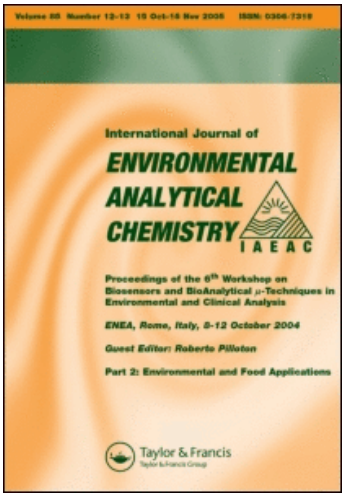

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Analytical and kinetic study of the aqueous hydrolysis of four organophosphorus and two carbamate pesticides

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ANALYTICAL AND KINETIC STUDY OF THE AQUEOUS HYDROLYSIS OF FOUR ORGANOPHOSPHORUS AND TWO CARBAMATE PESTICIDES

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The hydrolysis of six selected pesticides has been studied in aqueous solution. Four organophosphorus pesticides (disulfoton, isofenfos, isazofos and profenfos) and two *N*-methylcarbamate derivatives (oxamyl and ethiofencarb) were selected. Hydrolysis was performed in purified buffered water at different pH in the range 7.0–10.0 (ionic strength = 2.5 mM, $T = 25°C$). At pH = 8.0, isofenfos and disulfoton ($t_{1/2} \approx 4$ years, $t_{1/2} \approx 1$ year, resp.) were found to be far more stable than isazofos ($t_{1/2} \approx 5$ months), ethiofencarb and profenofos ($t_{1/2} < 1$ month), themselves more stable than oxamyl ($t_{1/2} \approx 1$ day). As expected, a strong dependence on pH was observed for all pesticides: the rate of degradation increased when the pH increased. Degradation products were identified by GC–MS and/or LC–MS. Possible structures are presented in the article.

Keywords: Organophosphorus; Carbamate; Pesticides; Hydrolysis; Kinetics; Degradation products

INTRODUCTION

The French West Indies Island, Martinique, is one of the main banana-producing areas in the world (277 000 tons in 1997). Great varieties and amounts of pesticides are applied for the control of soil-dwelling pest of banana crops (about 1300 tons/year according to the French Environmental Water Control Agency). The geographical context of the island (small land surface: 1100 km^2, banana fields very steep) and climatic conditions make the contamination of surface and ground waters a permanent risk. Organophosphorus and *N*-methylcarbamate pesticides were popular candidates to replace the more persistent organochlorine compounds suspected of being bio-accumulated [1,2]. The selected pesticides, used copiously in Martinique, are detected in significant amounts in river water from the island (French Environmental Water Control Agency).

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After release in the aquatic compartment, degradation via hydrolysis is among the main transformation pathways [3], and particularly for organophosphorus esters and carbamate derivatives. Hydrolysis may occur at several reactive centres in the pesticide molecule, OH^- or H_2O acting as nucleophilic reagents [4]. Organophosphorus pesticides possess two reactive centres: electron-deficient carbons and phosphorus atoms. Carbamate pesticide hydrolysis is known to proceed through alkaline catalysis, with reaction of the hydroxide ion with the carbonyl function or with abstraction of hydrogen in the α position with respect to the carbonyl [5–7]. These reactions lead to the formation of degradation products which may be more toxic than the starting material.

The main aim of this study was to determine the major degradation products of the selected pesticides (profenofos, isazofos, isofenfos, disulphoton, oxamyl and ethiofencarb) in weakly alkaline laboratory water. In addition, the kinetics of the alkaline process has been studied because it corresponds with that occurring in river water ($8.0 < pH < 9.0$).

EXPERIMENTAL

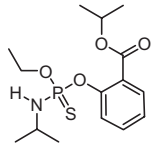
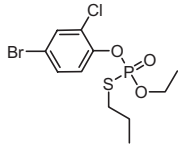
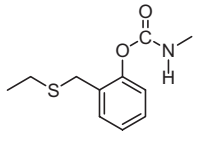
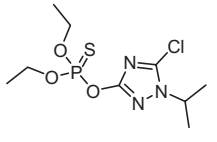
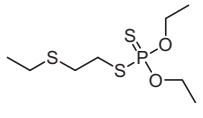
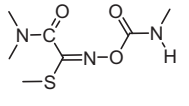
Reagents, Materials and Sample Preparation

