

Unequivocal Identification of Compounds Formed in the Photodegradation of Fenitrothion in Water/Methanol and Proposal of Selected Transformation Pathways

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The photodegradation of fenitrothion was examined in a mixture of distilled water/methanol (5:1). The UV irradiation was carried out with a high-pressure Hg lamp during 7 h. For the identification of further breakdown products, fenitrooxon and carboxyfenitrothion were also irradiated under experimental conditions identical to those for fenitrothion. The identification of the breakdown products formed was carried out by gas chromatography-mass spectrometry (GC-MS) with electron impact (EI) and comparison with authentic standards synthesized in the laboratory. A total of 21 photoproducts of oxidation, isomerization, denitration, and solvolysis that may be of concern in environmental studies were unequivocally identified. Among them were formyldenitrofenitrothion, carbomethoxydenitrofenitrooxon, and hydroxymethylidenitrofenitrooxon. A proposed mechanism of the process is presented. Selected pathways for the photodegradation of fenitrothion were examined: (i) degradation through hydrolysis, with eventual remethylation; (ii) P=S to P=O oxidation; (iii) denitration; and (iv) oxidation of the methyl substituent through hydroxymethyl and formyl to give the corresponding carboxy derivatives.

INTRODUCTION

Organophosphorus pesticides are being used as insecticides in animal husbandry and in many agricultural applications for crop protection or elimination of ectoparasites. As a consequence of their widespread use, residue levels varying from a few nanograms per liter to 10 $\mu\text{g/L}$ and from 10 ng/g to 1000 ng/g in water and soil samples, respectively, have been detected (Barceló et al., 1990, 1991; Durand and Barceló, 1991; Day, 1991). After application, their environmental fate is poorly understood, although several degradation pathways such as hydrolysis, photolysis, and microbial transformation may be possible. As an example, after aerial application of fenitrothion, the subject of the present study, several derivatives such as dimethylaminofenitrothion, *S*-methylfenitrothion, aminofenitrothion, and 3-methyl-4-nitrophenol have been detected at trace level in stream water (Day, 1991).

Photolysis is one of the major transformation processes affecting the fate of pesticides in the aquatic environment. In this context, three main light sources are used for carrying out model photolysis experiments, i.e., natural summer sunlight, suntest apparatus, and Hg lamp. It has been demonstrated that use of different light sources under identical aqueous conditions can produce similar degradation products with the only difference in the kinetics of formation (Chukwudebe et al., 1989; de Bertrand and Barceló, 1991; Pal et al., 1991). Although the use of a xenon arc lamp ($\lambda > 290 \text{ nm}$) is preferred, since the results obtained can be more easily compared to real sunlight conditions, mercury lamps, with λ close to 254 nm, have been used for convenience when the photodegradation of the compounds is too slow, leading to a faster photodegradation (Miller and Zepp, 1983; Zafiroiu et al., 1984).

As there is a need to identify as many photodegradation products as possible, large amounts of the parent pesticide

need to be photoirradiated and the availability of well-characterized standards is also convenient. In addition, due to the low water solubility exhibited by many of these organophosphorus pesticides, use of a photochemically inert organic cosolvent, such as acetonitrile or methanol, is mandatory (Choudry and Webster, 1985; de Bertrand and Barceló, 1991; Grunwell and Erickson, 1973). Because of this, and to avoid solubility problems, many studies have been conducted even in pure organic solvents such as benzene (Chukwudebe et al., 1989), methanol (Abdou et al., 1988; Pal et al., 1991), or oxygenated hexane (Greenhalgh and Marshall, 1976). The irradiation time is also very variable, from 1 to 72 h, and depends on the kinetics of the compound of interest.

Numerous studies on the photochemical transformations of a variety of organophosphorus pesticides, e.g., parathion-ethyl and -methyl, malathion, diazinon, iofenphos, fenthion, methidation, chlorpyrifos, chlormephos, and fenitrothion, in solution as well on plant and leaf surfaces have been reported (Chukwudebe et al., 1989; Greenhalgh and Marshall, 1976; National Research Council Canada, 1975; Buckland and Davidson, 1987; Walia et al., 1988, 1989a,b; Wang and Hoffman, 1991). It is known that the phosphorothioate (P=S) pesticides, such as parathion and fenitrothion, are converted by photooxidation into their oxon (P=O) analogues. These oxo compounds are of concern because they are the activated forms of the organophosphorus pesticides, with a considerably stronger inhibition of acetylcholinesterase activity than that exhibited by the parent compounds (Eto, 1974; Miyamoto et al., 1978). On the other hand, the *S*-methyl isomers, which also exhibit a different biological activity compared with that of their *O*-alkyl precursors, are produced by thermally induced isomerization. This isomerization can take place during the synthetic procedure or the storage of the pesticide or by photolysis (Wilkins, 1990). For the case of fenitrothion (V, see Scheme 2), other degradation compounds such as the carboxyfenitrothion (XX) and 3-methyl-4-nitrophenol

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(IX) have also been reported in photolysis studies (Greenhalgh and Marshall, 1976; National Research Council Canada, 1975; Takimoto, 1984; Mikami, 1985).

After photodegradation experiments have been completed, isolation of the reaction products is required with further identification by gas chromatography-mass spectrometry (GC-MS). One of the main problems in the identification of the photoproducts is that most of them are not commercially available. Therefore, structural confirmation needs to be carried out by comparison with authentic standards that should be independently synthesized. In fact, the lack of standards for the correct identification of the different photoproducts could lead to a misinterpretation of results obtained, as was pointed out in a recent paper about fragmentation of substituted phenyl phosphorothioates (Wilkins, 1990).

Although a partly qualitative identification by GC-MS of some photodegradation products of fenitrothion has been reported (Greenhalgh and Marshall, 1976; National Research Council Canada, 1975; Takimoto, 1984; Mikami et al., 1995), no other papers have appeared in the literature that confirm previously obtained results or find new photolysis compounds.

The purpose of our research was to examine the effects of a high-pressure mercury lamp jacketed with a water-cooled quartz filter (to obtain a maximum intensity of UV light close to 254 nm) on the transformation of fenitrothion in water-methanol, to isolate the transformation products, to perform their unequivocal identification by comparison with authentic standards from synthetic origin, and to propose a rational scheme of photodegradation. This work is a continuation of work from our group concerning pesticide photolysis studies in water (de Bertrand and Barceló, 1991; Durand et al., 1991a,b).

EXPERIMENTAL PROCEDURES

Synthesis of Compounds. The IR spectra were recorded with a Bomem MB-120 spectrometer. The ¹H (300 MHz), ¹³C (75 MHz), and ³¹P NMR (121 MHz) spectra were recorded with a Varian Unity 300 spectrometer. All NMR spectra were performed in neutralized deuteriochloroform solutions, and chemical shifts are given in parts per million downfield from either tetramethylsilane (for ¹H and ¹³C) or 1% trimethyl phosphite (deuteriochloroform solution in a capillary tube) (for ³¹P).

Preparation of Phosphorothioates IV, VII, X, XIII, and XXIII. General Procedure. These compounds were prepared from dimethyl chlorothiophosphate and the sodium salt of the corresponding phenol following the general procedure reported by Greenhalgh and Marshall (1976). Crude reaction mixtures were purified by flash chromatography on silica gel eluting with hexane/methyl *tert*-butyl ether mixtures.

