

Study of the removal of dichlorvos and dimethoate in a titanium dioxide mediated photocatalytic process through the examination of intermediates and the reaction mechanism

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Abstract

The photocatalytic oxidation of two selected organophosphorous insecticides (dichlorvos and dimethoate) has been investigated. The aim of the study was the identification of the intermediates that are formed during photocatalytic treatment. Intermediate products from the slurry system were identified by means of solid-phase extraction (SPE) coupled to gas chromatography–mass spectroscopy techniques (GC–MS). Nine possible by-products were identified for dimethoate and three for dichlorvos. A proposed degradation pathway for each insecticide is presented, involving mainly oxidation and dealkylation reactions. The results demonstrated that some of the transient intermediates formed (oxon derivatives, disulfide, chlorinated fragments), were more toxic compared to parent compounds whereas most of them are less toxic than the parent compounds.

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1. Introduction

Heterogeneous photocatalysis appears to be a very promising technique for the destruction of organic pollutants [1–3]. Among the semiconductors that have been tested, titanium dioxide demonstrates the most fulfilling results, exhibiting not only an outstanding catalytic efficiency but also low cost and resistance to photocorrosion [4]. Moreover, titanium dioxide is environmentally safe and gives the opportunity to use solar light as an energy source. The latter makes the process quite attractive especially to countries where solar irradiation is highly available.

The photocatalytic properties of the semiconductors are based on their electronic structure which is characterized by a filled valence band and an empty conduction band. When they are illuminated with energy greater than their band gap energy E_g , excited high-energy states of electron and hole pairs (e^-/h^+) are produced. These species can either recombine in the bulk of the semiconductor and dissipate the input energy as heat or they

can migrate to surface of the semiconductor's particles and react with adsorbed electron donors or electron acceptors. The photogenerated holes act as powerful oxidants and the electrons as powerful reductants and initiate a wide range of chemical redox reactions, which can lead to partial or total destruction of a great variety of organic pollutants [5].

In addition to the performance of the treatment process, the study of the formation of by-products is also important. In photocatalytic treatment of toxic pollutants, the monitoring of the disappearance rate of the parent compound is not the most appropriate parameter for classifying the efficacy of the process [6,7]. Information on the formation and decomposition of the intermediates or by-products is critical before a clean technology can be established [1]. The formation of intermediates with similar or even higher toxicity than the parent compounds during the photocatalytic degradation of pesticides was often reported [1,8,9].

Organophosphorous pesticides are comprised within the 10 most widely used pesticides all over the world. 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 [10,11]. Residue

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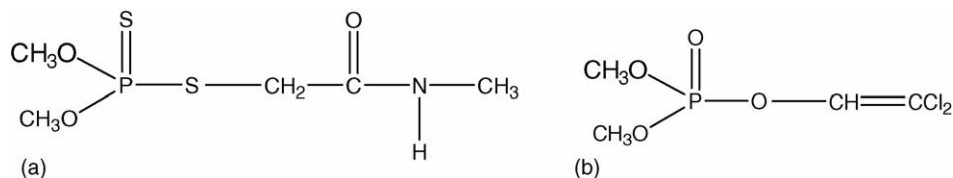


Fig. 1. The chemical structures of (a) dimethoate and (b) dichlorvos organophosphorous insecticides.

levels have been detected frequently in environmental waters [12,13] and their removal from water is in urgent demand.

In this study the photocatalytic degradation of two organophosphorous insecticides, dichlorvos (2,2-dichlorovinyl-*O,O*-dimethyl phosphate) and dimethoate (*O,O*-dimethyl *S*-methylcarbamoylmethyl phosphorodithioate) (Fig. 1), has been investigated. Although that the photocatalytic degradation kinetics and the operation parameters have been studied in the past [14–19] very limited information on the photocatalytic intermediates, end-products and reaction mechanisms are available [20,16,17]. Moreover, only the final products are discussed in these studies. Thus, major concern of this study is addressed to the determination of the main by-products using GC–MS techniques. In our previous studies, we showed that mineralization, especially for dimethoate, is not always possible or cost effective since it may require larger quantities of catalyst or very long irradiation times [14,15]. In that way, photocatalytic oxidation may be applied as a pre-treatment method thus rendering the identification of the intermediates as an indispensable task. In this study nine intermediates for dimethoate and three for dichlorvos have been determined during their photocatalytic treatment. Moreover, an attempt has also been made to correlate the identified photoproducts with toxicity measurements.

2. Experimental

2.1. Reagents and materials

Dichlorvos and dimethoate, both analytical grade (99.9% purity) were purchased from Riedel-de-Haen (Germany) and were used without any further purification. HPLC-grade solvents (acetonitrile, methanol and water) were supplied by Merck and pesticide grade solvents (dichloromethane and ethyl acetate) were from Panreac. Titanium dioxide P-25 Degussa (anatase/rutile: 65/35, non-porous, mean size 30 nm, surface area 56 m² g⁻¹) was used as received. HA 0.45 μm filters were supplied by Millipore (Bedford, USA). About 500 mg EnviCarb (non-porous GCB, 40–100 μm particle size, 100 m² g⁻¹ surface area; Supelco, Bellefonte, PA, USA) extraction cartridges were used for the by-products evaluation. HCl, NaOH and phosphate buffer pH 7 were used to adjust the pH when necessary. Doubly distilled water was used throughout the work. Stock solutions of dichlorvos and dimethoate (1000 mg L⁻¹) were prepared in water and protected from light.