Disulfoton, ethiofencarb, isofenfos, isazofos, profenofos, oxamyl, ethyl acetate, methanol, di-sodium hydrogenphosphate and sodium dihydrogenphosphate were commercial products of the purest grade available (Fluka–Riedel De Häeńs or Cluzeau Info Labo Paris-France). The chemical formulae of the pesticides are listed in Table I. All solutions were prepared with purified water (Millipore milli-Q system – Millipore αQ: resistivity 18 MΩ cm; dissolved organic carbon < 0.1 mg/L). A set of standards was prepared by dissolving each pesticide in methanol. Appropriate dilutions with purified water were performed to achieve the desired concentrations. The stability of methanolic solutions was controlled (care was taken to minimize the risk of organophosphorus pesticide transesterification [8]). Standards solutions were prepared weekly or daily and stored at 4°C in the dark. pH measurements were carried out using a Tacussel PHM 240 pH meter. The ionic strength (2.5 mM) and pH were controlled by using phosphate buffer. Hydrolysis experiments were performed in brown bottles to prevent photochemical processes. As soon as the solutions were prepared, the bottles were placed in a thermostated oven at 25°C. Samples were withdrawn at desired reaction times. Alkaline solutions of each pesticide were allowed to react ($pH = 9.0$, 25°C) to reach 30–40% of pesticide degradation for the analyses of hydrolysis products.

Chromatographic Analysis

High-performance liquid chromatography was used together with a diode array detector to quantify pesticides for kinetic studies (a Waters system equipped with a Waters 600 pump, Waters 717 autosampler and Waters 996 photodiode array detector). Two columns were used: Kromasil C_{18} 250 mm–4.6 mm, purchased from Alltech, and Omnispher C_{18} 100 mm–3.5 mm, purchased from Varian. The eluent was a mixture of methanol/water, the composition of which was adjusted to reach an optimal separation. The detection wavelength was chosen for each pesticide to obtain the best signal-to-noise ratio (Table I). The detection limits of the method are listed in Table I.

TABLE I Structure, detection limits of HPLC method, apparent first-order rate constant (k_{app}) and half-lives of pesticide hydrolysis determined at pH = 8.0 (standard deviations were determined from three measurements)

Pesticide	*Detection wavelength* *Detection limits*[a]	k_{app} (per hour)[b]	$t_{1/2}$[b]
Isofenfos 	220 nm 45 μg/L	$2.3 \pm 0.3 \times 10^{-5}$ ($R^2 = 0.936$)	1250 days
Profenofos 	220 nm 11 μg/L	$1.92 \pm 0.05 \times 10^{-3}$ ($R^2 = 0.994$)	15 days
Ethiofencarb 	220 nm 60 μg/L	$1.34 \pm 0.05 \times 10^{-3}$ ($R^2 = 0.996$)	22 days
Isazofos 	201 nm 128 μg/L	$2.1 \pm 0.3 \times 10^{-4}$ ($R^2 = 0.997$)	138 days
Disulfoton 	220 nm 28 μg/L	$1.2 \pm 0.2 \times 10^{-4}$ ($R^2 = 0.992$)	239 days
Oxamyl 	250 nm 9 μg/L	$2.18 \pm 0.02 \times 10^{-2}$ ($R^2 = 0.997$)	32 h

[a]Determined using a signal-to-noise ratio equal to 3. [b]At pH = 8.0 in phosphate buffer.

GC–MS and LC–MS apparatus were used to identify the degradation products. GC–MS experiments were performed with a Hewlett-Packard 5890 Serie II GC–Hewlett-Packard 5972 MS equipped with a Hewlett Packard 6890 autosampler. The injector was set at 225°C, in splitless mode (injected volume: 1 μL; splitless time: 0.5 min). The column was purchased from Alltech (AT-5-MS fused silica column (30 m × 0.25 mm i.d.) with 5% diphenyl–95% dimethylpolysiloxane (a film thickness of 0.25 μm)). The detector temperature was maintained at 200°C (transfer line at 280°C). The oven was programmed as follows: isotherm at 60°C for 3 min, ramp to