***O,O*-Dimethyl *O*-(3-Methoxycarbonyl)phenyl Phosphorothioate (IV).** Starting from 0.152 g (1 mmol) of methyl 3-hydroxybenzoate, 0.262 g of pure compound IV was obtained (95% yield). **IV:** IR (film) 2950, 1725, 1585, 1485, 1445, 1295, 1280, 1270, 1205, 1185, 1100, 1035, 990, 940, 840, 755 cm⁻¹; ¹H NMR δ 7.89 (dq, 1H, *J*₁ = 7.5 Hz, *J*₂ = 1.5 Hz), 7.82 (m, 1H), 7.46-7.36 (2H), 3.93 (s, 3H), 3.87 (d, 6H, *J*_{H-P} = 14 Hz); ¹³C NMR δ 166.1, 150.6 (d, *J*_{C-P} = 7 Hz), 131.8, 129.6, 126.5, 125.5 (d, *J*_{C-P} = 4.5 Hz), 122.0 (d, *J*_{C-P} = 5 Hz), 55.3 (d, *J*_{C-P} = 5 Hz), 52.3; ³¹P NMR δ 65.5.

***O,O*-Dimethyl *O*-(3-Formyl-4-nitro)phenyl Phosphorothioate (VII).** Starting from 0.151 g (1 mmol) of 5-hydroxy-2-nitrobenzaldehyde, 0.274 g of pure compound VII was obtained [92% yield, cf. Greenhalgh and Marshall (1976)]. **VII:** ¹H NMR δ 10.43 (s, 1H), 8.18 (d, 1H, *J* = 9 Hz), 7.67 (dd, 1H, *J*_{H-P} = 1.5 Hz, *J*_{H-H} = 2.5 Hz), 7.54 (ddd, 1H, *J*_{H-P} = 1.5 Hz, *J*_{H-H} = 2.5 Hz, *J*_{H-H} = 8.5 Hz), 3.90 (d, 6H, *J*_{H-P} = 14 Hz); ¹³C NMR δ 187.1, 154.8 (d, *J*_{C-P} = 7 Hz), 145.8, 133.5 (d, *J*_{C-P} = 1 Hz), 126.8 (d, *J*_{C-P} = 1 Hz), 125.5 (d, *J*_{C-P} = 5 Hz), 121.7 (d, *J*_{C-P} = 5.5 Hz), 55.6 (d, *J*_{C-P} = 6 Hz); ³¹P NMR δ 65.5.

***O,O*-Dimethyl *O*-(3-Methyl)phenyl Phosphorothioate (X).** Starting from 0.054 g (0.5 mmol) of *m*-cresol, 0.105 g of pure compound X was obtained [91% yield, cf. Greenhalgh and Marshall (1976)]. **X:** ¹H NMR δ 7.22 (m, 1H), 7.02-6.94 (3H), 3.85 (d, 6H, *J*_{H-P} = 14 Hz), 2.35 (s, 3H); ¹³C NMR δ 150.6 (d, *J*_{C-P} = 7 Hz), 139.8 (d, *J*_{C-P} = 1 Hz), 129.2 (d, *J*_{C-P} = 1 Hz), 126.1 (d, *J*_{C-P} = 1 Hz), 121.4 (d, *J*_{C-P} = 5 Hz), 117.7 (d, *J*_{C-P} = 5 Hz), 55.1 (d, *J*_{C-P} = 6 Hz), 21.3; ³¹P NMR δ 66.4.

***O,O*-Dimethyl *O*-(3-Formyl)phenyl Phosphorothioate (XIII).** Starting from 0.040 g (0.4 mmol) of 3-formylphenol, 0.085 g of pure compound XIII was obtained (95% yield). **XIII:** IR (film) 2950, 2845, 2730, 1700, 1585, 1485, 1450, 1240, 1030, 975 and 840 cm⁻¹; ¹H NMR δ 10.00 (s, 1H), 7.74 (dq, 1H, *J*₁ = 7.5 Hz, *J*₂ = 1.5 Hz), 7.68 (m, 1H), 7.54 (t, 1H, *J* = 7.5 Hz), 7.46 (m, 1H), 3.88 (d, 6H, *J*_{H-P} = 14 Hz); ¹³C NMR δ 191.1, 151.3 (d, *J*_{C-P} = 7 Hz), 137.8, 130.3, 127.1 (d, *J*_{C-P} = 4.5 Hz), 127.0, 121.3 (d, *J*_{C-P} = 4.5 Hz), 55.3 (d, *J*_{C-P} = 5.5 Hz); ³¹P NMR δ 65.5.

***O,O*-Dimethyl *O*-(3-Hydroxymethyl)phenyl Phosphorothioate (XXIII).** Starting from 0.124 g (1 mmol) of 3-(hydroxymethyl)phenol, 0.210 g of pure compound XXIII was obtained (85% yield). **XXIII:** IR (film) 3405, 2950, 1610, 1585, 1485, 1445, 1240, 1180, 1140, 1035, 960, and 830 cm⁻¹; ¹H NMR δ 7.33 (dt, 1H, *J*₁ = 8 Hz, *J*₂ = 0.5 Hz), 7.21-7.17 (2H), 7.09 (m, 1H), 4.69 (s, 2H), 3.86 (d, 6H, *J*_{H-P} = 14 Hz); ¹³C NMR δ 150.8 (d, *J*_{C-P} = 7 Hz), 142.9, 129.7, 123.6, 119.8 (d, *J*_{C-P} = 4.5 Hz), 119.1 (d, *J*_{C-P} = 4.5 Hz), 64.6, 55.1 (d, *J*_{C-P} = 6 Hz); ³¹P NMR δ 65.4.

***O,O*-Dimethyl *O*-(3-Carboxy-4-nitro)phenyl Phosphorothioate (XX).** This compound was prepared as described by Greenhalgh and Marshall (1976). **XX:** ¹H NMR δ 9.7 (br, 1H), 7.94 (d, 1H, *J* = 8.5 Hz), 7.62 (dd, 1H, *J*_{H-P} = 1.5 Hz, *J*_{H-H} = 2.5 Hz), 7.48 (ddd, 1H, *J*_{H-P} = 1.5 Hz, *J*_{H-H} = 2.5 Hz, *J*_{H-H} = 8.5 Hz), 3.90 (d, 6H, *J*_{H-P} = 14 Hz); ¹³C NMR δ 169.0, 153.4 (d, *J*_{C-P} = 7 Hz), 144.9 (d, *J*_{C-P} = 1.5 Hz), 128.2, 125.9 (d, *J*_{C-P} = 1 Hz), 124.5 (d, *J*_{C-P} = 5 Hz), 122.6 (d, *J*_{C-P} = 5.5 Hz), 55.6 (d, *J*_{C-P} = 5.5 Hz); ³¹P NMR δ 64.5.

