5-amino-2,4-pentadienal and resembles the characteristic n-π^* enamine aldehyde transition indicative of the opening of the pyridine ring.[29] The difference of the maxima of absorption might be because of the fact that our compound has substituents in the ring of the pyridine. The disappearance of this band might indicate the existence of a route to the mineralization of **3**, whose products would not be seen through chromatographic techniques as experimentally proved.

An analysis of the values obtained shows that the degradation of **3** does not complicate the measurement of the degradation rate of **1** since it is much faster, and the products do not absorb in the region of **1**. In the case of **2**, the degradation rate is of the order (actually it is slightly slower) than that of the parent molecule, and thus it could contaminate the value if no care is taken when determining the degradation rate.

3.3 | Photodegradation pathway

The experimental evidence led us to propose the photodegradation pathway shown in Scheme 2, which is also consistent with previous results in the literature. Compounds **2**, **3**, **4**, and **5** were found in the atmospheric degradation[3] of **1**. Among the products of the photodegradation of chlorpyrifos, Slotkin et al[23] found **3**, the diethylated analogous of **2**, **4**, and **5** and 3,6-dichloro-2-[pyridinyl-*O*, *O*-ethyl] thiophosphate, an analogous of **6**. Devi et al[24] proposed the formation of chlorpyrifos-oxon and **3** by photocatalytic degradation of chlorpyrifos; they also proposed the formation of **10** from **3** in the reaction medium, and that the final products of the decomposition of **3** were ammonium hydroxide,

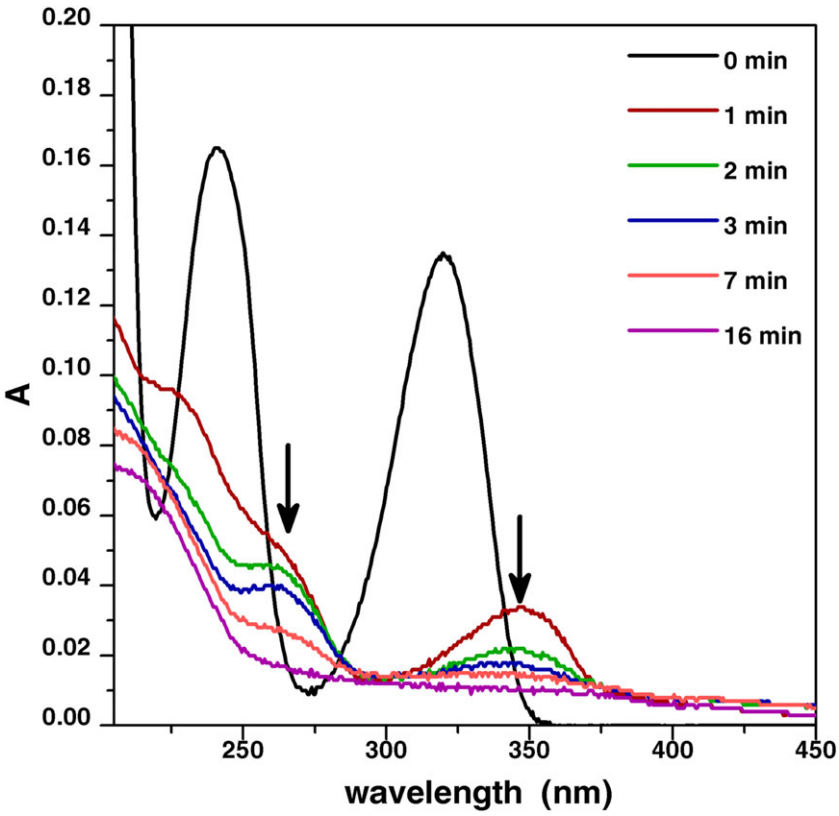


FIGURE 3 Spectra of **3** in 10% acetonitrile (ACN) at different irradiation times. $[3]_0 = 2 \times 10^{-5}$ M. Optical path = 1 cm

TABLE 1 Parameters regulated to some species of animals according to the Pesticide Properties Data Base[30]

