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Decomposition of ^{14}C-fenitrothion under the influence of UV and sunlight under tropical and subtropical conditions

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Abstract

The decomposition of ^{14}C-fenitrothion on silica gel chromatoplates as well as in polar and non polar solvents under sunlight and ultraviolet light was investigated, Its stability to sunlight on leaf surfaces of bean plants and on different surfaces (such as glass, quartz and plastic) was also determined. The main photoproducts were identified as carboxyfenitrothion, fenitrooxon, carboxyfenitrooxon and 3-methyl-4-nitrophenol and a small amount 3-caboxy-4-nitrophenol and methyl parathion. The addition of carbaryl and deltamethrin insecticides slightly accelerated the photodecomposition of fenitrothion on silica gel plates and in solution.

Keywords: Fenitrothion; Photodecomposition; Sun and UV lights; Different surfaces; Different solvents

1. Introduction

Organophosphorus compounds have recently been used as an alternative to organochlorine compounds for pest control. The widespread use of organophosphorus insecticides results in the release of their residues into natural water, thus inducing an environmental problem (Derbalah et al., 2004a).

Fenitrothion, first prepared by Sumitomo Chemical Co. has the structural formula [*O*,*O*-dimethyl-*O*-(3-methyl-4-nitrophenyl) phosphorothioate, I] is marketed under different trade names, e.g., Sumithion, Novathion and Metathion. It is a broad-spectrum organophosphorus insecticide that has been in use since 1959. It is considered to be a common river water pollutant, and its residues in natural water undergo photodegradation, resulting in the release of many toxic metabolites, some being more toxic than the parent compound to aquatic organisms (Eto, 1974; Amoros et al., 2000; Derbalah et al., 2004b).

Fenitrothion is considered somewhat toxic to fish (Thomson, 1989). And it is also employed in agriculture to control insects on rice, cereals, fruits, vegetables, stored grains and cotton. It is applied in public health measures to control flies, mosquitoes and cockroaches (WHO, 1992). It has been also used for the control of stored product insect pests in a number of countries (Snelson, 1987). The insecticide is non-systemic and non-persistent (Spencer, 1981; Hassall, 1990; Briggs and Council, 1992). The acute toxicity of fenitrothion to mammal is considered to be low (Spencer, 1981; Hayes, 1982; Hayes and Laws, 1990).

In Egypt, fenitrothion is used on cotton and other plants. Cotton receives, other than fenitrothion, insecticides such as carbaryl and deltamethrin, so the soil under the plant usually contain a mixture of the used insecticides. Therefore, we found it important to investigate the stability of fenitrothion in presence of carbaryl and deltamethrin in solution.

This paper studies the decomposition of fenitrothion by ultraviolet (UV) and sun light on silica gel surface and on bean foliage and when dissolved in organic solvents and water. Also, the effect of some pesticide chemicals usually used for spraying cotton plants (carbaryl and deltamethrin) on the photodecomposition of fenitrothion and stability of the insecticide fenitrothion on surfaces of glass, quartz and plastic was examined.

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The photodecomposition of fenitrothion has been reported by several authors (Durand et al., 1990, 1994; Barcelo et al., 1993; Burrows et al., 2002; Sakellarides et al., 2003; Matsushita et al., 2006). All these studies were carried out in temperate regions. In the present work we studied the photodecomposition under local conditions which are almost tropical (or subtropical), where the temperature reaches 37–41° in summer which is accompanied with a high degree of relative humidity (90–100%).

2. Materials and methods

2.1. Chemicals

^{14}C-methanol was obtained from Amersham International Corporation, United Kingdom. Thiophosphorylchloride was obtained from Fluka AG. All solvents and silica gel used were of chemical grades. (Merck Darmstadt, Germany). Labelled fenitrothion I (Nishizawa et al., 1963) Fenitrooxon II (Kim et al., 2000), 3-methyl-4-nitrophenol III (Akintonwa and Hutson, 1967), carboxyfenitrothion (IV) (Bowden et al., 1946) and carboxyfenitrooxon (V) (Greenhalgh and Marshall, 1976) were synthesized in the laboratory according to the procedures indicated.