2.2. Irradiation procedure

Irradiation experiments were carried out in a 500 mL Pyrex UV reactor equipped with a diving Philips HPK 125 W high-

pressure mercury lamp. The lamp was jacketed with a water-cooled Pyrex filter restricting the transmission of wavelengths below 290 nm. The tap water cooling circuit was used to remove IR radiation preventing any heating of the suspension (30–35 °C).

Dichlorvos or dimethoate solution (20 mg L⁻¹) was mixed with the appropriate amount of catalyst and was magnetically stirred before and during the illumination. The suspension was left for 30 min in the dark, prior to illumination, in order to achieve the maximum adsorption of the pesticide onto semiconductors surface. The pH was not adjusted unless otherwise stated.

A relatively low amount of TiO₂ (100 mg L⁻¹) was used in the experiments which enables to obtain slower kinetics and provide favorable conditions for the determination of by-products. Additionally, the initial herbicide concentration ($C = 20 \text{ mg L}^{-1}$) was selected to be high enough to facilitate the identification of intermediates.

2.3. Analyses

2.3.1. Kinetic studies

At specific time intervals samples were withdrawn from the reactor. In order to remove the TiO₂ particles the solution samples were filtered through a 0.45 μm filter. Pesticide concentrations were determined by a Shimadzu 10AD liquid chromatograph equipped with a variable wavelength UV detector using a 250 mm × 4.6 mm, C18 nucleosil 100-S column. The mobile phase was a mixture of acetonitrile and water (40/60 v/v for dimethoate and 50/50 v/v for dichlorvos) with a flow rate of 1 mL min⁻¹. The detection was realized at 210 nm. Standard solutions of pure compounds were used for quantitative analysis.

2.3.2. By-products evaluation

2.3.2.1. Sample preparation. For the GC–MS analysis, the SPE method was applied to the samples previous to the injection. Volumes of 50 mL of the treated samples were extracted by using 500 mg Envicarb extraction cartridges. Prior to extraction the water samples were acidified with sulfuric acid to pH 2 (for dimethoate solution) and to pH 1 (for dichlorvos solution). The cartridges were conditioned by elution with 2 mL × 4 mL of dichloromethane–methanol (80:20 v/v) and next, 2 mL × 6 mL of water, acidified to pH 2. After the passage of water samples, the cartridges were vacuum-dried for 30 min in order to remove traces of water. Elution of the analytes was conducted with 2 mL × 4 mL of dichloromethane–methanol (80:20 v/v). The eluate was evaporated to dryness, at room temperature, under a light stream of nitrogen and finally dissolved again, with

sonication, in ethyl acetate. The volume of the sample prior to injection was adjusted to 1 mL.

2.3.2.2. GC–MS. GC–MS analyses were performed on a Shimadzu QP 5000 instrument, equipped with a DB 5-MS column (J & W Scientific) of 30 m length and 0.25 i.d., coated with 5% phenyl 95% methylpolysiloxane. Separation of the by-products was conducted under the following chromatographic conditions: injector temperature 240 °C, oven temperature program 55 °C ramped at 5 °C/min to 200 °C followed by another ramp of 1 °C/min to 210 °C, held for 2 min and finally, to 270 °C at 20 °C/min (held for 3 min). Helium was used as carrier gas at a flow of 1 mL min⁻¹. The temperatures of the ion source and the interface were set at 240 and 290 °C, respectively. The MS operated in electron ionization mode with a potential of 70 eV and the spectra were obtained at a scan range from *m/z* 50–450 (full scan mode). The scan time was 47 min and 1.0 μL injections were made.

2.3.3. Toxicity measurements

The toxicity of the irradiated solution was examined by means of the Microtox toxicity test. The process that was followed is described in detail elsewhere [14,15].

3. Results and discussion

3.1. Kinetics

The kinetics of the selected insecticides disappearance, along with the factors affecting their photocatalytic degradation, have been examined and described in previous studies [14,15]. It has been proven that photocatalytic oxidation of dichlorvos and dimethoate follows first-order kinetics according to the Langmuir–Hinshelwood model as reported also for other organophosphorous insecticides [21]. The photocatalytic degradation of the selected insecticides is presented in Fig. 2, while in the insert, the logarithm of the ratio of the initial concentration (C_0) to the concentration at a given time (C) versus time (t) is plotted. The rate constant (k_{app}) was determined by calculating the slope of the line obtained.

Complete disappearance is observed within 30 and 120 min for dichlorvos and dimethoate, respectively. The calculated values of k_{app} and the linear regression coefficients R^2 are presented

Table 2
GC–MS–EI retention times (R_t) and spectral characteristics of dimethoate identified intermediates

Insecticide/photoproducts	R_t (min)	Characteristic ions (<i>m/z</i>)
1. <i>O,O</i> -dimethyl phosphonic ester	3.78	109, 95, 80, 79
2. <i>O,O,O</i> -trimethyl phosphoric ester	6.15	140, 109, 95, 79
3. <i>N</i> -methyl-2-sulfanylacetamide	9.87	105, 73, 58
4. <i>O,O,S</i> -trimethylphosphorothioate	10.61	156, 141, 126, 110, 95, 79
5. 2- <i>S</i> -methyl-(<i>N</i> -methyl) acetamide	11.06	119, 73, 61, 58
6. <i>O,O,S</i> -trimethyl thiophosphorothioate	12.6	172, 125, 93, 79
7. 1-Methyl-2-(acetyl- <i>N</i> -methyl-) methane disulfide	18.2	151, 105, 72, 58
8. Omethoate or dimethoxon (<i>O,O</i> -dimethyl- <i>S</i> -methylcarbamoylmethyl phosphorothioate)	24.1	213, 156, 141, 126, 110, 79, 58
Dimethoate (<i>O,O</i> -dimethyl- <i>S</i> methylcarbamoylmethyl phosphorodithioate)	27.15	229, 143, 125, 93, 87
9. 1,2-Bis(acetyl- <i>N</i> -methyl-) methane disulfide	34.43	208, 105, 73, 58