***O,O*-Dimethyl *O*-[3-(Methoxycarbonyl)-4-nitro]phenyl Phosphorothioate (VIII).** A solution of the carboxy derivative XX (0.090 g) in *tert*-butyl methyl ether (4 mL) was treated with an excess of diazomethane at 0 °C. When the reaction was complete (TLC monitoring), reagent excess and the solvents were removed under vacuum. The residue obtained was purified by flash chromatography to give pure compound VIII in almost quantitative yield (Greenhalgh and Marshall, 1976). **VIII:** IR (CCl₄) 2960, 2860, 1750, 1590, 1540, 1435, 1350, 1280, 1210, 1055, 1035, 980, 930, 840, 825 cm⁻¹; ¹H NMR δ 7.98 (d, 1H, *J* = 8.5 Hz), 7.47 (dd, 1H, *J*_{H-P} = 1.5 Hz, *J*_{H-H} = 2.5 Hz), 7.42 (ddd, 1H, *J*_{H-P} = 1.5 Hz, *J*_{H-H} = 2.5 Hz, *J*_{H-H} = 8.5 Hz), 3.94 (s, 3H), 3.89 (d, 6H, *J*_{H-P} = 13 Hz); ¹³C NMR δ 165.0, 153.7 (d, *J*_{C-P} = 7 Hz), 144.4 (d, *J*_{C-P} = 1 Hz), 129.9 (d, *J*_{C-P} = 1 Hz), 126.0 (d, *J*_{C-P} = 1 Hz), 123.6 (d, *J*_{C-P} = 5 Hz), 55.6 (d, *J*_{C-P} = 5.5 Hz), 53.5; ³¹P NMR δ 65.5.

***O,O*-Dimethyl *O*-[3-(Hydroxymethyl)-4-nitro]phenyl Phosphorothioate (XIX).** A solution of the methoxycarbonyl thiophosphate VIII (0.012 g) in anhydrous diethyl ether (2 mL) was added to a suspension of lithium aluminum hydride (0.003 g) in the same solvent (1 mL) at 0 °C. When the reaction was complete, workup of the crude reaction mixture led to a residue which was purified by flash chromatography to give pure compound XIX [0.008 g, 74% yield; cf. Greenhalgh and Marshall (1976)]. **XIX:** ¹H NMR δ 8.18 (d, 1H, *J* = 9 Hz), 7.60 (m, 1H), 7.25 (m, 1H), 5.04 (s, 2H), 3.90 (d, 6H, *J*_{H-P} = 14 Hz); ¹³C NMR δ 154.8 (d, *J*_{C-P} = 7 Hz), 140.1, 127.3, 127.2, 121.4 (d, *J*_{C-P} = 5 Hz), 120.3 (d, *J*_{C-P} = 4 Hz), 62.2, 55.5 (d, *J*_{C-P} = 5.5 Hz); ³¹P NMR δ 64.5.

***O*-Methyl *O,O*-Bis(3-methyl-4-nitro)phenyl Phosphorothioate (XXIV, Scheme 1).** A suspension of the sodium salt of 3-methyl-4-nitrophenol (2 mmol, generated with sodium hydride) in tetrahydrofuran (4 mL) was added to a solution of thiophosphoryl trichloride (0.169 g, 1 mmol) in the same solvent (4 mL). The mixture was stirred under reflux and inert atmosphere until reaction of the thiophosphoryl trichloride was complete (8 h, ³¹P NMR monitoring). Then the crude reaction mixture was cooled to 25 °C, sodium methoxide (1.2 mmol) was added in one portion, and stirring was prolonged for 2 h. Filtration of the crude reaction mixture through Celite and evaporation of solvent rendered a residue which was purified by flash chromatography to give pure bisfenitrothion XXIV (0.300 g, 75% yield) and a small amount (0.060 g) of fenitrothion. **XXIV:** IR (CCl₄) 1610, 1575, 1515,

1475, 1340, 1225, 1155, 1020, 970, 890, 820 cm^{-1} ; ^1H NMR δ 8.07 (d, 2H, $J = 8.5$ Hz), 7.22–7.16 (4H), 4.00 (d, 3H, $J_{\text{H-P}} = 14.5$ Hz), 2.64 (s, 6H); ^{13}C NMR δ 153.1 (d, $J_{\text{C-P}} = 7$ Hz), 146.4, 136.6, 126.9, 124.8 (d, $J_{\text{C-P}} = 5$ Hz), 119.2 (d, $J_{\text{C-P}} = 5$ Hz), 56.3 (d, $J_{\text{C-P}} = 6$ Hz), 20.9; ^{31}P NMR δ 56.8.

Isomerization of Bisfenitrothion: S-Methyl O,O-Bis(3-methyl-4-nitrophenyl) Phosphate (XXV). Following the general procedure reported (Rengasamy and Parmar, 1988), a mixture of compound XXIV (0.040 g, 0.1 mmol) and silica gel (0.020 g, 60–200 μm) in dry *N,N*-dimethylformamide (2 mL) was heated under reflux until the reaction was complete (30 min, TLC monitoring). The crude reaction mixture was concentrated under vacuum, redissolved in dichloromethane, filtered, and evaporated to give pure isobisfenitrothion XXV in quantitative yield. XXV (Greenhalgh and Shoolery, 1978): ^1H NMR δ 8.08 (d, 2H, $J = 10$ Hz), 7.32–7.26 (4H), 2.65 (s, 6H), 2.46 (d, 3H, $J_{\text{H-P}} = 17$ Hz); ^{13}C NMR δ 152.6 (d, $J_{\text{C-P}} = 7$ Hz), 146.4, 136.9, 127.1, 124.2 (d, $J_{\text{C-P}} = 5$ Hz), 118.7 (d, $J_{\text{C-P}} = 5$ Hz), 20.9, 13.3 (d, $J_{\text{C-P}} = 5$ Hz); ^{31}P NMR δ 20.9.

Preparation of Phosphates XI, XII, XIV–XVIII, XXI, and XXVI. These compounds were prepared from the corresponding phosphorothioates and dimethylthioxirane following the general procedure described by us (Sanchez-Baeza et al., 1990). The crude reaction mixtures were purified by flash chromatography to give the respective phosphates in nearly quantitative yield and high purity.

O,O-Dimethyl O-(3-Methyl-4-nitrophenyl) Phosphate (XI; Sanchez-Baeza et al., 1990).

O,O-Dimethyl O-(3-Methylphenyl) Phosphate (XII; Greenhalgh and Marshall, 1976): ^1H NMR δ 7.22 (m, 1H), 7.05–6.97 (3H), 3.86 (d, 6H, $J_{\text{H-P}} = 11.5$ Hz), 2.35 (s, 3H); ^{13}C NMR δ 150.5 (d, $J_{\text{C-P}} = 7$ Hz), 140.0 (d, $J_{\text{C-P}} = 1$ Hz), 129.4, 125.9 (d, $J_{\text{C-P}} = 1$ Hz), 120.4 (d, $J_{\text{C-P}} = 5$ Hz), 116.8 (d, $J_{\text{C-P}} = 5$ Hz), 54.9 (d, $J_{\text{C-P}} = 6$ Hz), 21.3; ^{31}P NMR δ -4.2.