2.1.1. Synthesis of fenitrothion (*I*)

^{14}C-fenitrothion labelled at the carbon atoms of the methyl groups was synthesized by a single vesseled reaction that involved the condensation of 0.28 ml (0.007 M) of ^{14}C-methanol in toluene with 0.315 ml (0.003 M) of thiophosphorylchloride in presence of triethylamine 0.81 ml (0.006 M) and the mixture was stirred at 5–10 °C for 30 min. After removal of the separated triethylamine hydrochloride by filtration, the filtrate was evaporated in a vacuum. The obtained (*O*,*O*-dimethylthiophosphoryl chloride) in toluene was allowed to react with 0.58 g (0.003 M) of potassium salt of 3-methyl-4-nitrophenol while stirring for 30 min at room temperature. This mixture was refluxed for 2–3 h at 60–80 °C, cooled, diluted with cold water and the organic layer was separated and dried over anhydrous sodium sulphate. Under reduced pressure the solvent was evaporated to give yellow-brown liquid bp 140–145 °C, 0.1 mmHg). The product was purified by preparative thin layer chromatography (TLC) (Silica gel 60 F_{254} pre-coated plates 20×20 cm; layer thickness 0.5 mm Art. 5744). The prepared ^{14}C-fenitrothion had a specific activity 2.96 MBq (0.08 µci/mg) and a radiometric purity 98% (Nishizawa et al., 1963).

Non-labelled fenitrothion was prepared as described above and its main degradation products were synthesized in our laboratory according to known procedures for comparison purposes (Fig. 1).

2.1.2. Synthesis of fenitrooxon (*II*)

Oxidation of fenitrothion was obtained by mixing fenitrothion solution (2 mM) in acetonitrile with a 10 times excess of bromine solution (20 mM) in acetonitrile followed by vortexing the mixture for a few seconds. The completion of the reaction was checked by silica gel TLC by using suitable mobile phases (Hexane: Benzene 1:2).