180°C (40°C/min) followed by a slower ramp to 280°C (10°C/min). High-purity helium was used as a carrier gas (1 mL/min). The mass spectrometer operates in the total ion chromatogram (with a mass range of 50–450 Da). *N*-methyl carbamates could not be analysed with GC–MS because they are known to be thermally decomposed [9]. LC–MS experiments were performed at the 'Service Central d'Analyses' of CNRS (Lyon, France) with a Hewlett-Packard HP1100-MSD system working in a positive or negative electrospray atmospheric pressure ionization source. Post-column additions (0.2 mL/min) were performed: formic acid/methanol for positive API and ammonium formate/formic acid buffer for negative API. Operating conditions for the nebulization were set as follows: capillary potential 4000 V, auxiliary gas N_2 at 11 L/min. The fragmenter was set at 20 V and 120 V alternatively after optimization. The column was a Varian Omnispher C_{18} 100 mm × 3.5 mm (3 μm) thermostated at 40°C.

Solid-Phase Extraction Procedure

Extractions were performed using single-use Waters Oasis cartridges (3 mL, 60 mg of solid phase). A 500 mL aliquot of solution was passed through an SPE cartridge (at a flow rate of about 2 mL/min), after preconditioning the cartridge with 2 mL of ethyl acetate followed with 2 mL of purified water. The adsorbed compounds were eluted with either 2 mL of ethyl acetate or 2 mL of methanol. The organic solution was collected in a 4-mL vial. The samples were then analysed by GC–MS (elution with ethyl acetate) or LC–MS (elution with methanol).

RESULTS AND DISCUSSION

Kinetics Studies

The hydrolysis of individual pesticides in aqueous buffered solutions was studied at 25°C and with an ionic strength of 2.5 mM (phosphate buffer). These values corresponded to the mean values recorded in river water of Martinique. A low concentration of phosphate buffer does not influence the rate of pesticide hydrolysis contrary to a high concentration of phosphate buffer, as demonstrated for phenylurea pesticide hydrolysis [10]. Samples were withdrawn at different reaction times and analysed immediately. Care was taken to avoid light exposure.

The hydrolysis of pesticides can be treated as a pseudo-first-order reaction in buffered solutions of constant pH. The following equation applies:

$$-\frac{d[\mathrm{C}]}{dt} = k_{\mathrm{app}}[\mathrm{C}]$$

the apparent rate constant k_{app} is usually assumed to be the sum of three terms $k_{\mathrm{a}}[\mathrm{H}^+]$, k_{n} and $k_{\mathrm{b}}[\mathrm{HO}^-]$, respectively, corresponding to acid, neutral and basic pathways [11]. Hence, the plot of the logarithm of the normalized concentration as a function of the reaction time (as shown in Fig. 1) gives straight lines, the slope of which identifies $-k_{\mathrm{app}}$. The values are listed in Table I. The half-lives calculated from these k_{app} values were about 4 and 1 year for isofenfos and disulfoton, respectively, about 5 months for isazofos, less than 1 month for ethiofencarb and profenofos, and

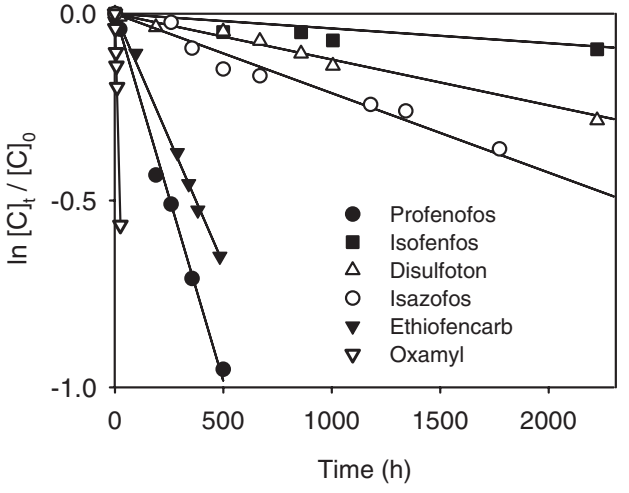


FIGURE 1 Hydrolysis kinetics of pesticide in pure buffered aqueous solutions (pH = 8.0) $[\text{pesticide}]_0 =$ 1.0 mg/L.

about 1 day for oxamyl, which was the most easily degraded. Similar values have been previously reported for oxamyl [12] and ethiofencarb [13].