Ecotoxicology	1	2	3
Mammals (rat)—acute oral LD_{50} (mg kg^{-1})	5000[a] (low)	869[b] (moderate)	3129[a] (low)
Birds (*Colinus virginianus*)—acute LD_{50} (mg kg^{-1})	923[a] (moderate)	34.75[c] (high)	>2000[a] (low)
Fish (*Oncorhynchus mykiss*)—acute 96 hour LC_{50} (mg L^{-1})	0.41[a] (moderate)	>0.0024[d] (high)	>12.6[a] (moderate)
Aquatic invertebrates (*Daphnia magna*)—acute 48 hour EC_{50} (mg L^{-1})	0.0006[a] (high)	-	10.4[a] (moderate)

[a]EU Regulatory & Evaluation Data as published by EC, EFSA (RAR, DAR & Conclusion dossiers), EMA (eg) EU Annex III PIC DGD (For example, see http://ec.europa.eu/sanco_pesticides/public/index.cfm or EFSA Scientific Publications https://www.efsa.europa.eu/en/publications).

[b]ChemID Online Databases (See http://chem.sis.nlm.nih.gov/chemidplus/) /IPCS INCHEM (See http://www.inchem.org/).

[c]Peer Reviewed Scientific Publications.

[d]U.S. EPA ECOTOX Database (see http://cfpub.epa.gov/ecotox/) /U.S. EPA Pesticide Fate Database (See http://cfpub.epa.gov/pfate/home.cfm) /Miscellaneous WHO documents.

carbon dioxide, and water, that is, complete mineralization. Meanwhile, Farner Budarz et al[21] assumed that chlorpyrifos-oxon and **3** are produced in the primary photodissociation of chlorpyrifos and studied only the kinetics of disappearance.

Although, we could not make a total quantification of the products, by following the photodegradation of **1** by ^{31}P NMR, we could observe that after 416 minutes of irradiation, the most abundant P containing product was compound **4** (Figure S18); therefore, if around 10% of the reaction goes through the direct formation of **2**, as roughly quantified from ^{31}P NMR, it seems necessary to have also a direct sulfur-oxygen interchange for the 90% coming from **5** to form compound **4**, a reaction path that remains open even in the absence of dissolved oxygen. Although the most abundant product indicates the breaking of a C-O bond, dechlorination reactions are also important and take place both from the reactant itself as well as from the pyridine ring as seen by the products formed.

Compounds **1**, **2**, and **3** are described in the Pesticide Data Base of the University of Hertfordshire, and some of their parameters for mammals, fish, birds, and aquatic invertebrates are listed[30] in Table 1. It is observed that the toxicity of **1** is low in mammals, moderate in birds and fish, and high in aquatic invertebrates. For **2** is moderate in mammals and high in birds and fish; and for **3** is low in mammals and birds and moderate in fish and aquatic invertebrates.

A coarse comparison about these different species let us to conclude that a detoxification process seems to pose no risk to the environment.

4 | CONCLUSIONS

The photodegradation at 254 nm of **1**, **2**, and **3** was studied. The kinetics of the degradation in 10% ACN/H_2O presented an average value of 2.38 and 7.2 hours for **1** and **2**, respectively. Experiments conducted in pure ACN allowed us to identify essentially all the photoproducts. These include **2**, **3**, the phosphate **4**, and thiophosphate **5** and compounds where one or two chlorine atoms are removed from **1**, **2**, or **3**.

Regarding compound **4**, we could not see the formation of phosphoric acid as postulated in the paper by Borras et al.[3] In that publication, they did not provide detailed mechanisms, so we believe that in our system, there will probably be an available channel that provides the hydrogen interchange more easily since we have an ACN solution.

Compounds **3**, **4**, and **5** are products of the metabolism of chlorpyrifos as well as of its environmental degradation. They are used as biomarkers of exposure to the insecticide by measuring its concentration in urine. In experiments conducted by Timchalk et al[31] where some rats were administered equal molar doses of chlorpyrifos, **3**, **4**, or **5**, observable cholinergic effects were noted only in those animals treated with chlorpyrifos. This can be taken as an indication that **4** and **5** are less toxic than chlorpyrifos. We could identify compound **10** as the only product after irradiation of **3**; thus, considering the results of Devi et al,[24] we think that mineralization to ammonium hydroxide, carbon dioxide, and water could occur.

Under the light of these results, we believe that, irradiation with UV light might be a useful method for detoxification of chlorpyrifos-Me solutions.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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