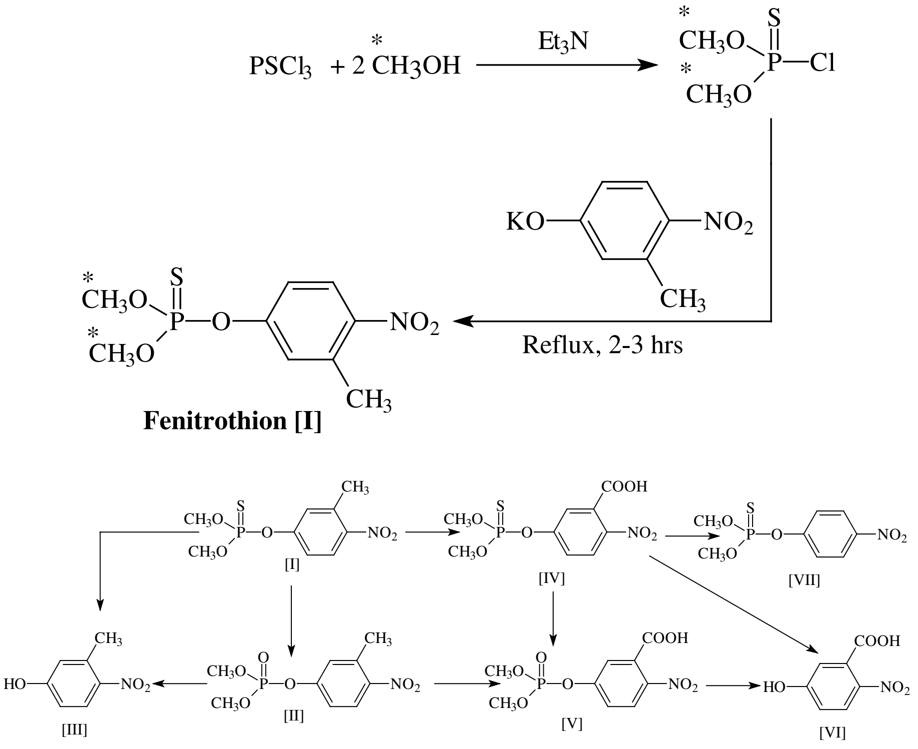

Fig. 1. Synthesis of ^{14}C-fenitrothion and its main degradation products by photodecomposition.

Isolation of the product was achieved by preparative TLC (silica gel) using the same mobile phases as used in analytical TLC (Kim et al., 2000). It gave colorless liquid (bp 146.5–148 °C, 0.7 mmHg).

2.1.3. Synthesis of 3-methyl-4-nitrophenol (*III*)

One gram of pure fenitrothion was dissolved in 10 ml of 5% alcoholic potassium or sodium hydroxide and heated on water bath for 30 min. After removal of the solvent, few drops of water were added and the undesirable materials were extracted with ether. After acidification of phenol salt with 2 N HCl, the solution was cooled over night and the pure phenol was obtained by crystallization from water (mp 125–128 °C) (Akintonwa and Hutson, 1967).

2.1.4. Synthesis of formylfenitrothion

Formylfenitrothion [*O*,*O*-dimethyl-*O*-(4-nitro-*m*-formylphenyl) phosphorothioate] was prepared by the dropwise addition of dimethyl chlorothiophosphate in dry acetone to an ice cold equimolar solution of 5-hydroxy-2-nitrobenzaldehyde in benzene containing 1.1 equiv of NaOH. The reaction mixture, maintained in an atmosphere of nitrogen, was allowed to come to room temperature when the addition was complete and then was refluxed for 8 h. The solvent was removed; the residues were cautiously suspended in water and then extracted three times with chloroform. The combined organic washes were dried (sodium sulfate), filtered and the solvent was removed to yield a pale yellow oil (Greenhalgh and Marshall, 1976).

2.1.5. Synthesis of carboxyfenitrothion (*IV*)

Carboxyfenitrothion [*O*,*O*-dimethyl-*O*-(4-nitro-*m*-carboxyphenyl) phosphorothioate] (IV) was obtained by oxidation of formyl-fenitrothion with 1.2 equiv of chromium trioxide/sulfuric acid in acetone (Bowden et al., 1946).

2.1.6. Synthesis of carboxyfenitrooxon (*V*)

Carboxyfenitrooxon [*O*,*O*-dimethyl-*O*-(4-nitro-*m*-carboxyphenyl) phosphate] (V) was prepared by oxidation of IV in acetone with an excess of potassium permanganate/magnesium sulfate at room temperature. The reaction was essentially complete after 15 min. Filtration of the crude reaction mixture and removal the solvent yielded a white crystalline material which can recrystallized from ether: mp 114–115 °C (Greenhalgh and Marshall, 1976).

2.2. Photodecomposition of fenitrothion

2.2.1. Effect of Ultraviolet Light

Fenitrothion solutions in distilled water at 14 ppm, 1.0% in 50% aqueous methanol, 1.0% in methanol, 1.0% fenitrothion in benzene and 1.0% in acetone were used.

Fenitrothion was individually spotted on silica gel plate (10 μg) (without fluorescent indicator) and then exposed to short UV-light (310 nm) for 15, 30, 60, 90 min at a distance of 25 cm. The photodecomposition was investigated in a glass apparatus with Quartz vessel used for irradiation (Rayoner chamber photo reactor with a wave length (6×3000 °Λ lamp, Ca. 800 w, 300 ± 10 nm).