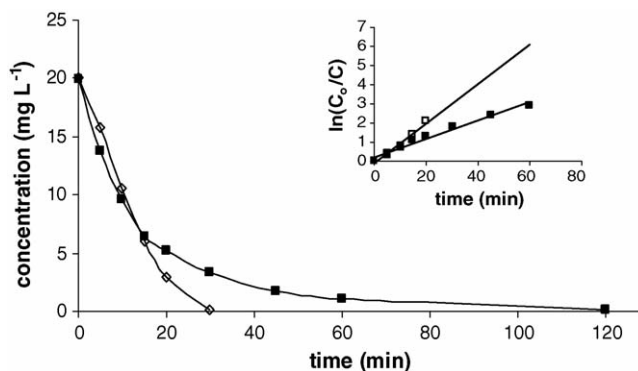


Fig. 2. Photodegradation kinetics of dimethoate (solid squares) and dichlorvos (empty squares) in the presence of TiO₂ (100 mg L⁻¹) particles.

Table 1

Photodegradation kinetic parameters (rate constants and linear regression coefficients R^2) for dimethoate and dichlorvos in the presence of TiO₂ = 100 mg L⁻¹

Insecticide	k_{app} (min ⁻¹)	R^2
Dimethoate	0.048	0.976
Dichlorvos	0.103	0.981

in Table 1. According to these values the appropriate first-order relationship appears to fit well.

3.2. Identification and evolution of degradation products

The photocatalytic oxidation of the selected insecticides yielded a number of organic intermediates. Nine by-products for dimethoate and three for dichlorvos have been identified using GC–MS–EI detection as possible degradation products. The determination of the derived intermediates was conducted (a) by using the identification program of NIST library with a fit value higher than 70% in all cases, (b) by comparing the spectra with previously reported spectra and (c) by interpretation of the mass spectra and investigation of their characteristic ions.

3.2.1. Dimethoate

Table 2 summarizes the identified intermediates of dimethoate along with their retention times and the characteristic ions of the mass spectra. Fig. 3 shows the mass spectra of dimethoate (DIM) and its degradation products (C1–C9) formed

