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Light induced transformations of selected organophosphorus pesticides on titanium dioxide: Pathways and by-products evaluation using LC–MS technique

P. Calza*, C. Massolino, E. Pelizzetti

Dipartimento di Chimica Analitica, Università di Torino, via P. Giuria 5, 10125 Torino, Italy

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ABSTRACT

Three organophosphorus pesticides (azinphos methyl, phosphamidon and methidathion) were degraded in aqueous solution using titanium dioxide as photocatalyst. The investigation had involved the identification of the intermediate compounds and the assessment of the mineralization. HPLC/MS was used to follow the disapperance of the initial pesticide and the formation of intermediate products and allowed the identification of some important photodegradation by-products. A tentative transformation mechanism has been proposed for the selected pesticides. As common pathways, in all cases hydroxylation, bihydroxylation and detachment of the organophosphorus moiety occurs. In addition, azinphos methyl and methidation had shown to give oxidation of P=S to P=O. Some additional pathways were however recognized. Phosphamidon is subjected to dechlorination, while methidathion is subjected to the ring opening of the triazolidine moiety. Azinphos methyl gives the N–C bond cleavage and its transformation proceeds through six concomitant pathways with the formation of 17 intermediate compounds.

Complete mineralization was achieved in all cases. While for azinphos methyl the mineralization process occurs within 3 h of irradiation, for phosphamidon up to 16 h are required. Measurement of phosphate, sulphate, chloride, nitrate and ammonium ions gave valuable information about how this process was achieved.

1. Introduction

The persistence of pesticide residues in agricultural products destined to human consumption is one of the most important problems connected to their use. Intoxications attributed to pesticides have been estimated to be as high as 3 million cases of acute and severe poisoning annually, with as many or more unreported cases and with some 220,000 deaths [1,2]. Organophosphorus pesticides (OP) constitute one of the most important groups of insecticides applied in agricultural areas for pest control. They have been used as an alternative to organochlorine compounds for pest control. However, they are considered as extremely toxic compounds acting on acetylcholinesterase activity [3]. Because of their widespread use and high toxicity, they have been included in several priority lists of pollutants and also in different groundwater monitoring programs, as a consequence of their frequent detection in environmental waters. Analytical chemistry of pesticides and their transformation studies in general, and LC/MS in particular, have become a fundamental tool for environmental, toxicological, food and biological studies [4,5].

On the other side, the employment of an appropriate technique for water decontamination is required. The use of AOPs for water treatment has been studied extensively [6,7]. Recently, researches have been focused on heterogeneous photocatalysis. The key advantage of photocatalysis lies in its destructive ability: it can be carried out under ambient conditions and has shown to be effective in the abatement of most organochloride compounds [8,9], as well as many pesticides [10]. The basic principles of photocatalysis have been extensively discussed elsewhere [11–13]. Among semiconductor solids, TiO_2 is widely used because it is non-toxic, inexpensive, as well as a biologically and chemically inert photocatalyst. Light induces the formation of reactive species on the surface of the photocatalyst (h^+, e^-, surface-adsorbed •OH), which results in the degradation and in most cases in the complete mineralization of a large variety of organic compounds. Such compounds are generally completely mineralized into non-toxic products like carbon dioxide, inorganic ions and water.

It is of great concern not only the achievement of pollutant abatement, but also the identification of the intermediate compounds formed during contaminant degradation, since during the photocatalytic treatment it was reported the formation of intermediates with similar, or even higher, toxicity than the parent compound [14]. Chemical oxidation processes produce numerous intermediates, due to the non-selectivity of the •OH radicals, and

* Corresponding author. Tel.: +39 0116707626; fax: +39 0116707615.
E-mail address: paola.calza@unito.it (P. Calza).

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several by-products, generally at quite low concentrations, whose kinetics of formation (and decomposition) need to be determined. Recently a great interest has developed about pesticide-related oxidative stress, leading to generation of free radicals and alteration in antioxidants, oxygen free radicals, the scavenging enzyme system, and lipid peroxidation [15].

The purpose of this study was to follow the fate of three selected organophosphorus pesticides, phosphamidon, methidathion and azinphos methyl, upon irradiation using TiO_2 as photocatalyst, through the identification of the transformation compounds and the assessment of total mineralization during the process. Phosphamidon (2-chloro-2-diethylcarbamoyl-1-methylvinyldimethyl phosphate) is a systemic organophosphorus compound with a broad spectrum of activity, which is mainly used to control sucking insects, stemborers in rice [16]. Methidathion (*S*-2,3-dihydro-5-methoxy-2-oxo-1,3,4-thiadiazol-3-ylmethyl-*O*,*O*-dimethyl-phosphorodithioate) is a non-systemic insecticide and acaricide, highly toxic [17], used to control a variety of insects and mites in many crops such as fruit, vegetables and sunflower. Azinphos methyl (*O*,*O*-dimethyl *S*-[(4-oxo-1,2,3-benzotriazin-3(4H)-yl)methyl] phosphorodithioate is one of the most toxic organophosphate insecticides and is highly persistent. It is a non-systemic insecticide used as a foliar application against leaf-feeding insects [18]. Phosphamidon and methidathion have not received much attention and only few works are available on its degradation [19–21], while no studies exist on their transformation products. Conversely, for azinphos methyl some studies on its phototransformation mechanism upon homogeneous photolysis have been recently reported [22,23], while under heterogeneous photocatalysis treatment it has only been investigated the removal efficiency, but not the identification of by-products [24].