The temperature of the chromatoplates irradiated with UV light was elevated to about 30°C. Experiments in the dark were carried out alongside as controls. All glass vessels used were pyrex.

2.2.2. Effect of sunlight

The other series of degradation experiments of the radio-insecticide in the same above solutions were studied following exposure to sunlight as follows: water solution for 1, 6, 12, 24 h and other solutions for 1, 6, 12, 24 h and two weeks.

Fenitrothion on silica plates (16 μg) were exposed to sunlight for 1, 3, 7, 15 days. Corresponding experiments in the dark were also carried out to serve as controls. Possible degradation products were investigated using thin layer chromatography.

2.2.3. Stability of fenitrothion on surfaces of glass, quartz and plastic

A solution of one mg of radioactive fenitrothion in hexane (2 ml) was allowed to evaporate in a Pyrex Petri dish. In a similar manner solution one mg of insecticide was placed on a quartz surface and on a plastic surface and then exposed to sunlight for two weeks.

2.2.4. Effect of various pesticides on fenitrothion photodecomposition

To examine the effect of various pesticides on fenitrothion photodecomposition, each of the pesticide (carbaryl and deltamethrin) chemicals was added on silica gel plate and/or added to fenitrothion solution as follows:

1. On silica gel

50 μg of each pesticide dissolved in methonal was spotted at the baseline of TLC plate and ^{14}C-fenitrothion (5 μg in methanol) was overspotted at the same position. The chromatoplates were exposed to sunlight for 2 days and then developed by the solvent systems. The percent of individual products was determined by LSC of radioactive gel regions.

2. In solution

(a) 10 μg fenitrothion was dissolved in water (5 ml),
(b) 10 μg fenitrothion + 1 mg carbaryl were dissolved in 5 ml water,
(c) 10 μg fenitrothion + 1 mg deltamethrin were dissolved in 5 ml water.

The three solutions were exposed to sunlight for one week (in July).

2.2.5. Photodecomposition of fenitrothion deposits on bean leaves

^{14}C-Fenitrothion (84.5 μg) in 50 μl of hexane was applied to the upper surface of each primary leaf by a micropepitte. After treatment, the plants were placed in a protected area for about 8 h each day. The residual radioactivity after various time intervals (1, 3, 6, 12 d) was removed by washing with two separate (50 ml) portions of methanol. The leaves after washing were frozen and then extracted twice with 10 ml of methanol. Extracts were subjected to LSC for the determination of the radioactivity and to TLC for the analysis of the radioactive products. The extracted residues were combusted using a Harvey Biological Oxidizer (Model-OX-600) followed by Liquid Scintillation Counting (LSC). For radio-thinlayer chromatography measurement, 1 cm zones of the plates were scrapped, mixed with scintillator and counted.

2.3. *Characterization of radioactive residues*

Residues were characterized by TLC on silica gel plates using toluene:ethyl acetate:acetic acid 5:7:1 (system 1) and toluene:acetic acid (7:1) (system 2).

Identification of substances was made by comparison with authentic reference samples, their R_f values and retention time are shown in Table 1. Analysis of fenitrothion and its degradation products was performed by high performance liquid chromatography (HPLC).

Spots were made visible by spraying the plates with vanillin/sulfuric acid reagent (2.5%), followed by heating at 110°C for 3 min. Fenitrothion and its metabolites gave different colours (pink and blue). Authentic samples were used for characterization of the residues.

Analysis by high performance liquid chromatography (HPLC) was done on a Helwtt Packard (1100 USA) equipped with gradient system pumping, solvent program-mmer, the stainless steel column (125 × 4 mm I.D) was packed with 5 μm ODS-Hypersil, variable-wavelength UV detector operated at 254 nm. The mobile phase consisted of a mixture of acetonitrile: water (1:1 v/v).