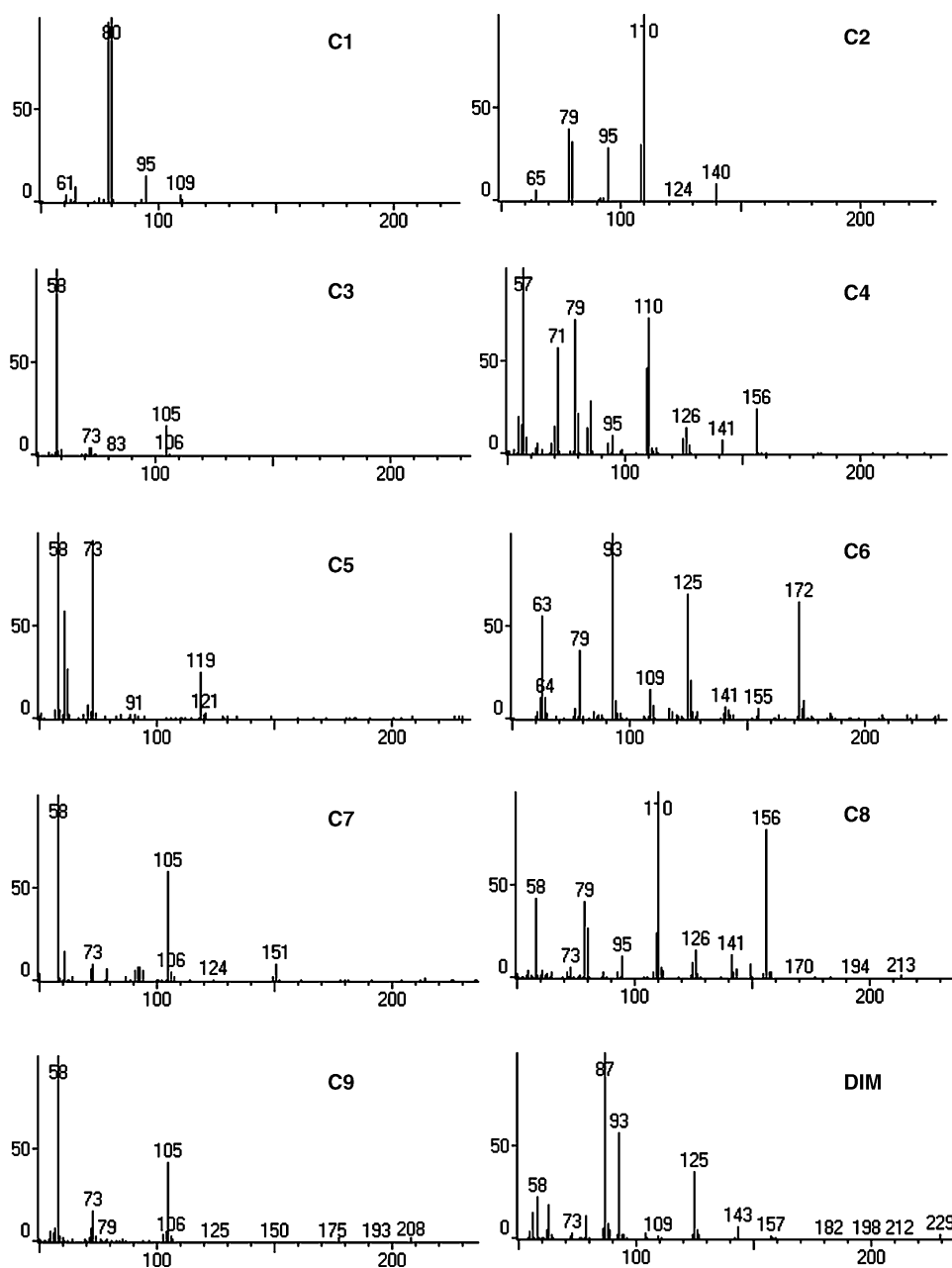


Fig. 3. Mass spectra of dimethoate (DIM) and degradation products (C1–C9) formed during the photocatalytic degradation in the presence of TiO_2 (100 mg L^{-1}) particles.

during the photocatalytic degradation of in the presence of TiO_2 (100 mg L^{-1}) particles. Compound **1** was identified as *O,O*-dimethyl phosphonic ester using the identification program of the NIST library exhibiting matching 90%. The ions at m/z 109 and 79 are characteristic of the phosphate esters and belong to the groups $[(\text{CH}_3\text{O})_2\text{P}(\text{O})]^+$ and $[\text{CH}_3\text{O}-\text{P}-\text{OH}]^+$, respectively [22]. Compound **1** was also detected as photocatalytic degradation product of other organophosphorous insecticides [23]. Compound **2** was identified as trimethyl phosphate by comparing the mass spectrum with previously reported spectrum as an identified intermediate during decomposition of various organophosphorous insecticides [9,24]. Moreover a comparison with the mass spectrum of the NIST library showed a fit

value of 75%. Compound **3**, which was identified as *N*-methyl-2-sulfanylacetamide, exhibits a peak at $m/z = 105$ which corresponds to the molecular ion $[M]^+$ and the characteristic ions at $m/z = 73$ and $m/z = 58$ that correspond to the loss of HSCH_2 - and HS -fragments, respectively. Compound **3** was also identified, in a previous study, as a by-product of dimethoate hydrolysis [25]. Compound **4** was also identified by a library search with a fit value of 75% and also by comparing the mass spectrum with previous published spectrum obtained after thermal decomposition of dimethoate [24]. Compound **5** was identified as 2-*S*-methyl-(*N*-methyl)acetamide and it exhibits ions at $m/z = 119$ that correspond to the molecular ion $[M]^+$ and the characteristic ions $m/z = 73$ and $m/z = 58$ that are identical with

compound **3** fragmentation. In addition, the mass spectrum of compound **5** has the same ions with its isomer, carbamothioic acid-(*N*-methyl)-*S*-methylthiomethyl ester, which is detected as by-product of dimethoate thermal decomposition [24]. Compound **6** was also identified by a library search with a fit value of 78% and also by comparing the mass spectrum with the spectrum of its isomer (*O,S,S* trimethyl phosphorothioate) which has been identified as an intermediate during thermal decomposition [24]. The two isomers exhibit the same characteristic ions. The main difference is the presence of an $m/z = 93$ ion which corresponds to the $[(\text{CH}_3\text{O})_2\text{P}]^+$ group indicating the formation a thiophosphorothioate and not a phosphorodithioate [26]. Compound **7** exhibits a peak at $m/z = 151$ which corresponds to the molecular ion $[M]^+$ and the characteristic ions $m/z = 105$, $m/z = 73$ and $m/z = 58$ that are identical with compound **3** fragmentation.

The identification of omethoate (dimethoxo, compound **8**) is carried out by the comparison with the spectrum of the NIST library exhibiting a fit value higher than 86%. Omethoate gives a characteristic rearrangement ion peak at $m/z = 156$ due to the migration of hydrogen to phosphoryl oxygen accompanied with the loss on *N*-methyl isocyanate as the neutral species. Another intense peak is at $m/z = 110$ and is due to α -cleavage accompanied by the rearrangement of hydrogen.

Finally, compound **9** that had the higher retention time was identified as the product of dimerization of compound **3** exhibiting a peak at $m/z = 208$ which corresponds to the molecular ion $[M]^+$. The rest of the fragmentation pattern (m/z 105, 79, 58) is identical to the one of compound **3**.