2. Experimental

2.1. Material and reagents

Experiments were carried out using TiO_2 Degussa P25 as the photocatalyst. Azinphos methyl, methidathion and phosphamidon were purchased from Dr. Ehrenstorfer. HPLC grade water was obtained from MilliQ System Academic (Waters, Millipore). Acetonitrile HPLC grade (BDH) was filtered through a 0.45 μm filter before use. Formic acid reagent grade was purchased from Fluka Chemie (Sigma).

2.2. Irradiation procedures

The irradiation experiments were carried out in Pyrex glass cells, filled with 5 mL of a suspension containing the pesticide (15 mg L^{-1}) and TiO_2 (200 mg L^{-1}). The illumination was performed using a 1500 W Xenon lamp (CO.FO.MEGRA, Milan, Italy) equipped with a 340 nm cut-off filter simulating AM1 solar light. Temperature reached during the irradiation was 38 °C. The entire content of each cell was filtered through a 0.45 μm filter and then analysed by the appropriate technique.

2.3. Analytical procedures

2.3.1. Liquid chromatography

Pesticides and their transformation products were analysed by HPLC/MS. The chromatographic separations followed by a MS analyzer were run on a C18 column Lichrosphere, 250 mm × 4.0 mm. Injection volume was 20 μL and flow rate 1000 μL/min. Gradient mobile phase composition was adopted: 80/20 to 20/80 in 10 min formic acid 0.05% in water/acetonitrile.

A Surveyor mass spectrometer (Thermo Finnigan) equipped with an atmospheric pressure interface and an ESI ion source was used. The LC column effluent was delivered into the ion source using nitrogen as sheath and auxiliary gas. The cone voltage was set at 50 V value. The heated capillary value was maintained at 300 °C. The acquisition method used was previously optimized in the tuning sections for the parent compound (capillary, magnetic lenses and collimating octapoles voltages) in order to achieve the maximum of sensitivity. The tuning parameters adopted for ESI source have been the following: capillary voltage 2.5 V, RF Lens Bios 0.3 V, ion energy 1 V. Mass spectra were collected in full scan positive mode in the range of 60–700 *m*/*z*.

The chromatographic analysis for benzene derivatives were followed by a UV–vis detector (Merck Hitachi L-4200) and were accomplished by an HPLC using a Rheodyne injector, a RP C18 column (Lichrochart, Merck, 12.5 cm × 0.4 cm, 5 μm packing) and a gradient made by two high pressure pumps (Merck Hitachi L-6200 and L-6000 pumps).

2.3.2. Ion chromatography

A Dionex instrument was employed, equipped with a conductimeter detector. Determination of ammonium ions was achieved using a CS12A column and 25 mM metansulphonic acid as eluent, at a flow rate of 1 mL/min. In these conditions the retention time of ammonium was 5.02 min. The anions were analysed using a AS9HC anionic column and K_2CO_3 9 mM at a flow rate of 1 mL/min. In these experimental conditions the retention time of chloride, nitrate, phosphate, sulphate were 7.10, 13.98, 19.60, and 22.60 min, respectively. The measurement of anions have been performed on the solution basified at pH 12 with NaOH.

2.3.3. Total organic carbon analyzer

Total organic carbon (TOC) was measured on filtered suspensions using a Shimadzu TOC-5000 analyzer (catalytic oxidation on Pt at 680 °C). Calibration was achieved by injecting standards of potassium phthalate.

3. Result and discussion

3.1. Photoinduced transformation of phosphamidon

Fig. 1 shows the disappearance of phosphamidon in the diverse experimental conditions as a function of the irradiation time. The experiments were realized in ESI positive mode, which appears to

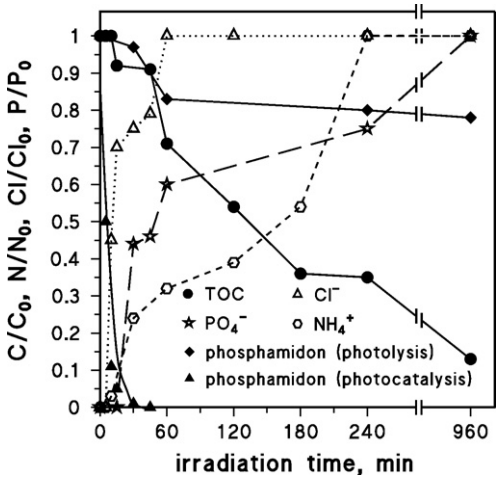


Fig. 1. Degradation of phosphamidon 15 mg L^{-1} on TiO_2 200 mg L^{-1}; disappearance of the initial compound, TOC profile and evolution of phosphate, chloride and ammonium ions as a function of the irradiation time.