Effect of pH on the Rate of Hydrolysis

As previously mentioned, hydrolysis may be catalysed in acid or basic medium according to the chemical structure of compounds. We focused our investigation on the alkaline process because of the pH of river water of Martinique. Experiments have been performed in the pH range 7.0–10.0. The apparent first-order constants, k_{app}, were determined by plotting the logarithm of the normalized concentration *vs.* the reaction time, for each pH value. Then, k_{app} values were plotted *vs.* pH in semi-logarithmic form (Fig. 2). Straight lines were obtained for three pesticides: profenofos, ethiofencarb and oxamyl. The slope of the straight lines was about 1.0, indicating that the hydrolysis was of first order with respect to hydroxide ions (slopes equal to 0.31, 0.53 and 0.70 were determined for disulfoton, isazofos and isofenfos, respectively, but with a low accuracy, as shown by a regression coefficient lower than 0.90). From the y-intercept, second-order rate constants for the reaction between hydroxide ions and pesticides can be determined: 1.17 M/s, 2.67 M/s, 0.53 M/s for profenofos, oxamyl and ethiofencarb, respectively.

Hydrolysis Products

Phosphate-buffered solutions containing the pesticide (1 mg/L) were aged until 30–40% of pesticide degradation. Then, evaporation under reduced vacuum or extraction using SPE cartridges with 500 mL of solution passed through and 2 mL of methanol or ethyl acetate was performed to increase the concentration of major hydrolysis products.

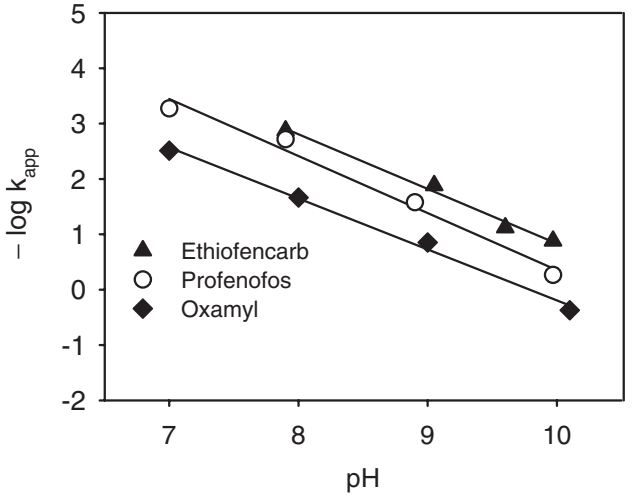


FIGURE 2 Apparent rate constants of pesticide hydrolysis as a function of the pH of the solution.

Degradation Products of Oxamyl and Ethiofencarb

LC–MS analyses of aged solutions of oxamyl in positive electrospray revealed a unique degradation product with $MH^+ = 163$ Da and $MNa^+ = 185$ Da. This is in agreement with the structure of the oxime derivative (2-dimethylamino-*N*-hydroxy-2-oxo-thioacetimidic acid methyl ester-R-OH derivative) as mentioned by Harvey and Han [12].

Analyses of aged solutions of ethiofencarb by LC–MS showed the formation of a unique degradation product with $MNa^+ = 191$ Da (API+) and $M\text{-}H^+ = 167$ Da (API-) corresponding to 2-ethylsulphanylmethylphenol (R-OH derivative) as described by Sanz-Asenzio *et al.* [13].

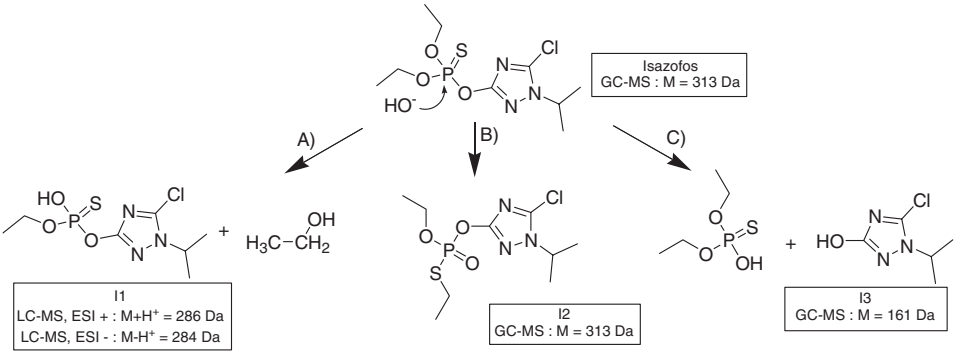
The formation of these two degradation products (R-OH derivatives) involves the same mechanism corresponding to either an addition of HO^- onto the carbonyl with a further elimination of the RO^- leaving group or an abstraction of the hydrogen of the methyl carbamate moiety again evolving with elimination of the RO^- group.