Based on the previous structure identification of the transformation products, a tentative photocatalytic degradation pathway is proposed for dimethoate in TiO_2 suspensions (Fig. 4). Compound **3** is formed by the scission of the thioester bond through a hydrolytic pathway. Formation of thiols was reported also for the hydrolytic degradation of other organophosphorous insecticides [27,28]. This hydrolytic pathway (pathway C) could proceed via the formation of sulfide cation radicals by attacking of positive holes initiating the series of reactions. The formation of cation radicals was observed also in the photocatalytic degradation of thiocarbamate pesticides [29] and thioethers [30]. The interfacial transfer of a single electron from the sulfur atom initiate P–S or C–S cleavage as a mechanism (Fig. 4). The scission of P–S bond leads to the formation of $\cdot\text{SCH}_2\text{C}(\text{O})\text{NHCH}_3$ radicals that are the precursor of compound **3**. The formation of such radicals has been previously reported by Oae [31]. Similarly, the formation of compound **5** involves the cleavage of P–S bond as above, followed by addition of a methyl radical from the

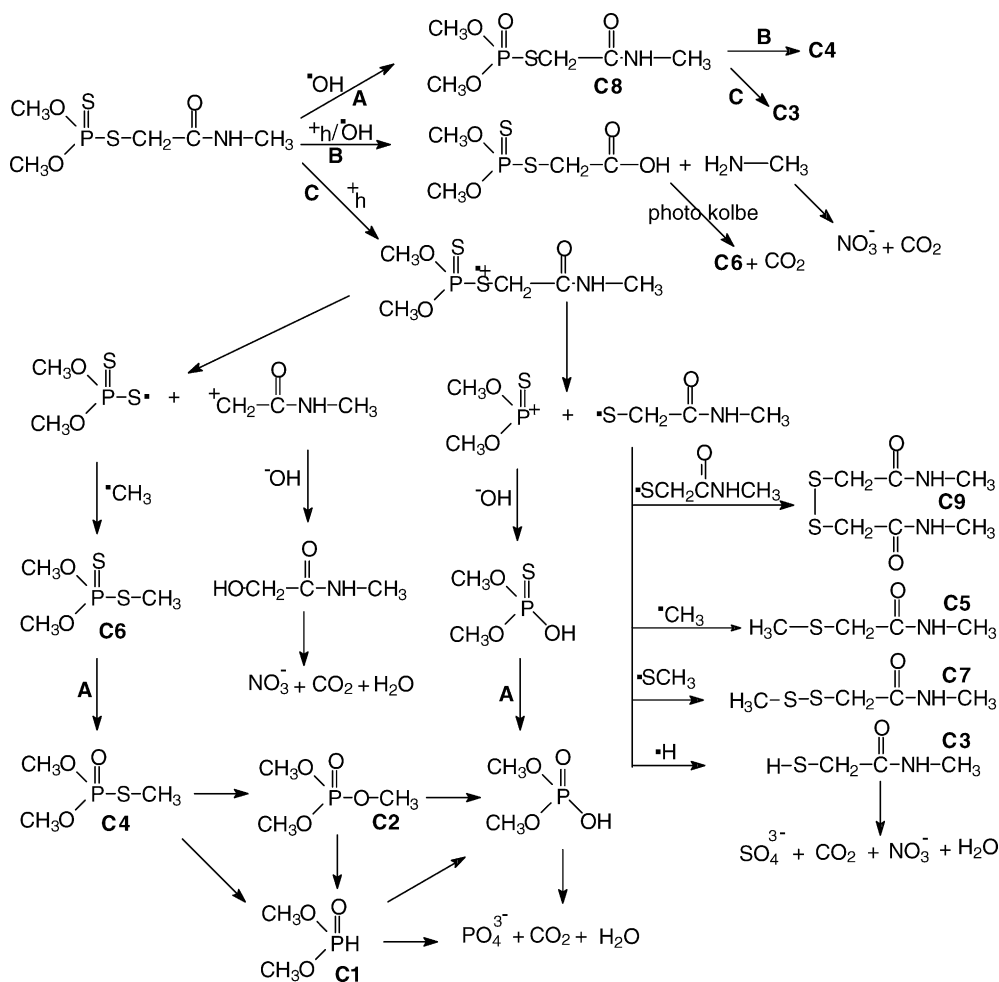


Fig. 4. Tentative photodegradation scheme of dimethoate during the photocatalytic degradation over TiO_2 suspensions.

medium. Compound **7** is formed also by a recombination of free radicals present in the reaction medium i.e. $\bullet\text{SCH}_2\text{C}(\text{O})\text{NHCH}_3$ and $\text{CH}_3\text{S}\bullet$. The recombination of $\bullet\text{SCH}_2\text{C}(\text{O})\text{NHCH}_3$ radicals could form dimers such as compound **9**. The dimerization of thiol radicals has been reported also in the case of the photocatalytic degradation of thiocarbamate pesticides [32]. In addition, disulfides were detected during the oxidation of similar organophosphorous insecticide molecules such as disulfoton and phorate [27,28] through hydrolysis. The formation of disulfide could be also attributed to the oxidation of the resulting thiol by oxygen as reported elsewhere [28]. Finally, mechanisms of free radicals recombination was also demonstrated in the sonolytic degradation of thioethers [33].

The formation of compound **6** could be explained by two possible reaction pathways (a) via the scission of the C–S bond as previously described, and the addition of methyl radical from the reaction media and (b) through the scission of the amide bond by positive holes and the addition of $\bullet\text{OH}$ radicals to form the corresponding acid which is subsequently decarboxylated into CO_2 and $(\text{CH}_3\text{O})_2\text{P}(\text{S})\text{SCH}_2\bullet$ via the well known photo-Kolbe decarboxylation (pathway B) (Fig. 4). Moreover, the nucleophilic attack of the RS^- group after the cleavage of P–S bond to alkyl phosphoroesters have been proposed also in the hydrolysis of disulfoton [27].