Table 1
Identified transformation products in phosphamidon photocatalytic degradation: $[M+H]^+$, maxima amounts and the time for their formation/disappearance

$[M+H]^+$	Name	R_t (min)	Maximum amount (area) and t_{max} (min)	Time (min) of disappearance
300	2-Chloro-2-diethylcarbamoyl-1-methylvinyldimethyl phosphate	14.57	0 (128.330.212)	30
316	2-Chloro-2-ethylhydroxyethyl carbamoyl-1-methylvinyldimethyl phosphate	12.19	5 (4.931.908)	30
332	2-Chloro-2-dihydroxyethyl carbamoyl-1-methylvinyldimethyl phosphate	11.90	5 (595.168)	10
282	2-Hydroxy-2-diethylcarbamoyl-1-methylvinyldimethyl phosphate	13.10	5 (47.381)	10
192	Crotonamide, 2-chloro-*N*,*N*-diethyl-3-hydroxy-	11.29	10 (987.471)	15

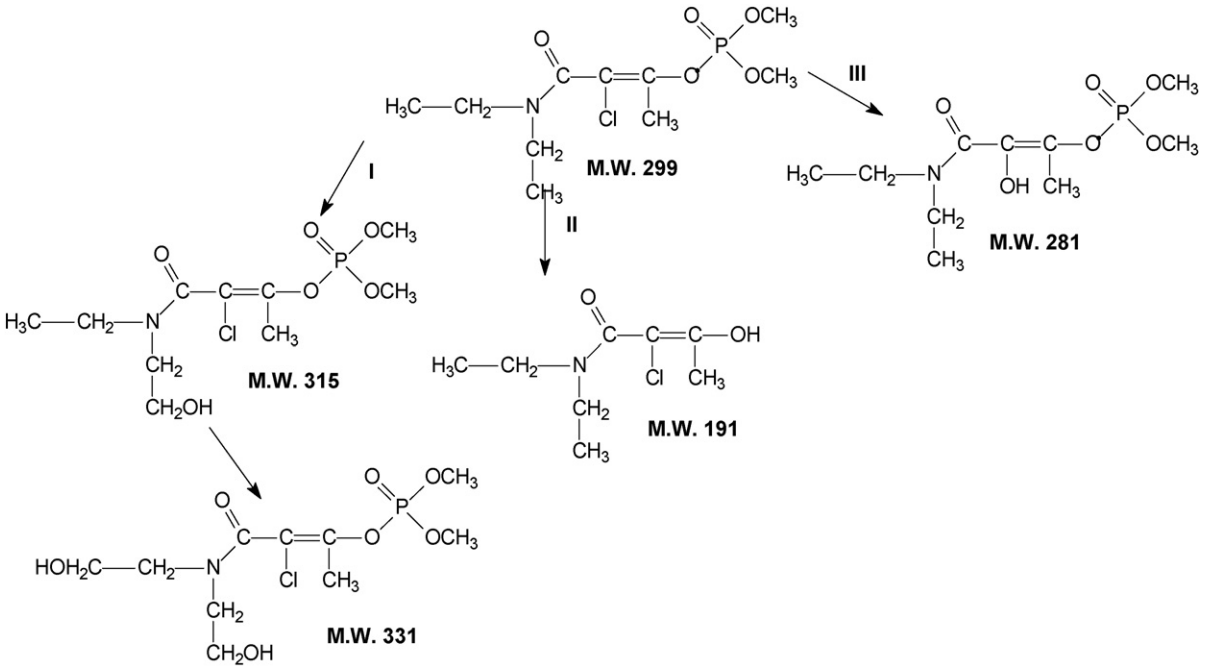
be more sensitive and suitable for the parent compound as well as for the majority of photogenerated products. Dark experiments and direct photolysis experiments were preliminarily run, with the aim of assessing if direct photolysis or thermal decomposition may contribute to the pesticide decomposition. Phosphamidon had shown to be stable and only 20% was degraded over the time interval considered (16 h). Conversely, the disappearance of phosphamidon under heterogeneous photocatalysis easily occurs and followed a pseudo first-order rate law. The calculated half-time was 5 min, while the complete degradation of the initial compound occurred within 30 min.

Along with the phosphamidon degradation, four intermediate compounds were formed and are shown in Table 1. The chromatographic retention times of the observed peaks are consistent with the behaviour of molecules more hydrophilic than the initial compound. Even if a quantification of the intermediates cannot be done, the predominant transformation pathway should be tentatively defined on the basis of their relative abundance. The most abundant intermediate was the species at $[M+H]^+$ 316. A difference of 16 amu respect to the parent compound suggests the formation of the hydroxyl derivative. The analysis of the corresponding MS spectrum did not provide useful information to assign the OH group position. However, on the basis of the nature of the substituent, the ethyl group seems to be the part of the molecule more reactive toward the attack by OH radical. So, the structure reported in Scheme 1 can be tentatively proposed. A species at $[M+H]^+$ 332 was also formed and was identified as the bihydroxylated phosphamidon; the same considerations as above can be done.

Two species at lower molecular weight were also formed. The first one at $[M+H]^+$ 282 was consistent with the detachment of the chlorine atom, as assessed by the absence in its MS spectrum of the typical chlorine isotopic pattern and was recognized as 2-hydroxy-2-diethylcarbamoyl-1-methylvinyldimethyl phosphate. For instance, the compound at $[M+H]^+$ 192 should be formed through the detachment of the organophosphorus moiety. This hypothesis found support in the contemporaneous formation of phosphate ions.

The identified compounds can be formed through the occurrence of three concomitant transformation pathway, as summarized in Scheme 1. The first one leads to the formation of the mono and bihydroxylated derivatives. A second pathway leads to the detachment of the organophosphorus moiety, with the formation of the species at $[M+H]^+$ 192. A third pathway proceeds through the formation of dechlorinated product with $[M+H]^+$ 282.

All the identified intermediates were easily degraded and until 30 min of irradiation they were completely disappeared (see Table 1). Conversely, mineralization was a longer process and up to 16 h were required to obtain the complete organic carbon abatement. Inorganic ions showed different formation rates. Chloride ions were easily formed and the stoichiometric release is obtained until 1 h of irradiation. At that time, only 30% of the nitrogen was released as ammonium ions and the stoichiometric concentration was achieved until 4 h of irradiation. The formation of ammonium ions was in agreement with the fate followed by alkylamines, that are known to be photoconverted predominantly to ammonium ions [25]. Therefore, the remaining organic carbon does no more



Scheme 1. Transformation pathways of phosphamidon during the photocatalytic degradation over TiO_2 suspensions.