O,O-Dimethyl O-[3-(Methoxycarbonyl)-4-nitro]phenyl Phosphate (XIV): ^1H NMR δ 8.00 (d, 1H, $J = 9$ Hz), 7.52 (dd, 1H, $J_{\text{H-P}} = 1$ Hz, $J_{\text{H-H}} = 2.5$ Hz), 7.48 (ddd, 1H, $J_{\text{H-P}} = 1$ Hz, $J_{\text{H-H}} = 2.5$ Hz, $J_{\text{H-H}} = 8.5$ Hz), 3.94 (s, 3H), 3.91 (d, 6H, $J_{\text{H-P}} = 11.5$ Hz); ^{13}C NMR δ 165.0, 153.8 (d, $J_{\text{C-P}} = 6$ Hz), 144.1, 130.3, 126.3, 122.4 (d, $J_{\text{C-P}} = 5$ Hz), 120.9 (d, $J_{\text{C-P}} = 5$ Hz), 55.4 (d, $J_{\text{C-P}} = 6$ Hz), 53.5; ^{31}P NMR δ -5.1.

O,O-Dimethyl O-(3-Formyl-4-nitrophenyl) Phosphate (XV; Greenhalgh and Marshall, 1976): ^1H NMR δ 10.41 (s, 1H), 8.18 (d, 1H, $J = 9$ Hz), 7.69 (dd, 1H, $J_{\text{H-P}} = 1$ Hz, $J_{\text{H-H}} = 3$ Hz), 7.60 (ddd, 1H, $J_{\text{H-P}} = 1$ Hz, $J_{\text{H-H}} = 3$ Hz, $J_{\text{H-H}} = 8.5$ Hz), 3.91 (d, 6H, $J_{\text{H-P}} = 11.5$ Hz); ^{13}C NMR δ 187.0, 154.7 (d, $J_{\text{C-P}} = 6$ Hz), 145.7, 133.7, 127.0, 124.4 (d, $J_{\text{C-P}} = 4.5$ Hz), 120.6 (d, $J_{\text{C-P}} = 6$ Hz), 55.5 (d, $J_{\text{C-P}} = 6$ Hz); ^{31}P NMR δ -6.1.

O,O-Dimethyl O-(3-Hydroxymethyl)phenyl Phosphate (XVI): ^1H NMR δ 7.31 (t, 1H, $J_1 = 8$ Hz), 7.22 (br, 1H), 7.16 (d, 1H, $J = 8$ Hz), 7.10 (br, d, 1H, $J = 8$ Hz), 4.66 (s, 2H), 3.85 (d, 6H, $J_{\text{H-P}} = 11.5$ Hz); ^{13}C NMR δ 150.6 (d, $J_{\text{C-P}} = 6.5$ Hz), 143.3, 129.8, 123.5, 118.8 (d, $J_{\text{C-P}} = 4.5$ Hz), 118.2 (d, $J_{\text{C-P}} = 4.5$ Hz), 64.4, 55.0 (d, $J_{\text{C-P}} = 6$ Hz); ^{31}P NMR δ -5.2.

O,O-Dimethyl O-(3-Formyl)phenyl Phosphate (XVII): ^1H NMR δ 10.00 (s, 1H), 7.75–7.71 (2H), 7.58–7.49 (2H), 3.90 (d, 6H, $J_{\text{H-P}} = 11.5$ Hz); ^{13}C NMR δ 191.0, 151.2 (d, $J_{\text{C-P}} = 7$ Hz), 138.0, 130.5, 126.6, 126.0 (d, $J_{\text{C-P}} = 5$ Hz), 120.3 (d, $J_{\text{C-P}} = 5$ Hz), 55.1 (d, $J_{\text{C-P}} = 6$ Hz); ^{31}P NMR δ -5.3.

O,O-Dimethyl O-(3-Methoxycarbonyl)phenyl Phosphate (XVIII): ^1H NMR δ 7.91–7.84 (2H), 7.46–7.42 (2H), 3.93 (s, 3H), 3.89 (d, 6H, $J_{\text{H-P}} = 11.5$ Hz); ^{13}C NMR δ 166.0, 150.5 (d, $J_{\text{C-P}} = 7$ Hz), 131.9, 129.8, 126.3, 124.5 (d, $J_{\text{C-P}} = 4.5$ Hz), 121.0 (d, $J_{\text{C-P}} = 5$ Hz), 55.0 (d, $J_{\text{C-P}} = 6$ Hz), 52.3; ^{31}P NMR δ -5.3.

O,O-Dimethyl O-(3-Carboxy-4-nitrophenyl) Phosphate (XXI; Greenhalgh and Marshall, 1976): ^1H NMR δ 9.0 (br, 1H), 7.92 (d, 1H, $J = 8.5$ Hz), 7.62 (d, 1H, $J_{\text{H-H}} = 1.5$ Hz), 7.44 (dd, 1H, $J_{\text{H-H}} = 1.5$ Hz, $J_{\text{H-H}} = 8.5$ Hz), 3.93 (d, 6H, $J_{\text{H-P}} = 11.5$ Hz); ^{13}C NMR δ 166.4, 153.0 (d, $J_{\text{C-P}} = 6$ Hz), 144.7, 129.9, 126.1, 122.8 (d, $J_{\text{C-P}} = 7$ Hz), 121.4 (d, $J_{\text{C-P}} = 5$ Hz), 55.8 (d, $J_{\text{C-P}} = 6$ Hz); ^{31}P NMR δ -6.5.

O-Methyl O,O-Bis(3-methyl-4-nitrophenyl) Phosphate (XXVI): ^1H NMR δ 8.05 (d, 2H, $J = 8.5$ Hz), 7.24–7.18 (4H), 4.02 (d, 3H, $J_{\text{H-P}} = 12$ Hz), 2.63 (s, 6H); ^{13}C NMR δ 152.8 (d, $J_{\text{C-P}} = 6$ Hz), 146.2, 136.9, 127.1, 123.7 (d, $J_{\text{C-P}} = 5$ Hz), 118.1 (d, $J_{\text{C-P}} = 5$ Hz), 56.2 (d, $J_{\text{C-P}} = 6$ Hz), 20.9; ^{31}P NMR δ -13.3.

Photolysis Experiments. Fenitrothion (V, 99.7%) and fenitrooxon (XI), analytical grade standards, were gifts from Sumitomo Chemical Co. (Osaka, Japan), and parathion-methyl (X) was purchased through Promochem (Wesel, Germany). Pesticide grade ethyl acetate, acetone, methanol, and *n*-hexane were obtained from Merck (Darmstadt, Germany). Silica gel was also obtained from Merck.

Fenitrothion showed a slow photodegradation in distilled water plus 2–4% methanol when the suntest apparatus was used and without the use of acetone as photosensitizer (Durand et al., 1991b). As a consequence, to identify the possible photodegradation products, the fenitrothion solution was irradiated with a higher intensity light source (a HPK 125-W high-pressure mercury lamp), jacketed with a water-cooled quartz filter to get a maximum intensity of UV light close to 254 nm. Since fenitrothion has a limited solubility in water (14 mg/L) and the purpose of this work was to identify as many degradation compounds as possible, water/methanolic solutions of fenitrothion were employed. Thus, 100 mg of fenitrothion was dissolved in 600 mL of a mixture of water/methanol (5:1). After 7 h of irradiation, the fenitrothion solution was extracted with 150 mL of dichloromethane, then with 150 mL of *n*-hexane, and finally with 150 mL of dichloromethane, and the fractions were combined. The remaining water solution was concentrated to dryness and redissolved in 0.5 mL of ethyl acetate. This solution is called water extract under Results and Discussion. The dichloromethane/hexane extracts were concentrated under vacuum, and the residue was placed on a semipreparative silica gel column (52 \times 1.5 cm i.d.), from which 88 fractions were collected using eluent mixtures of *n*-hexane/ethyl acetate. After fractionation was complete, the different fractions were analyzed by liquid chromatography with UV detection at 254 nm. The extracts that were found to be mixtures of the same compounds under LC were combined and the solvent was removed. The residues were redissolved in 250 μL of ethyl acetate and directly injected onto the GC-MS using the experimental conditions described below.