Omethoate represents one of the most expected intermediates since previous studies showed that the oxidant attack of the $\bullet\text{OH}$ radicals on the P=S bond occurs firstly in the case of phosphorothioates, resulting to the formation of the oxon derivatives which in most cases are more toxic than the parent compounds [1,23,34]. Thus, the formation of omethoate is attributed to oxidative desulfuration by $\bullet\text{OH}$ attack (pathway A) (Fig. 4). Similarly, the oxidative desulfuration of compound **6** by $\bullet\text{OH}$ attack yield the formation of compound **4**. Continuous attack of h^+ and $\bullet\text{OH}$ lead to the formation of compounds **1** and **2**.

The study of the photoproducts evolution profiles offers useful information to support the proposed mechanisms. The temporal evolution profile of dimethoate photoproducts is presented in Fig. 5a and b. It is obvious, that most dimethoate intermediates exhibit a peak until the first 15 min of irradiation. Compounds **5** and **9** are completely disappeared after 60 min of illumination time while dimethoate is more than 90% degraded (Fig. 2). Compounds **3** and **4** present a slight increase at 60 min and after that time their concentration decreases slowly. This could be attributed to the enhanced degradation of compounds **8** and **9** at the same time. On the other hand, compounds **1** and **2** appear to be preserved in small concentrations even after complete dis-

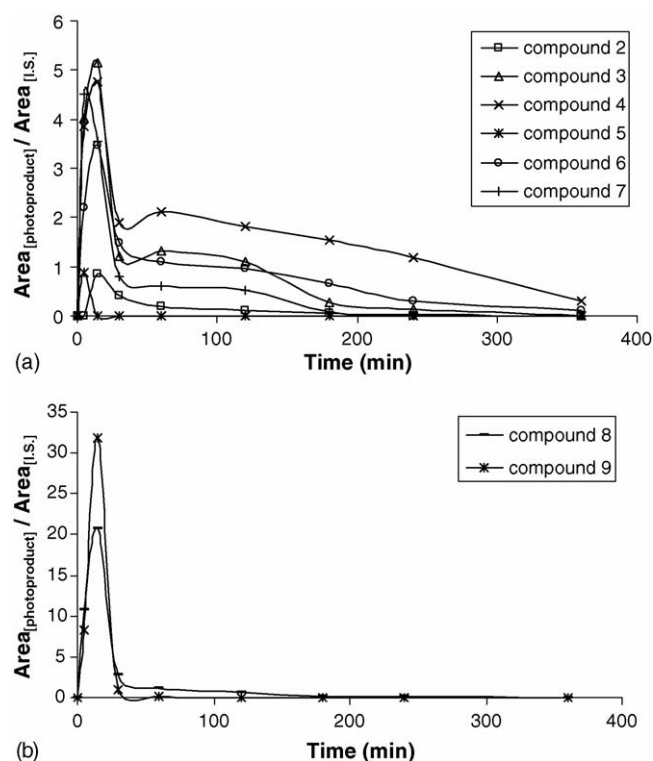


Fig. 5. (a and b) Profile of dimethoate photocatalytic intermediates.

appearance of dimethoate. Especially compound **1** was detected only in traces.

The degradation of dimethoate proceeds simultaneously for most intermediates whereas their decay generates secondary intermediates such as compounds **1**, **2** and **4**. This is further supported by previous findings [14] demonstrating that formation of sulfate and phosphate ions proceeds rather simultaneously in the first 2 h but then sulfates maintain the high rate and reach their maximum after 6 h while phosphate ions release proceeds slower and finally they reach the 90% of the expected amount. As shown in Fig. 5a and b, the decrease rate of compounds **2**, **4** and **6** after 120 min is slower than the decrease rate of compounds **3** and **7** that contained only sulfur.

3.2.2. Dichlorvos

Table 3 summarizes the identified intermediates of dichlorvos along with their retention times and the characteristic ions of the mass spectra. The dimethoate photoproducts **1** and **3** were also identified as intermediates during photocatalytic treatment of dichlorvos using the identification program of NIST library with

Table 3
GC–MS–EI retention times (R_t) and spectral characteristics of dichlorvos identified intermediates

Compound	R_t (min)	Characteristic ions (m/z)
1. <i>O,O</i> -dimethyl phosphonic ester	3.78	109, 95, 80, 79
2. Desmethyl dichlorvos (2,2-dichlorovinyl <i>O</i> -methylphosphate)	4.90	207, 96, 95, 79, 65, 64
3. <i>O,O,O</i> -trimethyl phosphoric ester	6.15	140, 109, 95, 79
Dichlorvos (2,2-dichlorovinyl- <i>O,O</i> -dimethyl phosphate)	14.81	220, 185, 145, 109, 79

a fit value of 85% and 70%, respectively. Trimethyl phosphate has also been identified as an intermediate of the photocatalytic oxidation of dichlorvos elsewhere [16].

Compound **2** was identified as the desmethyl dichlorvos and exhibited the $[M]^+$ ion at $m/z = 207$ that corresponds to the loss of a methyl group ($M - 14$) from dichlorvos and the characteristic ions of $[\text{CH}_3\text{OP}(\text{OH})_2]^+$, $[\text{CH}_3\text{OP}(\text{O})\text{OH}]^+$, $[\text{CH}_3\text{O}-\text{P}-\text{OH}]^+$, $[\text{P}(\text{OH})_2]^+$ and $[\text{O}=\text{P}-\text{OH}]^+$ at $m/z = 96, 95, 79, 65$ and 64 , respectively. Desmethyl dichlorvos has also been identified as a metabolite of dichlorvos in mammals [35]. The molecular structure of the degradation products and the tentative photocatalytic degradation pathway of dichlorvos are presented in Fig. 6.