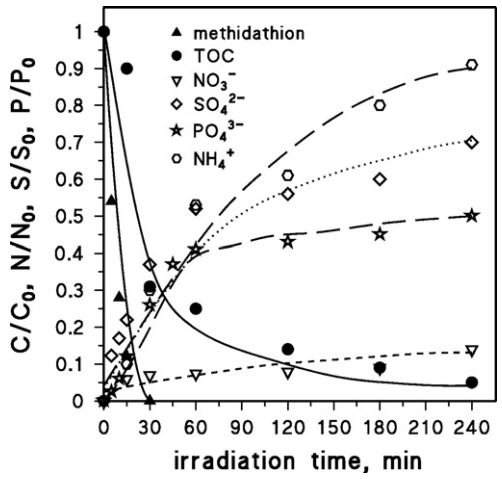


Fig. 2. Degradation of methidathion 15 mg L^{-1} on TiO_2 200 mg L^{-1}; disappearance of the initial compound, TOC profile and evolution of sulphate, phosphate, ammonium and nitrate ions as a function of the irradiation time.

contain the nitrogen and should be linked to the formation of small-oxidized molecules, i.e. crotonic or oxalic acid. On the other side, phosphate ions were initially formed at smaller amount. The phosphate anion is a target ion in the organophosphorus degradation, since phosphorous toxic compounds, i.e. trimethyl phosphate esters [22], could be formed. The phosphate stoichiometric amount was reached after 16 h of irradiation. Phosphate ions at actual pH (6.2) is known to remain adsorbed on the TiO_2 surface, therefore the measurement were performed on the basified solution (pH 12).

3.2. Photoinduced transformation of methidathion

Preliminary experiments were carried out to evaluate the extent of hydrolysis and photolysis processes on the methidathion transformation (data not shown). Results obtained by the adsorption in the dark, as well as direct photolysis for a time period of 4 h, proved that the above abiotic processes were scarcely responsible for the fast transformations observed when the solution was irradiated in the presence of titanium dioxide (see Fig. 2). These results were in agreement with the data available on methidathion hydrolysis [26] and photolysis [27]. Abiotic hydrolysis, that involves the cleavage of the S–P bond, occurs only at alkaline pH, while at this pH value (6.3) does not take place. In the presence of TiO_2 the disapperance of the initial compound followed a pseudo-first order law decay. The calculated half-life for methidathion from the fitting curve was 10 min and it was completely degraded within 30 min of irradiation.

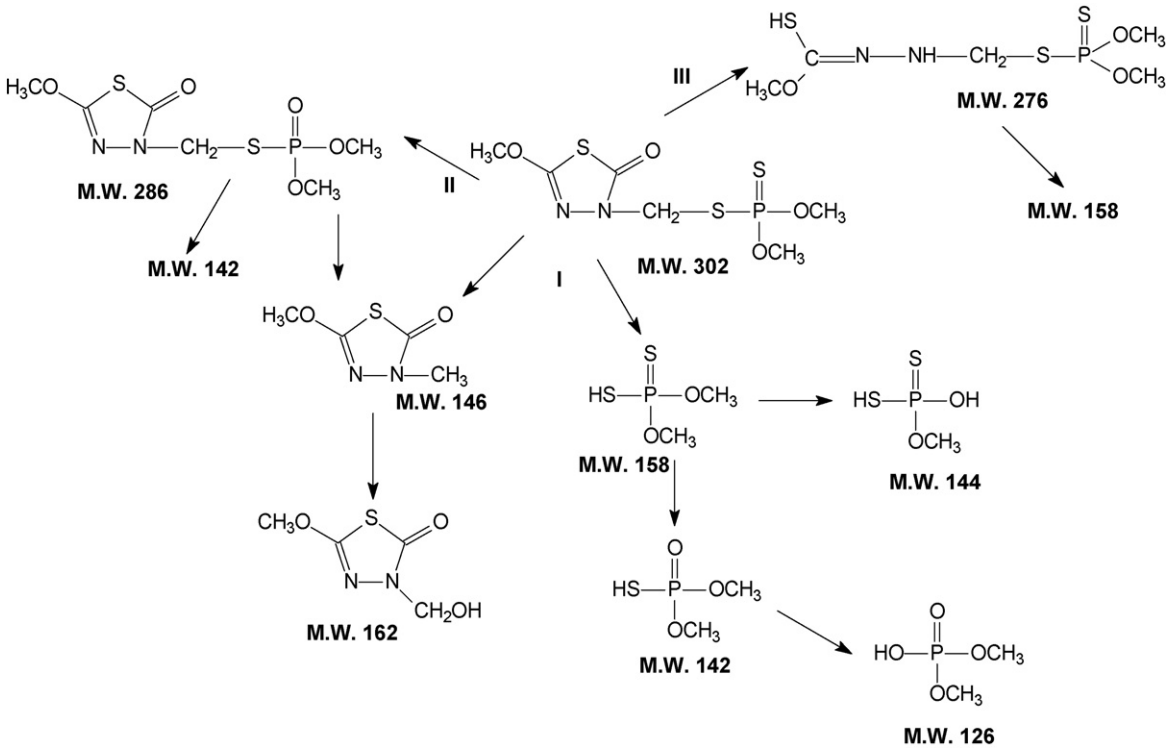
Several intermediates were formed along with the insecticide degradation and are summarized in Table 2 and Scheme 2. Their formation involved the cleavage of the C–S or P–S bond. The former leads to the contemporaneous formation of the species at $[M+H]^+$ 147, recognized as 1,3,4-thiadiazol-2(3H)-one, 5-methoxy-3-methyl and at $[M+H]^+$ 159, *O*,*O*-dimethylhydrogen dithiophosphate (see pathway I). The proposed structures found support in their concomitant presence, signal of the C–S bond cleavage, and on their MS spectra, that show a modified number of sulphur atoms (two and one sulphur atoms for the species at $[M+H]^+$ 159 and 147, respectively). The latter brings about the formation of the species at $[M+H]^+$ 287. Its MS spectrum shows the typical isotopic distribution of two sulphur atoms. The oxidation of P=S to P=O is also confirmed by its MS/MS spectrum, which eliminates CO (*m*/*z* 259) and SH-$PO(OCH_3)_2$ (*m*/*z* 145), instead of the peculiar loss of methidathion (product ion at *m*/*z* 145, that eliminates $SHPS(OCH_3)_2$). It was then recognized as *S*-2,3-dihydro-5-methoxy-2-oxo-1,3,4-thiadiazol-3-ylmethyl-*O*,*O*-dimethyl-phosphorothioate (see pathway II). The formation of this intermediate compound was also documented in soil [28]. The formation of oxon derivatives is of concern, since the oxon analogous of organophosphorus pesticides were found to be activated forms with a considerably stronger inhibition of cholinesterase activity than that exhibited by the parent compound [29]. Through a further transformation, the formation of 3,4-thiadiazol-2(3H)-one, 5-methoxy-3-methyl could be realized.

