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Photocatalytic pollutant removal in water at room temperature: case study of the total degradation of the insecticide fenitrothion (phosphorothioic acid O,O-dimethyl-O-(3-methyl-4-nitro-phenyl) ester)

Mikhail Kerzhentsev [1], Chantal Guillard, Jean-Marie Herrmann *, Pierre Pichat

URA au CNRS Photocatalyse, Catalyse et Environnement, Ecole Centrale de Lyon BP 163, 69131 Ecully Cedex, France

Abstract

The photocatalytic purification of water containing fenitrothion has been performed in TiO_2 aqueous suspensions. The mineralization into CO_2, $H_2PO_4^-$, SO_4^{2-}, NO_3^- was achieved. Several intermediates have been identified by HPLC and GC/MS. They illustrate the transformation of P=S into P=0, the splitting between the phosphorous part and the aromatic moiety and the transfer of methyl or methoxy groups. Formate ions, principally produced from the CH_3O and CH_3 groups and acetate ions were also detected as intermediate products.

Keywords: Photocatalytic pollutant removal; Insecticides; Fenitrothion

1. Introduction

Many chemical compounds, among which pesticides, are successfully destroyed by heterogeneous photocatalysis [1–3]. Organophosphorous compounds, which are known as inhibitors of acetylcholinesterase [4,5], are principally used as insecticides. Most of them are highly toxic for human beings and mammals [5]. In the environment, they progressively disappear by hydrolysis of their ester functionality [4]. In water they are either not degradable [6,7] or hardly decomposed by biological treatment [7,8].

Two organophosphorous insecticides, DDVP (dimethyl-2,2-dichlorovinyl phosphate) and DEP (dimethyl-2,2,2-trichloro-1-hydroxyethyl phosphonate) have been reported to be totally degraded by photocatalysis [8]. More recently, the disappearance of DEP and of fenitrothion, the title insecticide, by photocatalytic treatment combined with ozonation was also studied [9]. The photocatalytic treatment alone was a little more rapid than ozonation for pesticide disappearance but it was evidenced that the rate of TOC reduction was increased by ozonation followed by the photocatalytic degradation.

Several other phosphorous-containing insecticides (paraoxon or 4-NPDEP or 4-nitrophenyl diethylphosphate [10,11]; parathion or diethyl-p-nitrophenyl thiophosphate; malathion or 0,0-dimethyl-S- (1,2-dicarbethoxyethyl) phosphorodithioate; 4-nitrophenylethylphenyl phosphinate and 4-nitrophenylisopropylphenyl phos-

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* Corresponding author.

[1] Permanent address: Institute of Catalysis, Novossibirsk, 630090, Russia

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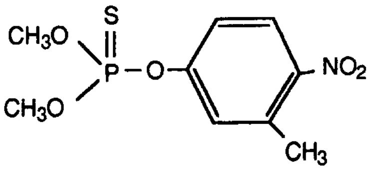
phinate [11]) were also photocatalytically mineralized. The disappearance rate was dramatically increased by addition of strong inorganic oxidants ($K_2S_2O_8$, H_2O_2, $NaIO_4$ and $KBrO_3$). However, no attempt was made to identify the organic intermediates. Chlorinated organophosphorous insecticides such as dichlorvos (2,2-dichlorvinyl dimethyl phosphate) [8,12] and tetrachlorvinphos ((Z)-2-chloro-1-(2,4,5-trichlorophenyl, ethenyl dimethyl, ethenyl dimethyl phosphate) [13] were also totally mineralized. In the latter case, several organic intermediates were identified. Other organophosphorous compounds such as pesticide precursors [7] or surfactants [14] were also successfully eliminated in aqueous suspensions of TiO_2.

The photocatalytic destruction of various aromatic compounds has been previously carried out in our laboratory [15] with the aim of evaluating the efficiency of the process, identifying the nature of the intermediates and elucidating the reaction pathways. This study concerns the degradation of fenitrothion



which contains four types of heteroatoms. The objective was to determine whether these heteroatoms are mineralized and to attempt to determine the fate of each element of the molecular structure.

2. Experimental

2.1. Materials

Fenitrothion (99.3% purity) was obtained from the Institute Organic of Industrial Chemistry (Warsaw) and used as received, whereas most degradation intermediates were purchased from Aldrich. The photocatalyst was TiO_2 Degussa P-25 (non porous, mainly anatase, 50 $m^2\ g^{-1}$).