To identify further photodegradation products and also to better clarify the photodegradation pathway of fenitrothion, fenitrooxon (XI) and carboxyfenitrothion (XX) were independently irradiated under conditions identical with those used for fenitrothion. In these two cases, after 7 h of irradiation, the *n*-hexane/dichloromethane extract was concentrated to dryness, redissolved in ethyl acetate, and directly injected onto the GC-MS, with fractionation.

GC-MS Determinations. A 30 m \times 0.25 mm i.d. fused silica capillary column coated with chemically bonded phenyl-cyanopropyl-methyl DB 1701 (J&W Scientific, Folsom, CA) was programmed from 90 to 280 $^{\circ}\text{C}$ at 6 $^{\circ}\text{C}/\text{min}$, and it was used for the GC-MS determinations. The injection volume was 2 μL , and the injection mode was splitless.

A Hewlett-Packard 5995 instrument (Palo Alto, CA) interfaced to a 59970C data system was used for GC-MS in the EI. The same fused silica column described above was used and directly introduced into the ion source. Helium was used as the carrier gas (30 cm/s). The ion source and the analyzer were held at 200 and 230 $^{\circ}\text{C}$, respectively. EI spectra were obtained at 70 eV.

The different compounds identified in the GC-MS traces were determined by selected ion monitoring using fenitrothion as internal standard. The final percentage of the different photoproducts obtained was as follows: fenitrothion, compounds II and VIII accounted for 10% each; *S*-methyl fenitrothion, compounds I and III accounted 3% each, whereas the rest was below 1% with respect to the initial irradiated fenitrothion concentration. The unextracted residue might correspond to highly polar compounds which are slightly or not soluble in ethyl acetate. In this sense, the presence of formic acid in this unextracted residue has been reported by Mikami et al. (1985). Preliminary results from our group using liquid chromatography-mass spectrometry have shown the presence of dimethylphosphoric acid in this fraction.

RESULTS AND DISCUSSION

A selection of the EI spectra of the different photodegradation products is shown in Figure 1.

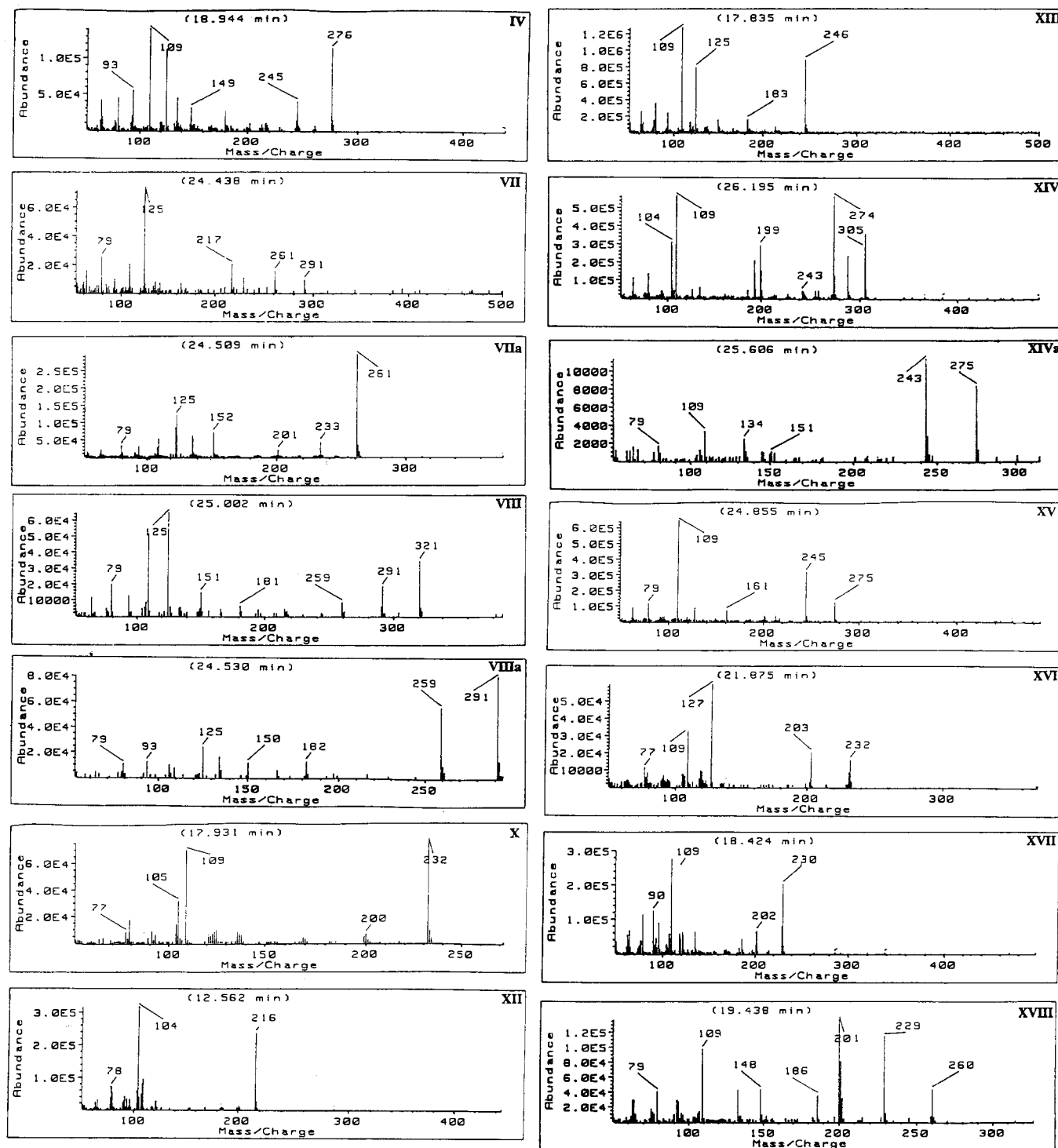
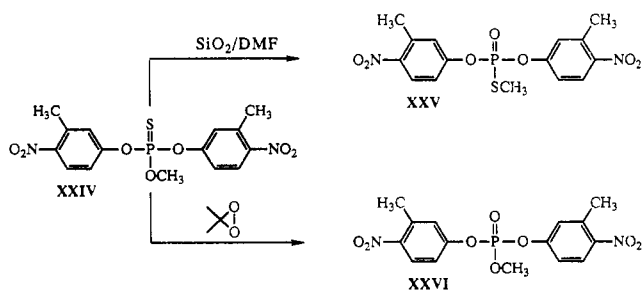


Figure 1. EI spectra of selected transformation products of fenitrothion identified by coelution with an authentic standard.