Degradation Products of Profenofos

GC–MS and LC–MS analyses revealed the formation of a unique product: 4-bromo-2-chlorophenol. This is formed by reaction of a hydroxide ion with a phosphorus atom followed by a rearrangement leading to the formation of the phenol derivative after elimination of the phosphorus-containing moiety. This classical pathway has been frequently mentioned [14,15].

Degradation Products of Isazofos

Three structures can be proposed according to mass spectra obtained from GC–MS and LC–MS experiments (Scheme 1). This indicates a reaction of hydroxide ion with phosphorus atom, followed by the elimination of the $R\text{-}O^-$ group thus leading to the formation of I1 (elimination of $^-O\text{-}Et$) and I3 (corresponding to the other $R\text{-}O^-$ anion). It is worth noting the formation of the isomer of isazofos (I2). Checks were



SCHEME 1 Proposed pathway for the degradation of isazofos.

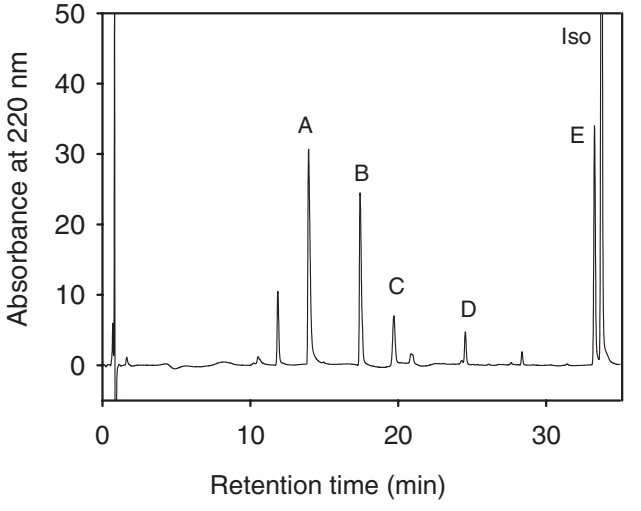
carried out to ensure that this product was not present after the preparation of the solution and that it did not correspond to an analytical artefact. Isazofos isomer could be formed by a rearrangement of a reaction intermediate after the addition of HO^-. I3 seemed to be the major degradation product. This has already been mentioned for the degradation of isazofos in soils described by Somasundaram *et al*. [16].

Degradation Products of Isofenfos

Figure 3 presents the LC–UV chromatogram obtained upon analysis of an aged solution of isofenfos (40% of conversion). LC–MS experiments allow the proposition of the structures as mentioned in Fig. 3. GC–MS analysis reveals the presence of E and of an additionnal product: isopropylsalicylate (IPS). These structures show that hydroxide ion may react with three different sites on the isofenfos molecule. The product B arises from reaction of hydroxide with the carbonyl ester function followed by further elimination of the $^-$O-iPr group. Addition onto the P=S moiety leads to the formation of IPS after elimination of the $^-$O-aryl group. The formation of D involves the elimination of the iPr-NH^- moiety. A further reaction of D with hydroxyde ions leads to A. Hydroxyl ions may also abstract the hydrogen of the amino part leading to E after an intramolecular rearrangement with the elimination of the $^-$O-iPr group [14,17]. According to LC–UV data, the products A, B and E should represent the major degradation products.

Degradation Products of Disulfoton

Four structures can be proposed according to the results of the analysis of disulfoton aged aqueous solutions by GC–MS and LC–MS after solid-phase extraction (Scheme 2). Reaction of hydroxide ions with the phosphorus atom leads to D1 and D2, the latter further dimerizing to D3 [18]. A second possible pathway involves the reaction of hydroxyde ion with CH_2 in the α position of the thiophosphoryl ester [9,19], followed by a cross-reaction leading to D4. A similar reaction was observed by the Pehkonen's team [9,18–20] upon hydrolysis of phorate and terbufos, but this was not found for disulfoton. Sn_1 or $SN_{intramolecular}$-type mechanisms were proposed to explain the formation of D4 from phorate or terbufos, and it was thought that the presence of the additional CH_2- between the two sulphur atoms disadvantages these