2.2. Photoreactor

The reaction was carried out in a static batch photoreactor (ca. 90 cm^3). The radiant flux was provided by a Philips HPK 125 W UV-lamp, filtered by water (2.2 cm thick) and, unless otherwise indicated, a Corning 0.52 filter transmitting wavelengths >340 nm. It was measured with a calibrated radiometer and found to be equal to 50 mW/cm^2. It corresponded to about 1.6×10^{17} photons/s potentially absorbable by TiO_2. The volume of solution was 20 cm^3 and the mass of TiO_2 was 50 mg.

2.3. Analyses

Fenitrothion was analyzed by GC-FID (Intersmat chromatograph model IGC 120 FL) using a DB-17 column, 0.545 mm i.d., 1.0 μm film thickness, at 523 K. Anions and cations were analyzed by HPLC using a Waters 501 isocratic pump and a Waters 431 conductivity detector. For the analysis of anions, a IC-PAX anion column (5 cm long, 4.6 mm i.d.) was used with lithium benzoate as eluent (1 ml/min) for the detection of acetate, formate, NO_2^- and NO_3^-; lithium gluconate was chosen as eluent (1 ml/min) for the detection of SO_4^{2-}, HPO_4^{2-}, NO_2^- and NO_3^-. The analysis of cations was performed by using a Vidac column with HNO_3 (2.5 mmol/l, 1.5 ml/min) as eluent. The kinetics of H^+ formation was monitored with an ionoprocessor (Tacussel Electronique). CO_2 evolution was followed by on-line gas chromatography using a GC-catharometer (Intersmat, model GC 121 MB) equipped with a Porapak Q column, 3 m long, 6.3 mm i.d..

To identify the intermediates after various periods of irradiation, the suspension was filtered, acidified with HCl to pH = 2–3 and the organics were extracted by dichloromethane. The solution was then concentrated using a rotatory evaporator (the volume was decreased from 20 cm^3 to 10–50 μl) and injected in a GC/MS analyzer (HP 5890 and 5971A) connected to a microprocessor HP 386 and equipped with a CP-Sil-5CB column, 25 m long, 0.32 mm i.d., 1.2 μm film thickness and an ion generator (electron ionization 70 V).

2.4. Degradation procedures

The suspension was first agitated in the dark for 30 min to reach equilibrated adsorption of fenitrothion on titania. Most results were obtained with an initial fenitrothion concentration of 15 ppm (5.41×10^{-5} mol l^{-1}).

3. Results and discussion

3.1. Effects of UV-irradiation on fenitrothion disappearance with or without TiO_2

At $\lambda > 340$ nm the disappearance of fenitrothion was negligible in the absence of TiO_2 and occurred in its presence (Fig. 1). The mineralization of fenitrothion into CO_2 was obtained in a much shorter time by photocatalysis at $\lambda > 340$ nm than by direct photolysis at $\lambda > 290$ nm (Fig. 2).

Therefore the degradation carried out at $\lambda > 340$ nm with TiO_2 can be considered to be uniquely due to the photocatalysis and although the usage of shorter wavelengths can be of practical interest with titania, wavelengths > 340 nm were employed to study the photocatalytic degradation.

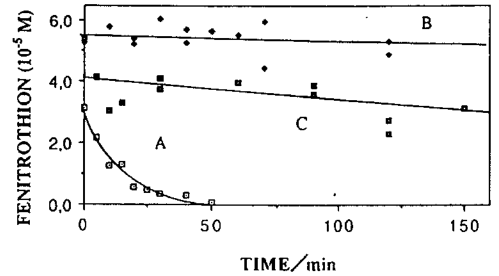


Fig. 1. Photocatalytic (curve A) and photolytic (curve B) degradation of fenitrothion ($\lambda > 340$ nm, $\phi > 50$ mW/cm², $C_0 = 15$ ppm). Curve C was obtained with TiO_2 in the dark.

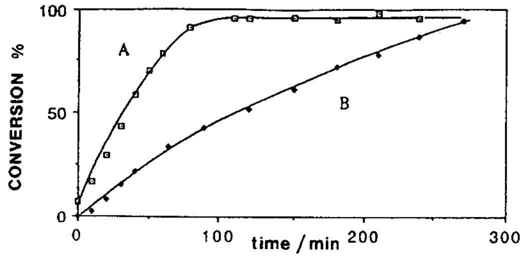


Fig. 2. Conversion of fenitrothion into CO_2 by photocatalytic degradation at $\lambda > 340$ nm (curve A) and by direct photolysis at $\lambda > 290$ nm (curve B).