Synthesis of Standards of Photolysis Products. Phosphorothioates IV, VII, X, XIII, and XXIII were synthesized in good conversion yields according to the procedure reported elsewhere (Greenhalgh and Marshall, 1976). A similar procedure was used for the preparation of the phosphorothioate containing two aromatic substituents [bisfenitrothion (XXV); see Scheme 1]. On the other hand, phosphorothioates XX, VIII, and XIX were synthesized from the formyl phosphorothioate VII. Thus, oxidation of VII led to the carboxy derivative XX, which was methylated with diazomethane to give the corresponding ester VIII. Reduction of this ester afforded the corresponding hydroxymethyl derivative XIX. Compounds were fully characterized by their spectral data (IR, ¹H, ¹³C, and ³¹P NMR, MS).

Scheme 1. Synthesis of Dimeric Structures Related to Fenitrothion



With the exception of phosphate XXV, which was prepared by isomerization of phosphorothioate XXIV in

the presence of silica gel [Scheme 1; cf. Rengasamy and Parmar (1988)], the different phosphorothioates were converted into their respective phosphates in nearly quantitative yields by treatment with dimethyldioxirane according to our previously reported procedure (Sanchez-Baeza et al., 1990). In these cases, the shift of approximately 70 ppm upfield in the ^{31}P NMR spectra of the reaction products confirmed the conversion of the P=S into the corresponding P=O moiety (Tebby, 1987). In addition, the ^1H NMR spectra of the phosphate compounds showed a lower value of the $J_{\text{H-P}}$ coupling constants in comparison with those of the corresponding phosphorothioate derivatives, which agrees with the charge density decrease on the phosphorus atom in the P=O bond.

Identification of Fenitrothion Photoproducts. (A) *Water Extract.* The EI spectra of the different photolysis products identified in the water extract of the irradiated fenitrothion were assigned to compounds with molecular weights of 140, 156, and 234, respectively. These compounds were identified as trimethyl phosphate (I), *O,O,S*-trimethyl phosphate (II), and tetramethyl pyrophosphate (III), respectively. The spectrum of trimethyl phosphate matches previous EI data on this compound (Desmarchelier and Lacey, 1985) and the EI spectra of all three compounds match with EI spectra of the three main photolysis products of parathion-methyl (Chukwudebe et al., 1989). The formation of identical water-soluble photoproducts for fenitrothion and parathion-methyl is explained by the fact that both compounds contain the same basic functional group structure. It should be noticed that the m/z value of 126 in II corresponds to $[(\text{CH}_3\text{O})_2\text{PSH}]^+$, whereas for III it corresponds to $[(\text{CH}_3\text{O})_2\text{P}(\text{O})\text{OH}]^+$. A significant observation is that these photolysis products were never identified in previous photolysis experiments carried out with fenitrothion (Greenhalgh and Marshall, 1976; National Research Council Canada, 1975; Mikami et al., 1985). In addition, the present work reflects more what can happen in real environmental conditions since photolysis was conducted in water instead of pure organic solvents as reported by Greenhalgh and Marshall (1976).

(B) *Organic Extract.* (1) *Carbomethoxydenitrofenitrothion* (IV) was identified by its ions at m/z values of 63, 79, 93, 109, and 125, indicating the presence of the phosphorothioate moiety (Takimoto, 1984; Stan et al., 1977; Damico, 1966; Desmarchelier et al., 1976). The ion at m/z 109 was enhanced as compared to usual phosphorothioate pesticides, e.g., fenitrothion. This enhancement can be attributed to the fact that a COOCH_3 group is in the *meta* position that can more easily magnify the m/z 109 rearrangement ion as compared with a CH_3 substituent (as for fenitrothion V) (Wilkins, 1990). A second abundant ion at m/z 245 was also formed, and it has been attributed to a OCH_3 loss.

(2) As expected, fenitrothion (V, MW 277), with a OH loss at m/z 260 and the characteristic ions of the phosphorothioate group, was identified (Greenhalgh and Marshall, 1976; National Research Council, Canada, 1975).

(3) The *S*-methyl isomer of fenitrothion (VI) was also obtained. Its identification was pointed out by different facts: (i) The spectrum of VI had features in common with the one of fenitrothion, with ions at m/z 125 as base peak and 260. Both structures exhibited the $(\text{CH}_3\text{S})\text{-(CH}_3\text{O)P}(\text{O})$ moiety, which corresponds to the same molecular weight as fenitrothion structures. (ii) The main difference corresponded to the absence of the m/z 109 ion, which could not be formed for this compound since the $(\text{CH}_3\text{O})_2\text{P}(\text{O})$ structure was not present. (iii) The *S*-methyl

isomer of fenitrothion exhibited a longer retention time than fenitrothion (24.6 vs 22.3 min). All of the assumptions made here concerning the identification of the *S*-methyl isomer coincide with the results reported elsewhere for the photodegradation of fenitrothion (Greenhalgh and Marshall, 1976; National Research Council Canada, 1975) and also are supported by the formation of *S*-methyl isomers of other phosphorothioate pesticides, e.g., parathion-methyl by ultraviolet light (Chukwudebe et al., 1989).

(4) *Compound VII* was identified as formylfenitrothion. It contained typical ions of organo-P, at m/z values of 79 and 125. Other important ions were obtained at m/z 217 and 261, corresponding to $[\text{M} - \text{NO}_2 - \text{CO}]^+$ and $[\text{M} - \text{NO}]$, respectively. This EI spectrum partly agreed with that from Greenhalgh and Marshall (1976). Compound VIIa was formed during chromatography—probably in the injection block—and it corresponded to one in which a formal loss of NO has occurred. A very similar compound to VIIa had been postulated to be formed under photolysis (Takimoto, 1984). The loss of NO enhances the abundance of the base peak at m/z 261 corresponding to $[\text{M} - \text{NO}]$, and consequently the abundances of typically organo-P diagnostic ions, e.g., at m/z 125, and decreased, similar to the findings reported by Wilkins (1990). The ion formed at m/z 136 was attributed to the characteristic ion of the 3-methyl-4-nitrophenol structure, whereas the ion formed at m/z 233 corresponded to $[\text{M} - \text{CO}]^+$. It should be indicated that compounds VII and VIIa were found in the same fractions, after photolysis, and also when pure standard VII was injected onto the GC-MS. The detection of both compounds can be attributed to several factors: (i) some degradation during injection to give the new compound by NO loss due to the presence of an electronegative C=O group in the ortho position with respect to NO_2 ; (ii) the use of a GC capillary column that enhances resolution as compared with previous studies of fenitrothion, thus permitting their detection.

(5) *Carbomethoxyfenitrothion* (compound VIII) was identified by its EI spectrum (Greenhalgh and Marshall, 1976). Besides the typical ions common to the phosphorothioate moiety, three characteristic ions at m/z values of 151, 181, and 321 were obtained. The fragment ion at m/z 290, attributed to a loss of CH_3O , is similar to the formation of m/z 245 in IV. On the other hand, compound VIIIa is thought to be formed by a process similar to that described above for product VIIa. In this case, the new compound formed corresponded to a product at m/z 291; this peak was assigned to the fragment $[\text{M} - \text{NO}]^+$. The second abundant ion at m/z 259 corresponded to a loss of CH_3OH .