The primary mechanisms for the photocatalytic oxidation of dichlorvos via hydroxyl radical attack, are hydrogen abstraction (pathway I_A), addition–elimination (pathway I_B) and addition to the unsaturated bond (pathway III). The first two pathways were also reported for the photocatalytic degradation of dimethyl methyl phosphonate [36]. Pathways II and IV are initiated by electron transfer followed by $\bullet\text{OH}$ addition–elimination reaction series. The formation of desmethyl dichlorvos (C2) could proceed via pathways I_A, I_B and II as shown in Fig. 6. Desmethyl dichlorvos was detected only during the first stages of the photocatalytic degradation and in low concentrations. This could be explained considering that addition–elimination mechanism is not significant under aqueous conditions [37] and electron transfer reactions in TiO_2 photocatalysis are also limited compared to hydroxyl radical or positive hole reactions. Hydrogen

abstraction from $\text{CH}_3\text{O}-$ groups is more probable although that hydrogen should be abstracted from primary carbons, because the dichlorovinyl group activates the H atom abstraction. Similarly, photoproducts C1 and C3 are not the major photoproducts produced and were detected only in traces.

The formation of dimethyl phosphate and dichloroacetaldehyde were also expected based on advanced oxidation of dichlorvos and other organophosphorous insecticides [38–40]. The formation of these compounds proceeds probably via pathway III (addition of $\bullet\text{OH}$ to $\text{C}=\text{C}$ bond) but it can be also performed following II_d and IV_b routes. Dichlorovinyl alcohol is primarily formed but quickly tautomerize to dichloroacetaldehyde that sequentially react with $\bullet\text{OH}$ to form dichloroacetic acid [38]. Although that the solution pH value was fixed to 1, the dimethylphosphate ($\text{p}K_{\text{a}} = 1.25$), dichloroacetaldehyde and dichloroacetic acid ($\text{p}K_{\text{a}} = 1.3$) cannot be detected using GC–MS technique. Summarizing, dimethyl phosphate and dichloroacetaldehyde were considered as primary major intermediates. The above-described mechanism is also in agreement with previous studies [15] which showed that the release of chlorine ions is a rapid process and probably responsible for dichlorvos disappearance since almost the 80% of the expected amount was observed in 60 min. Thus, cleavage of the dichlorovinyl group proceeds more rapidly than *O*-demethylation. From 60 min to 6 h, dechlorination proceeded at a slower rate probably due to the formation of more resistant chlorinated intermediates and reached the maximum concentration after 6 h of irradiation.

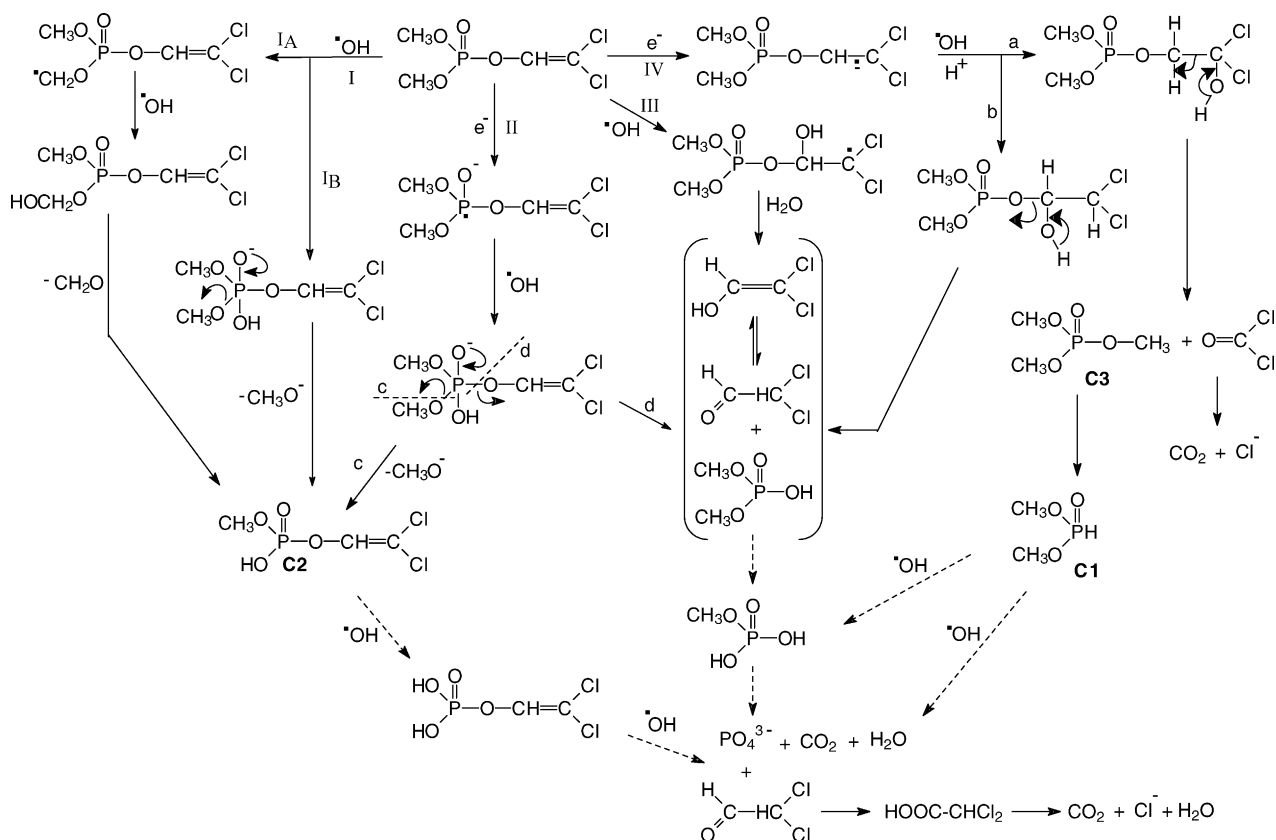


Fig. 6. Tentative photodegradation scheme of dichlorvos during the photocatalytic degradation over TiO_2 suspensions.