A parallel transformation involves the breakage of the thiadiazolic ring, with the formation of a species at $[M+H]^+$ 277, that still contains three sulphur atom (see pathway III). The elimination of a molecule of CH_3OCH_2SH in its MS/MS spectrum supports the hypothesis of the ring cleavage. Analogously to pathway I, the molecule could then break down with the release of *O*,*O*-dimethylhydrogen dithiophosphate.

Afterward, the transformation pathway I proceeds through the hydroxylation/demethylation with the formation on one side of the species at $[M+H]^+$ 163, that contains only one sulphur atom 1,3,4-thiadiazol-2(3H)-one, 3-(hydroxymethyl)-5-methoxy and on the other side the species at $[M+H]^+$ 143 and 145, recognized as *O*,*S*-dimethyl phosphorothioate and *S*,*S*-methyl hydroxy phosphorodithioate. The species at $[M+H]^+$ 143 should be formed from two independent pathways: (1) the transformation of the species at *m*/*z* 286 through the cleavage of C–S bond; (2) the transformation of the species at $[M+H]^+$ 159, through the oxidation of the P=S to P=O. Subsequently, its degradation proceeds with the formation of the species at $[M+H]^+$ 127, recognized as dimethyl phosphate. The absence of sulphur atoms typical isotopic distribution in its MS spectrum proves the proposed structure. The delayed times for the formation of these species (maxima concentration reached after 1 h of irradiation) confirms that they were further transformation products.

Table 2
Identified transformation products in methidathion photocatalytic degradation: $[M+H]^+$, fragments coming from MS^2 spectra, maxima amounts and the time for their formation/disappearance

$[M+H]^+$	Name	R_t (min)	MS/MS	Maximum amount (area) and t_{max} (min)	Time (min) of disappearance
303	*S*-2,3-Dihydro-5-methoxy-2-oxo-1,3,4-thiadiazol-3-ylmethyl-*O*,*O*-dimethyl-phosphorodithioate	12.71	145:-$HSPS(OCH_3)_2$	0 (5.915.614)	30
287	*S*-2,3-Dihydro-5-methoxy-2-oxo-1,3,4-thiadiazol-3-ylmethyl-*O*,*O*-dimethyl-phosphorothiolate	9.41	259: (-CO) 145: (-$HSPO(OCH_3)_2$)	15 (5.381.706)	120
147	1,3,4-Thiadiazol-2(3H)-one, 5-methoxy-3-methyl	9.52	–	15 (332.854)	60
159	*O*,*O*-Dimethylhydrogen dithiophosphate	2.52	–	30 (488.666)	120
145	*O*-Methyl hydroxy phosphorodithioate	9.32	–	10 (6.579.258)	180
143	*O*,*O*-Dimethyl-phosphorothioate	4.88	–	90 (8.029.864)	180
277	Methoxymercapto idrazone *O*,*O*, dimethylphosphorodithioate	8.49	199: (-CH_3OCH_2SH)	30 (830.796)	180
163	1,3,4-Thiadiazol-2(3H)-one, 3-(hydroxymethyl)-5-methoxy	8.73	–	60 (1.080.115)	180
127	Dimethylphosphate	1.75	–	120 (4.467.044)	240



Scheme 2. Transformation pathways followed by methidathion under TiO_2 treatment.

The most abundant intermediate was the one involving the P=S oxidation (pathway II), while the other two pathways seemed to occur in a lesser extent. The lower molecular compounds seemed to be formed at high amount, probably due to their formation through several independent pathways.