(6) *Compound IX* was identified as 3-methyl-4-nitrophenol by library search. This compound has been previously identified as one of the photolysis products of fenitrothion (Greenhalgh and Marshall, 1976; National Research Council Canada, 1975); it gives an EI spectrum with m/z 153 and 136 characteristic ions.

(7) A compound with a molecular weight of 232 was identified as denitrofenitrothion (X). As reported previously (Greenhalgh and Marshall, 1976), denitrofenitrothion is likely to be formed under photolysis at an amount below 5%. In our case, the amount of this compound is lower than 1%, which can be attributed to the use of water instead of an organic solvent. Its EI spectrum exhibited an abundance of m/z 125 much lower than other ions at m/z values of 232, 109, and 105. The m/z 125 ion exhibited a lower relative abundance than in compound IV. Owing to an energetically favorable

fragmentation pathway, the COOCH₃ group of IV can more easily stabilize the *m/z* 125 ion as compared to the CH₃ group of denitrofenitrothion (X) (Wilkins, 1990).

(8) *Fenitrooxon* (XI) was identified by its typical feature of the EI spectrum which showed *m/z* ions at 79 and 109 with no formation of *m/z* ion at 125, since no S is in the molecule. Also, a significant *m/z* 244 was present, corresponding to a loss of OH similar to fenitrothion (Greenhalgh and Marshall, 1976; National Research Council Canada, 1975).

(9) For the first time in photodegradation studies of fenitrothion (Greenhalgh and Marshall, 1976; National Research Council Canada, 1975; Takimoto, 1984), compound XII was identified as *denitrofenitrooxon*. Two main ions were observed at *m/z* values of 104 and 216. This second ion corresponded to [M]⁺, whereas the ion at *m/z* 104 probably was a rearrangement ion and corresponded to [C₆H₅CH=CH₂]⁺, as noticed for other phosphates (Desmarchelier and Lacey, 1985), and it was also reported for carbomethoxyfenitrooxon XIV (Greenhalgh and Marshall, 1976).

(10) *Compound XIII (formyldenitrofenitrothion)* was identified by its typical ions at *m/z* values of 109 and 125, corresponding to the phosphorothioate moiety. The ion obtained at *m/z* 246 corresponded to the molecular ion and had a relative abundance of 70%.

(11) *Carbomethoxyfenitrooxon* (compound XIV) has been also previously reported (Greenhalgh and Marshall, 1976). Most of the ions at *m/z* values of 104, 109, 199, 274, and 305 matched previous results, although with differences in the relative abundance. Ions at *m/z* 305, 288, and 274 corresponded to [M]⁺, [M - OH]⁺, and [M - CH₃O]⁺ structures, respectively. XIVa is a decomposition product of XIV obtained, as in the case of VII and VIII, by degradation during injection, thus giving rise to a compound exhibiting an important peak at *m/z* 275, which was assigned to [M - NO]⁺. The base peak obtained at *m/z* 243 corresponded to [M - NO - CH₃OH]⁺. It should be mentioned that compound XIVa was never identified, and its present identification can be due to a similar phenomenon as indicated above for compounds VIIa and VIIIa.

Three possible dimeric structures derived from fenitrothion were also synthesized, as indicated in Scheme 1. Although these dimers had been mentioned as possible transformation products of fenitrothion (National Research Council Canada, 1975), they could not be detected as photodegradation products under our experimental irradiation conditions. Formation of dimers had been reported for coumaphos, another organophosphorus pesticide, under UV irradiation conditions similar to those in the present experiments, but with an irradiation time of 300 h (Abdou et al., 1988), and also for monuron, a phenylurea herbicide (Marcheterre et al., 1988), after 25 h of irradiation. In the present experiments the irradiation time was only 7 h; thus, additional irradiation hours could be needed for the formation of such dimers for fenitrothion.

The use of relatively high amounts of fenitrothion in photolysis studies, as reported in this study, can lead to the formation of solvent adducts and dimers. We need to indicate, as mentioned above, that we were only able to identify solvent adducts but not dimers.

Tentative Photodegradation Pathways. The tentative photodegradation pathways of fenitrothion (V) in water/methanol with the labels of the different photoalteration products identified are shown in Scheme 2. To confirm the proposed degradation pathways observed in this scheme, further irradiation experiments were carried

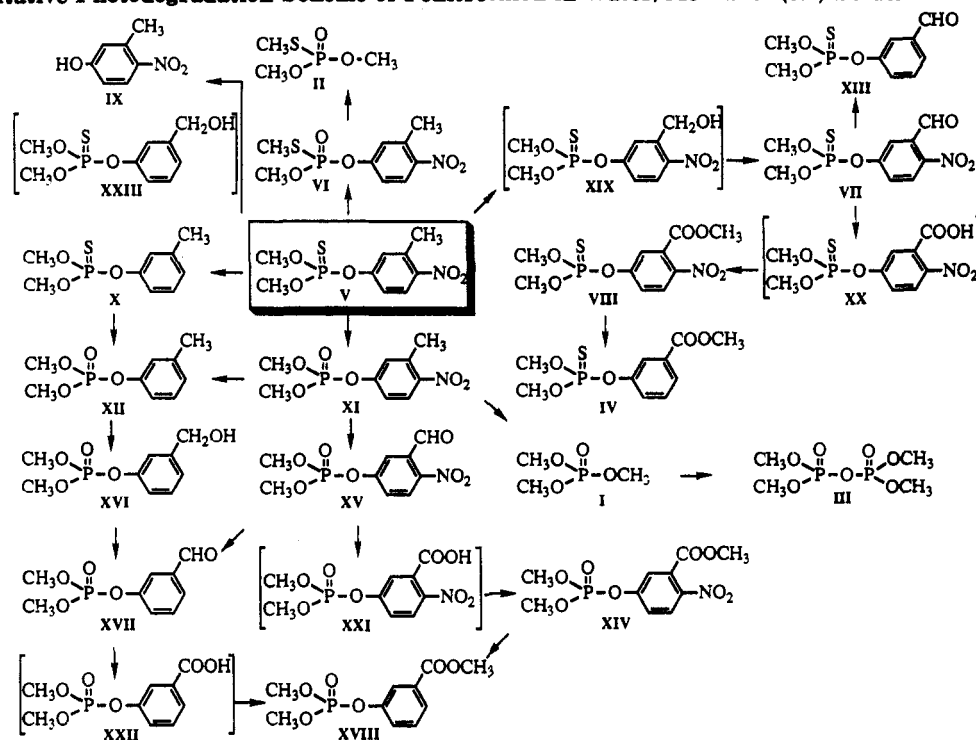
out, which allowed a concomitant identification of new photoproducts formed.