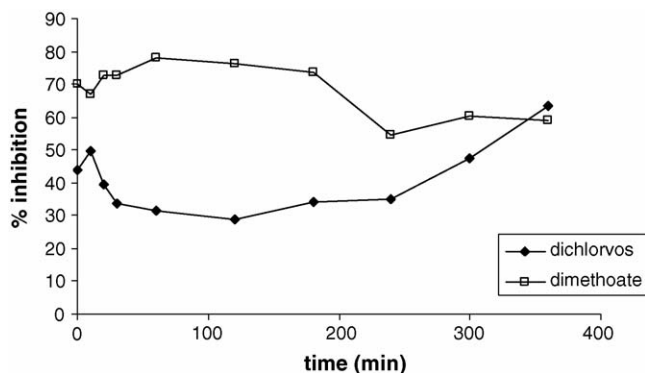


Fig. 7. Toxicity evolution as a function of irradiation time in the presence of $\text{TiO}_2 = 100 \text{ mg L}^{-1}$, $C_{\text{insect}} = 20 \text{ mg L}^{-1}$ [7,8].

3.3. Toxicity evaluation

Our previous studies proved that photocatalytic treatment was not always capable of reducing the toxicity of dimethoate or dichlorvos solutions [14,15]. On the contrary, a slight increase could sometimes be observed especially when no other additives like oxidants (for example hydrogen peroxide or peroxydisulfate) were present. Photocatalytic treatment with TiO_2 suspensions could not always lead to complete detoxification of the treated solutions probably requiring longer irradiation times or higher quantities of catalyst. Therefore identification of intermediates during photocatalysis proved to be an indispensable task in order to obtain integrated knowledge concerning toxicity evaluation.

Fig. 7 presents the variation of % inhibition of bioluminescence versus time. In the case of dimethoate a slight increase of the toxicity is observed until 180 min of irradiation that can be attributed to the formation of the oxon derivative (omethoate), the disulfide and *O,O,S*-trimethyl thiophosphorothioate. Omethoate has been proven to be 10 times more toxic than its parent compound and it is more of a potential inhibitor to cholinesterase activity than dimethoate [41,42]. Moreover, the disulfide derivative of phorate is found to be about two and a half times as toxic as phorate on a molar basis [28]. In addition, extrapolating the result that diethyldithiophosphate was more toxic than disulfoton [43] it can be considered that *O,O,S*-trimethyl thiophosphorothioate could enhance the toxicity of the reaction mixture. Finally, it was observed that phosphorothiolates such as compounds **4** and **6** exhibit delayed toxicity in mammals that is not attributable to acetylcholinesterase inhibition [44]. The other sulfur degradation products of the side chain showed lower toxicity in the case of disulfoton [43]. Since the maxima of the more toxic compounds were attained at 15 min the continuous increase of toxicity until 60 min could be attributed to probable synergistic effect of all different intermediates of the reaction media. On the other hand, the explanation for the increased toxicity in dichlorvos solution is difficult since the identified by-products appear to be less toxic than the parent compound. However, considering the by-products resulted as possible fragments of dichlorvos that are not detected in this study (phosgene, dichloroacetaldehyde, dichloroacetic acid), the

increase of toxicity could be explained. It is observed that during the photocatalytic degradation of chlorinated ethenes more toxic phosgene is generated as one of the products [45]. In more prolonged times, dichloroacetaldehyde and dichloroacetic acid are formed that are also toxic compounds and in this case, synergistic effects with methylphosphates may take place increasing the toxicity of the treated solution. It is also worthy to note that combination of organophosphorous esters resulted in synergistic effect in aquatic organisms and enzymes [46,47]. Finally, some of the by-products detected (i.e. compounds **1** and **3**) are suspected carcinogens [24].

Other studies [48] dealing with the toxicity monitoring of dichlorvos solution treated by photocatalysis, presented similar trend and was higher under acidic than under alkaline conditions. The photoconversion intermediates produced at pH 4 were more toxic than the parent compound. Eventually, after 3-h treatment, toxicity increased 2.5 times related to the inhibition of the parent compound [46]. In conclusion, it seems reasonable to say that the potential of seemingly environmentally friendly organophosphorous insecticides to be the precursors to toxic compounds has been underestimated.

4. Conclusions

The major degradation products formed during the photocatalytic treatment of dimethoate and dichlorvos were identified and the reaction pathways were examined. Most of the identified intermediates are less toxic compounds than the parent compounds. The increased toxicity of the dichlorvos treated solution is probably attributed to synergistic effects of chlorinated photoproducts with methylphosphates.

The identification of intermediates during photocatalysis appear to be a necessary process in order to achieve complete knowledge concerning the mineralization of the parent compound and thereby to be able to evaluate the final outcome of the treatment. Therefore, by-product evaluation combined with toxicity assessment is the key to optimize each treatment and to maximize the overall process.

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