Methidathion underwent complete mineralization within 4 h of irradiation. Along with organic carbon disappearance, the evolution of inorganic ions occurred. Looking closer to the fate of the nitrogen, it was released mainly as ammonium ions. The sum of nitrate and ammonium ions amount accounts for 85% of the stoichiometric amount. The release of nitrogen in triazolidine derivatives was reported to give N_2 gas formation [30], so that the missing nitrogen was probably lost as N_2 gas. Sulphur was partially recovered as sulphate (70%), while the lacking amount was probably released as H_2S, that was not possible to detect it in our experimental condition. The release of sulphur as H_2S could find support in the formation of sulfidic intermediates (see compounds at *m*/*z* 277, 159, 143 and 145).

3.3. Photoinduced transformation of azinphos methyl

Under sunlight, azinphos methyl is subjected to photolysis (half-life of 8 days) [31]. However, homogeneous photolysis does not induce degradation of the selected pesticide in the considered time (4 h) and no transformation products were identified. The degradation curve of azinphos methyl in the presence of titanium dioxide was similar to phosphamidon and methidathion, with a calculated half-life of 3 min and the total abatement obtained within 15 min of irradiation (see Fig. 3).

Along with the azinphos methyl degradation, numerous intermediates were identified, whose profiles as a function of irradiation time are shown in Fig. 4. They are summarized in Table 3 and Scheme 3. Some of them were also found under UV irradiation [23] and are indicated in red. These photoproducts were formed through the S–C–N bonds cleavage, with formation of *N*-methylbenzazimide ($[M+H]^+$ 162) and 1,2,3-benzotriazin-4(3H)-one ($[M+H]^+$ 148) [22,23]. These triazinic products are known pollutants in the environment, due to their use as herbicides [32,33]. Similar pathways also occurred under heterogeneous photocatalysis, with the formation of the species at $[M+H]^+$ 148, recognized as 1,2,3-benzotriazin-4(3H)-one, further transformed into the hydroxyl derivative at $[M+H]^+$ 164 (pathway I). The introduction of an OH group found support on their MS/MS spectrum, that shows water as peculiar loss. At the same time, other routes proceed through the formation of the species at $[M+H]^+$ 162 (see pathway II) or the detachment of an esther group (pathway IV) with the formation of *O*-methyl *S*-[(4-oxo-1,2,3-benzotriazin-3(4H)-yl)methyl] phosphorodithioate ($[M+H]^+$ 304), also recognized under UV irradiation [23].

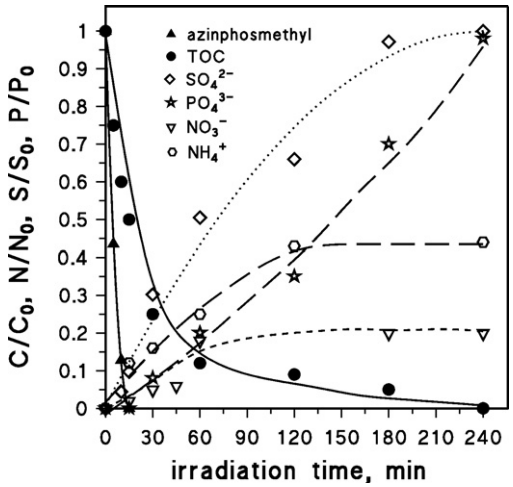


Fig. 3. Degradation of azinphos methyl 15 mg L^{-1} on TiO_2 200 mg L^{-1}; disappearance of the initial compound, TOC profile and evolution of sulphate, phosphate, ammonium and nitrate ions as a function of the irradiation time.

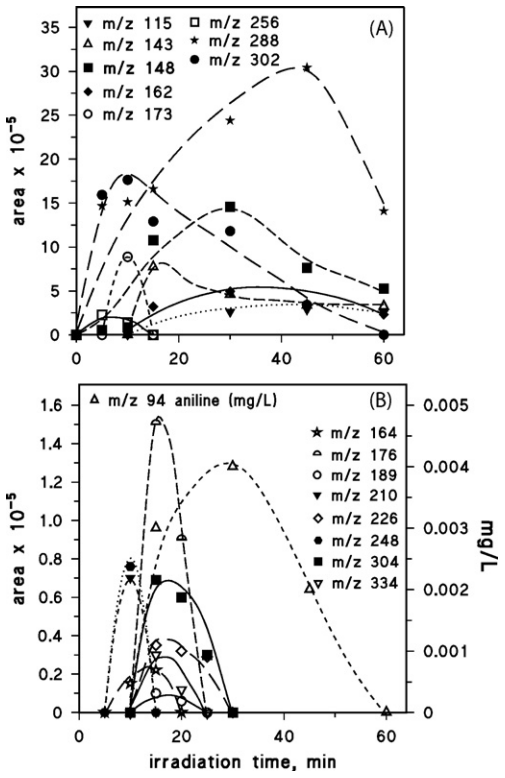


Fig. 4. Intermediates formed from azinphos methyl degradation as a function of the irradiation time.

In addition to these transformation pathways followed under both homogeneous and heterogeneous photocatalysis, the presence of titanium dioxide starts additional pathways. A pathway proceeds through the oxidation of the P=S to P=O (pathway III) with the formation of the species at $[M+H]^+$ 302. This species produced in MS/MS experiment an intense product ion corresponding to the elimination of SH-$PO(OCH_3)_2$ (*m*/*z* 160), instead of the typical loss of azinphos methyl (product ion at *m*/*z* 160, eliminates $SHPS(OCH_3)_2$) and was recognized as *O*,*O*-dimethyl *S*-[(4-oxo-1,2,3-benzotriazin-3(4H)-yl)methyl] phosphorothioate. By analysing the pathways III and IV, the formation of a species at $[M+H]^+$ 288 occurs. An help in attributing an identity comes from its MS/MS spectrum, which eliminates only methanol, so proving that a modification in the phosphorous moiety had occurred, and permits to propose the structure showed in Scheme 3.