First, irradiation of fenitrooxon (XI) under the same experimental conditions as fenitrothion led to the identification of several new photoproducts, such as the formyl derivative XV, the alcohol XVI, the denitroaldehyde XVII, and the carbomethoxy derivative XVIII. Probably these photoproducts were also formed during irradiation of fenitrothion but at very low concentration, so they could not be detected under the usual conditions of analysis. The EI mass spectrum of these products is reported in Figure 1. All of these compounds, derivatives of fenitrooxon, exhibited the typical ions of the oxon structure at *m/z* values of 79 and 109. Other characteristic ions at *m/z* values of 245 and 275 corresponding to [M - NO]⁺ and [M]⁺, respectively, were assigned to formylfenitrooxon (XV). For hydroxymethylidenitrofenitrooxon (XVI) the base peak was the *m/z* 127 ion, corresponding to the structure (CH₃O)₂P(OH)₂, also indicative of organophosphorus pesticides with an oxo group (Stan et al., 1977). Other ions at *m/z* 203 and 232 corresponded to the loss of CHO and to [M]⁺, respectively. The spectrum of formyldenitrofenitrooxon (XVII) exhibited ions at *m/z* 202 and 230, corresponding, respectively, to [M - CO]⁺ and [M]⁺ ions. Finally, the spectrum of carbomethoxydenitrofenitrooxon (XVIII) exhibited the ions at *m/z* 201, 229, and 260, corresponding to [M - COOCH₃]⁺, [M - OCH₃]⁺, and [M]⁺, respectively, with a fragmentation behavior similar to that reported for compound IV.

A third irradiation experiment, also under the same conditions as for fenitrothion (V) and fenitrooxon (XI), was performed for the acid derivative of fenitrothion XX. The identification of compounds IV and VIII proved that the formation of the ester derivatives occurred via this acid and also that afterward a loss of NO₂ took place, leading to compound IV.

Therefore, as result of all the irradiation experiments performed and the unequivocal identification of the photoproducts described above, some selected pathways for the photodegradation of fenitrothion in an aqueous/methanolic medium could be proposed. Thus, degradations through hydrolysis (with eventual remethylation due to the presence of methanol as cosolvent) (i.e., V to give IX, XI to give I, VI to give II), isomerization (i.e., V to give VI), and P=S to P=O oxidations (V to give XI) were observed. With respect to the latter oxidations, the fact that the ester of fenitrooxon XIV was not detected after irradiation of acid from fenitrothion XX would suggest that the transformation of its methyl ester VIII into XIV could be absent or greatly diminished. Other possible P=S to P=O oxidations not explicitated in Scheme 2 (i.e., X to give XII, VII to give XV) cannot be discarded. In any case, it appears that the phosphorothioate to phosphate conversion was particularly favored for the case of the parent organophosphorus compound, probably due to its still higher concentration in the samples after 7 h of irradiation.

As indicated in the Introduction, some of the above degradation pathways had been previously described for fenitrothion (Greenhalgh and Marshall, 1976; National Research Council Canada, 1975; Takimoto, 1984; Mikami et al., 1985) or for other organophosphorus pesticides. Denitration constituted another photodegradation pathway observed in our experiments (i.e., V to give X, XV to give XVII, VIII to give IV, VII to give XIII, XIV to give XVIII). Although the formation of X from V had been reported (Greenhalgh and Marshall, 1976) and it was indicated to be a minor degradation pathway, no other

Scheme 2. Tentative Photodegradation Scheme of Fenitrothion in Water/Methanol (5:1) Solution^a

^a Compounds in parentheses have not been identified in the different fractions analyzed but, with the exception of acid XXII, they have been available as synthetic standards.

one of these denitrated compounds was previously reported. Such nitro group elimination from an aromatic moiety was also observed in photodegradation studies of pendimethalin, and it was attributed to a homolytic fission of the nitrogen-carbon bond with an abstraction of a hydrogen radical from the medium. The displacement of the nitro group has been explained by either a free-radical or ionic mechanism (Pal et al., 1991).

Finally, it has been proved that the methyl group present in the aromatic substituent of fenitrothion can undergo a stepwise oxidation through hydroxymethyl and formyl to give the corresponding carboxy derivative (i.e., V → XIX → VII → XX, XII → XVI → XVII → XXI) or XI → XV → XXI). In our experiments, similar to findings reported previously for the photodegradation of fenitrothion (Greenhalgh and Marshall, 1976), we have unequivocally identified formylfenitrothion (VII). However, we did not find (hydroxymethyl)fenitrothion (XIX) since it is a compound photolytically unstable and rapidly oxidized to formyl- (VII) and carboxy- (XX) fenitrothion. For the oxo compounds XII and XI, this pathway of photooxidation has been reported for the first time. In this respect it is worth noting that irradiation of acid XX did not produce the corresponding product of decarboxylation, i.e., methyl-parathion, which could suggest that this degradation pathway does not operate in this type of compound. The potential loss of the alkyl substituent through a decarbonylation from its corresponding formyl derivative is now under investigation in our laboratory.

CONCLUSIONS

This study is in line with earlier literature precedents reporting the important role of photodegradation in the fate of pesticides in the aquatic environment. In recent years, considerable interest has been generated concerning the effects of photolysis in pesticide degradation. The

present work has expanded considerably the list of photolysis products observed for fenitrothion in previous photodegradation studies and provides useful information for a more detailed knowledge of the mechanism of the degradation in the environment. This is due to the use of a more aqueous environment in our case vs pure organic solvents, as reported by Greenhalgh and Marshall (1976).

With the combined use of an extensive fractionation step followed by synthesis of the different photoalteration products and GC-MS characterization, a characterization of the complex mixtures of the different photolysis products formed is feasible. Among them are trimethyl phosphate (I), *O,O,S*-trimethyl phosphate (II), tetramethyl pyrophosphate (III), carbomethoxydenitrofenitrothion (IV), the formyl fenitrothion derivative VII, the carbomethoxyfenitrothion derivative VIII, denitrofenitrooxon (XII), formyldenitrofenitrothion (XIII), the carbomethoxy fenitrooxon derivative (XIV), formylfenitrooxon (XV), hydroxymethyldenitrofenitrooxon (XVI), formyldenitrofenitrooxon (XVII), and carbomethoxydenitrofenitrooxon (XVIII). Considering that photodecomposition of fenitrothion in artificial sunlight yields polar compounds, it appears reasonable to expect these compounds to be found in soil, plants, or water exposed to this insecticide. However, it is not expected that solvent adducts with methanol are found under real environmental conditions.

It is our plan to carry out future photodegradation studies with lower concentrations of fenitrothion in the micrograms per liter level, much closer to environmental levels, and by using real environmental waters containing pesticides and also spiked samples. At the same time on-line solid-phase extraction with liquid chromatography-mass spectrometry will be developed to achieve a better limit of quantitation which should facilitate the determination of a great number of highly polar transformation products.

ACKNOWLEDGMENT

G.D. is the recipient of a fellowship from Fundació Caixa de Pensions (Barcelona, Spain). J.L.A. is the recipient of a fellowship from the Ministerio de Educación y Ciencia, CICYT (Grant AGR-89-532). This work has been financially supported by the Environment Programme from the Commission of the European Communities (EV5V-CT92-0105).

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Received for review January 11, 1993. Revised manuscript received July 16, 1993. Accepted November 18, 1993.*

* Abstract published in *Advance ACS Abstracts*, January 15, 1994.