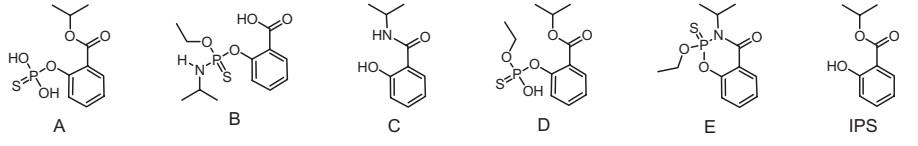
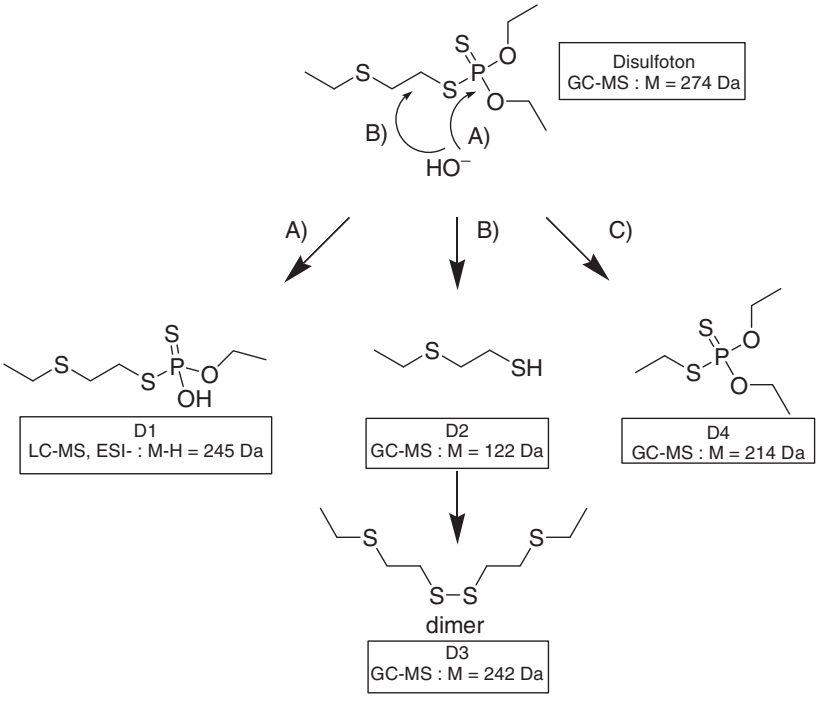


FIGURE 3 HPLC chromatogram at 220 nm of an aqueous solution of isofenfos (40% of conversion), extracted with OASIS™ HLB SPE cartridges. *Iso* stands for Isofenfos. IPS was not shown in the LC chromatogram.



SCHEME 2 Proposed pathway for the degradation of disulfoton.

processes [18]. No information can be given concerning the yield of the different hydrolysis products because of the absence of standards.

Conclusion

The hydrolysis of the selected pesticides is greatly influenced by the pH: the more alkaline the solution, the faster the hydrolysis. Oxamyl appears to be degraded very rapidly. Second-order rate constants for the reaction between hydroxide ion and pesticide have been found to be 1.17 M/s, 2.67 M/s and 0.53 M/s for profenofos, oxamyl and ethiofencarb, respectively. The general trends of organophosphorus and carbamate pesticides were already known, but our study evidenced the degradation products of the six starting compounds. The hydrolysis reaction seems to be a quite simple process for profenofos, oxamyl and ethiofencarb: order 1 with respect to pesticide and hydroxide ion and only one degradation product. It seems to be different to the three other organophosphorus pesticides: no integer order with respect to hydroxide ion and many degradation products. Carbamate pesticides undergo the classical hydrolysis pathway with the elimination of the methyl carbamate moiety to the formation of the R-OH derivative: the oxime and phenol derivative for oxamyl and ethiofencarb, respectively. A general behaviour is shown for the hydrolysis products of organophosphorus pesticides, corresponding to the reactivity of hydroxide ion with the P=S bond and leading to the cleavage of ester bonds. Profenofos did not shown this behaviour because it already presented a P=O bond. Additionally, specific reactions or rearrangements are also observed according to the chemical structure of the pesticide. All the degradation products are far more stable than the initial compound.

Acknowledgements

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