At the same time, another route (labelled V) leads to the formation of the hydroxyl derivative ($[M+H]^+$ 334). A parallel initial pathway (labelled VI) involves the cleavage of the S–P bond, with the formation of the species at $[M+H]^+$ 210 and 226. Their formation is consistent with the occurrence of the hydroxylation and bihydroxylation on the benzenic ring, since these two compounds may derive from the hydroxyl derivative at $[M+H]^+$ 334, through the detachment of the organophosphorus moiety. Afterward, the molecule breakdown occurs.

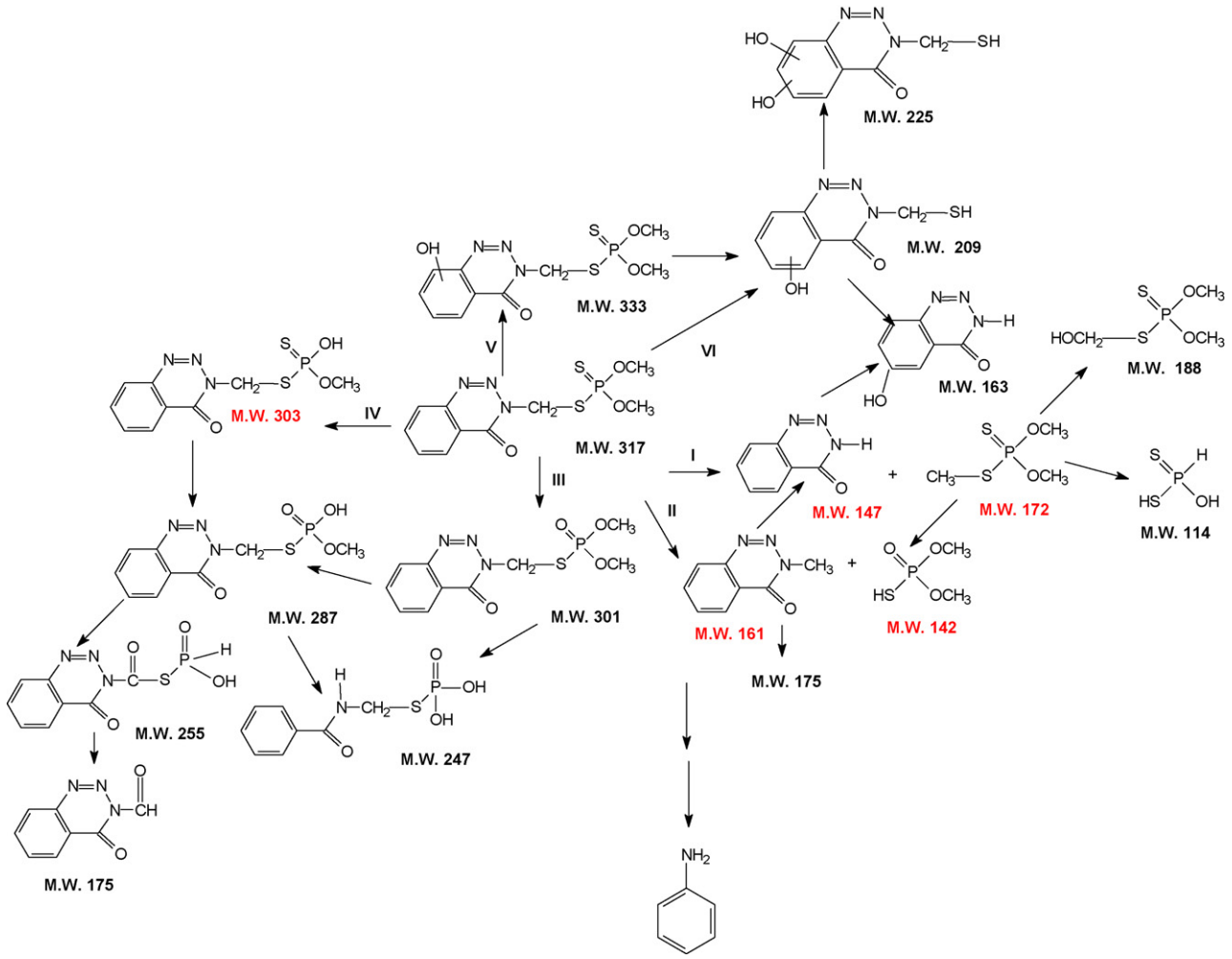
Through these six pathways the transformation of azinphos methyl then proceeds with the formation of numerous smaller molecules. The intermediate at $[M+H]^+$ 288 could be transformed into the species at $[M+H]^+$ 256 and 248. The species at $[M+H]^+$ 256 was attributed to 1,2,3-benzotriazin-4(3H)-one,1-oxo-3-[(phosphonothio)]. The presence of a keto group in the proposed structure found support in the formation of a species at $[M+H]^+$ 176, that should be formed from $[M+H]^+$ 256 through the detachment of the organophosphorus group. The organic compound at $[M+H]^+$ 248 was probably formed through the breaking of the benzotriazinic moiety with the detachment of the azo group. Its formation could found support in the evolution of N_2 gas discussed below. Looking closer to the species at $[M+H]^+$ 176, it could be alternatively formed through the pathway IV (see species $[M+H]^+$ 256), as a consequence of the detachment of the organophosphorus group or through the pathway II (see species $[M+H]^+$ 162), due to the oxidation of the methyl group to a keto group.