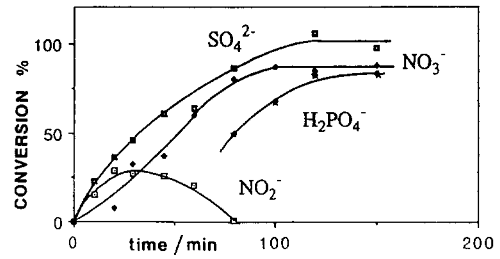


Fig. 3. Kinetics of formation of inorganic ions during fenitrothion photocatalytic degradation (in % of the expected amounts for the total mineralization). To detect phosphate ions, the suspension was basified at pH = 12 after irradiation (see text).

The kinetics of fenitrothion disappearance followed an apparent first-order kinetics, which is consistent with a Langmuir–Hinshelwood mechanism at a low coverage resulting from low concentrations.

3.2. Total mineralization

In agreement with the overall reaction:

$$C_9H_{12}O_5NPS + 13/2O_2 \rightarrow 9CO_2 + 3H_2O + NO_3^- + SO_4^{2-} + H_2PO_4^- + 4H^+$$

the inorganic anions NO_3^-, SO_4^{2-} and $H_2PO_4^-$ (Fig. 3) and CO_2 (Fig. 2) were progressively formed.

Dihydrogenophosphate ions were not found in the liquid phase at a pH below 6, since they are known to remain adsorbed on TiO_2 in acidic media [16–18]. Upon increasing the pH to 12 with NaOH, ca. 80% of the expected amount of phosphate was recovered. The stoichiometric quantities of SO_4^{2-} ions (Fig. 3) and of CO_2 (Fig. 2) expected from total mineralization were obtained within irradiation times of ca. 100 min. The nitro group was first mineralized into nitrite which was progressively oxidized into NO_3^- (Fig. 3). Ammonium ions were also detected (2 to 4% with respect to nitrate).

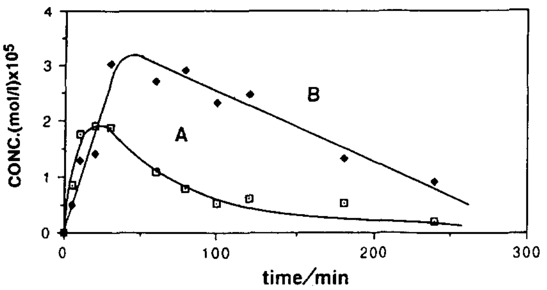
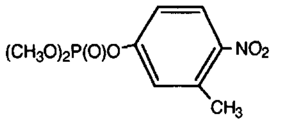
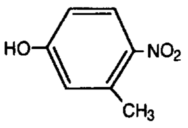
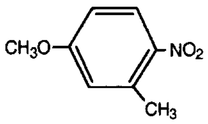
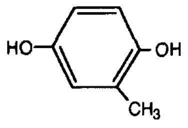
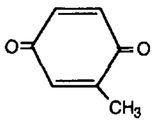


Fig. 4. Kinetics of formation and disappearance of formate (A) and acetate (B) anions during fenitrothion photocatalytic degradation.

Table 1
GC-MS identified intermediates in fenitrothion photocatalytic degradation

1. fenitrooxon	
2. 3-methyl-4-nitrophenol	
3. 3-methyl-4-nitroanisole	
4. 2-methylhydroquinone	
5. 2-methyl-1,4-benzoquinone	
6. phosphonic acid dimethyl ester	$(CH_3O)_2P(O)H$
7. phosphorothioic acid, O,O,S-trimethyl ester	$(CH_3O)_2(CH_3S)PO$

Compounds 2–5 were identified by comparison with authentic compounds; the mass spectra of compounds 1 and 7 were in accordance with the mass of the MS library; the formula of compound 6 is derived from our interpretation of the mass spectrum.

3.3. Identification of intermediates

HPLC peaks corresponding to acetate and formate ions were detected as a result of the fenitrothion photocatalytic degradation. Their kinetics of formation/disappearance is shown in Fig. 4.

The maximum of formate was obtained at 25 min of UV-irradiation, whereas that of acetate was obtained at a treatment time ca. twice longer. These observations suggest that formate would originate from the methoxy and methyl groups of fenitrothion, whereas acetate ions would result from the degradation of the aromatic ring.

The other intermediates identified by GC-MS are listed in Table 1. The identifications were made by comparison with commercially available standards (compounds 2–5) or with mass spectra reported in the literature (compound 1,7) or, if no matching spectrum was found, by interpretation of the mass spectrum (compound 6). The main mass peaks of fenitrooxon, listed in decreasing order of intensity, were respectively : $m/z=244$, 109, 261, 127, 79 and 150. $(CH_3O)_2P(O)H$ (retention time 4.9 min) corresponded to the typical fragments at $m/z=79$, 80, 47, 29, 95, 66, 109 and 110, while the mass fragments of $(CH_3O)_2P(O)\text{-}SCH_3$ (retention time 13.9 min) were at $m/z=110$, 79, 156, 47, 126, 95 and 141, with a confidence limit of 94% with respect to the literature mass spectrum included in the spectrometer library (Fig. 5).