The further photoinduced transformation leads to the formation of aniline $[M+H]^+$ 94, whose identity was assessed through the injection of a standard solution. It was as well quantified and accounts for the conversion of less than 1% of the benzenic moiety.

The fate of the organophosphorus moiety was also followed. All the observed organophosphorus derivatives should come from the compound $[M+H]^+$ 173, formed through the pathway I. Its transformation then proceeds with: (1) hydroxylation of the methyl group, with the formation of *S*-hydroxymethyl *O*,*O*-dimethyl phosphorodithioate ($[M+H]^+$ 189); (2) the detachment of the two methoxy groups with the formation of the species at $[M+H]^+$ 115, that still possesses two sulphur atoms, as assessed by its MS spectrum, and was identified as phosphorothioic acid; (3) the oxidation of P=S

Table 3
Identified transformation products in azinphos methyl photocatalytic degradation

$[M+H]^+$	Name	R_t (min)	MS/MS
318	*O*,*O*-Dimethyl S-[(4-oxo-1,2,3-benzotriazin-3(4H)-yl)methyl] phosphorodithioate	17.50	160: (–$HSPS(OCH_3)_2$); 132: (–N_2– $HSPS(OCH_3)_2$); 118: (–N_2– $CH_3SPS(OCH_3)_2$)
334	*O*,*O*-Dimethyl S-[(4-oxo-1,2,3-hydroxy3(4H)-yl)methyl] phosphorodithioate	16.10	–
304	*O*-Methyl *S*-[(4-oxo-1,2,3-benzotriazin-3(4H)-yl)methyl] phosphorodithioate	14.02	–
302	*O*,*O*-Dimethyl *S*-[(4-oxo-1,2,3-benzotriazin-3(4H)-yl)methyl] phosphorothioate	14.10	160: (–$HSPO(OCH_3)_2$) 132: (–N_2– $HSPO(OCH_3)_2$)
288	1,2,3-Benzotriazin-4(3H)-one,3-[(phosphonothio)methyl]	13.23	256: (–CH_3OH)
248	Methylbenzamide- phosphorothioic acid	8.61	–
256	1,2,3-Benzotriazin-4(3H)-one,1-oxo-3-[(phosphonothio)]	8.65	–
176	1,2,3-Benzotriazin-4(3H)-one, 3-formile	7.15	
162	*N*-Methyl-benzazimide	6.01	
164	Hydroxy-1,2,3-benzotriazin-4(3H)-one	4.78	118: (–N_2, –H_2O)
148	1,2,3-Benzotriazin-4(3H)-one	5.29	120: (–N_2)
226	1,2,3-Hydroxybenzotriazin-4(3H)-one, 3-(mercaptohydroxymethyl)	4.36	–
210	1,2,3-Hydroxybenzotriazin-4(3H)-one, 3-(mercaptomethyl)	4.11	–
189	*S*-Hydroxymethyl *O*,*O*-dimethyl phosphorodithioate	5.89	–
173	*O*,*O*,*S*-Trimethyl esther	6.73	–
143	*O*,*S*-Dimethyl phosphorothioate	4.09	–
115	Phosphorothioic acid	2.60	–
94	Aniline	5.77	–



Scheme 3. Transformation pathways followed by azinphos methyl under TiO_2 treatment. Compounds indicated in red were also identified though homogeneous photolysis [23].

to P=O, with the formation of the species at $[M+H]^+$ 143, that possesses only a sulphur atom, as assessed by typical isotopic distribution in its MS spectrum. This compound should be formed from the pathways I or II.

By taking into account the relative abundances of the identified organic compounds, the main pathways seemed to be those involving the cleavage of the P–O bond (pathway IV), the oxidation of P=S to P=O (pathway III) and the cleavage of the N–C bond, with the molecule breakdown (pathway I), that coincide with those occurring also under homogeneous photolysis. The additional pathways, that involve the molecule hydroxylation and the cleavage of the S–P bond, seemed to be only secondary routes.

Complete mineralization was achieved within 4 h of irradiation. Sulphur atom was recovered as sulphate, phosphor atom as phosphate and their stoichiometric concentration were reached after 3 h or 4 h of irradiation, respectively. When azinphos methyl was entirely disappeared, phosphor was still bond in organic compounds, while sulphur was partially released (15%). It means that the initial transformation does not involve the cleavage of the organophosphorus group, while the P–S is partially oxidized to P–O, in agreement with the identified intermediates. Nitrogen was partially converted to nitrate and ammonium ions, formed in a ratio 1:2, while the lacking nitrogen (40%) is probably released as N_2 gas. The nitrogen of N=N containing structure is known to give N_2 gas formation [25].

4. Conclusions

On the basis of the obtained results, it can be found a degradation pathway followed by all the structures, apart from the nature of the substituents. Common pathways are represented by the detachment of the organophosphorus moiety and by the oxidation of P=S to P=O. The formation of oxon derivatives is of concern, since the oxon analogous of organophosphorus pesticides were found to be toxic compounds. Hydroxylation occurred in all cases. Some additional pathways were however recognized. Phosphamidon was subjected to dechlorination, methidathion was subjected to the triazolidinic ring opening, while azinphos methyl gave the N–C bond cleavage. Complete mineralization was achieved in all cases.

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