Fenitrooxon seems to be one of the primary products formed during the photocatalytic degradation of fenitrothion, since the difference between the two compounds is only the substitution of sulfur by oxygen in the P=S bond and since no other P=S group-containing compounds were found. The other aromatic intermediates listed in Table 1 result from the splitting of the phosphorus-phenoxy bond with or without the removal of the nitro group. Considering previous results on the degradation of substituted benzenes [3,15], formation of these intermediates was expected.

Note that 2-methylhydroquinone and 2-methyl-1,4-benzoquinone were also observed or proposed

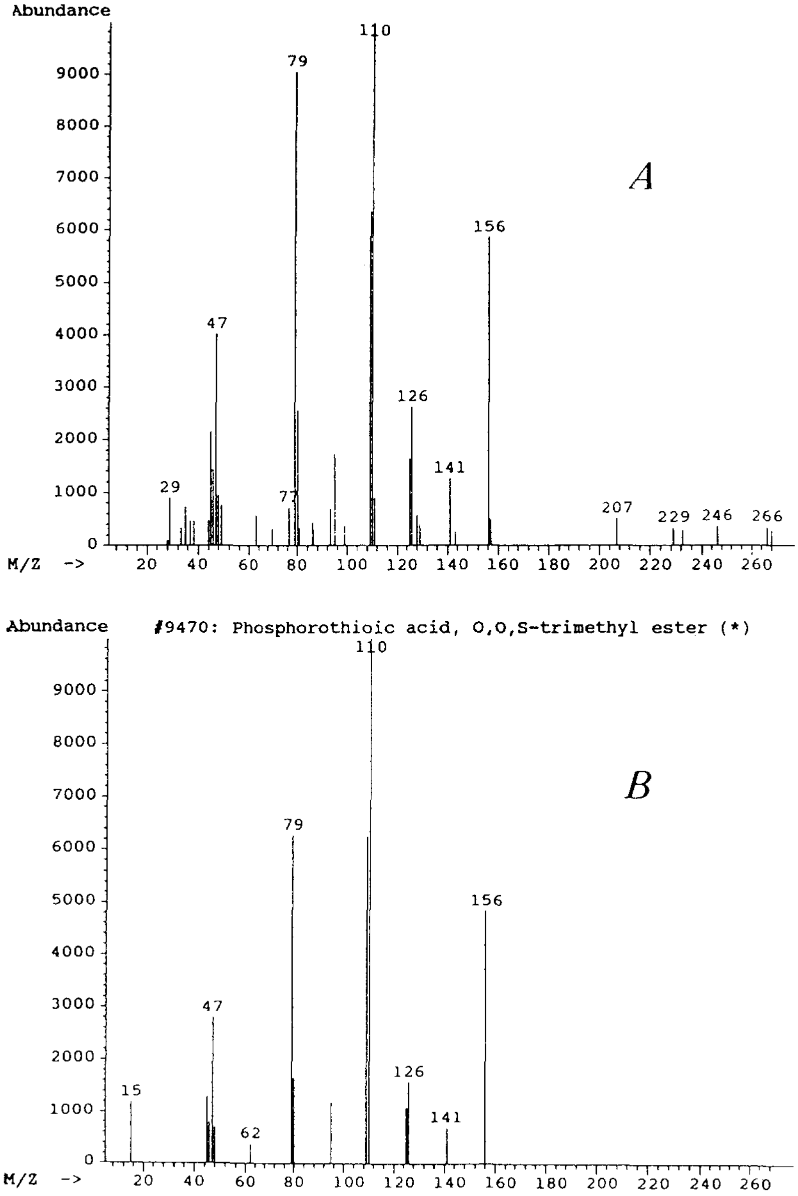


Fig. 5. Mass spectrum (A) corresponding to the GC peak attributed to phosphorothioic acid, O,O,S-trimethyl ester; (B) mass spectrum of this compound in the GC-MS library. Mass spectrum A was recorded only for $28 \leq m/z \leq 270$.

as intermediates when fenitrothion was degraded by bacteria [19]. The formations of 3-methyl-4-nitroanisole and of phosphorothioic acid O,O,S-trimethylester imply the transfer of methyl or methoxy groups. The presence of compound 6 indicates the reduction of P^V into P^{III}, possibly by H atoms, whose existence might also be at the origin of NH_4^+ formation. These reactions illustrate the complexity of the photocatalytic degradation in water.

Acknowledgements

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