3. Results and discussion

3.1. *Photodecomposition products from irradiation of ^{14}C-fenitrothion in various solutions with UV light*

Fenitrothion dissolved in various solutions was found to be relatively stable when kept in the dark. It readily decomposed upon UV-irradiation showing variable rates of photodecomposition. The rate of degradation in polar solutions decreased in the order: water solution > 50% methanol > acetone and methanol solutions. In benzene solution, on the other hand, the insecticide decomposed less readily. When ^{14}C-fenitrothion in acetone solution was irradiated with UV at 310 nm six products, in addition to parent compound, were detected. The nature and percentage of the products are listed in Table 2. On exposure of ^{14}C-fenitrothion to sunlight in water solution, the insecticide disappeared rapidly and Table 3 shows the percentage of the individual degradation products. Carboxyfenitrothion was the main product.

Table 1
TLC solvent systems and R_f values and retention time (R_t) for fenitrothion and its photoproducts

Compounds	R_f values		R_t
	A	B	C
Fenitrothion [I]	0.92	0.75	9.32
Fenitrooxon [II]	0.67	0.40	2.47
3-Methyl- 4-nitrophenol [III]	0.80	0.35	2.24
Carboxyfenitrothion [IV]	0.60	0.22	–
Carboxyfenitrooxon [V]	0.15	0.08	–
3-Carboxy-4-nitrophenol [VI]	0.37	0.05	–
Methylparathion [VII]	0.92	0.75	–

Solvent system A = toluene:ethylacetate:acetic acid (5:7:1).
B = toluene:acetic acid (7:1).
C = HPLC: UV detector 254 nm, mobile phase acetonitrile:water (1:1).

Okowa et al. (1974) showed that photolysis involved oxidation of the aryl methyl group to give carboxyfenitrothion. The rate of photodecomposition of the insecticide varies according to the solvent used but not the nature of the products. Solvents polarity affected both the rate and the nature of products formed. Irradiation of fenitrothion in non polar solvents appeared to favor oxidation of the P=S to P=O, whereas in polar solvents oxidation occurred at the aryl methyl group (Kormali et al., 2004).

Fenitrothion residues in natural water undergo photodegradation, resulting in the release of several toxic metabolites, some being more toxic to aquatic organisms than

Table 2
Photodecomposition of ^{14}C-fenitrothion in acetone solution irradiated with UV light

Photoproduct	% of recovered radiocarbon as indicated products			
	Irradiation time (min)			
	15	30	60	90
Fenitrothion [I]	85	70	48	30
Fenitrooxon [II]	0.8	1	1.0	1.5
3-Methyl- 4-nitrophenol [III]	Detected by colour			
Carboxyfenitrothion [IV]	5	10	20	25
Carboxyfenitrooxon [V]	0	2	3.5	6
3-Carboxy-4-nitrophenol [VI]	Detected by colour			
Methylparathion [VII]	0	0	0.5	1
Unknown (origin)	5	8	15	18
Total	95.8	91	88	81.5

Table 3
Photodecomposition of ^{14}C-fenitrothion in water solution exposed to sunlight

Photoproduct	% of recovered radiocarbon as indicated products				
	Exposure time (h)				
	1	6	12	24	Dark
Fenitrothion [I]	88	75	50	20	95
Fenitrooxon [II]	1	3	5	7	0.4
3-Methyl- 4-nitrophenol [III]	Detected by colour				
Carboxyfenitrothion [IV]	2	8	15	28	0.3
3-Carboxy-4-nitrophenol [VI]	Detected by colour				
Unknown (origin)	3	6	13	28	0.1
Total	94	92	83	75	95.8

the parent compound (Eto, 1974; Amoros et al., 2000; Derbalah et al., 2004b).

The results obtained show that fenitrothion when irradiated with UV or sunlight undergoes the following photochemical reactions:

(1) oxidation of the P═S group to P═O group, (2) oxidation of m-methyl group to carboxyl group, (3) cleavage of P–O-aryl linkage to give the corresponding phenol. The photodecomposition pathways of fenitrothion deduced from the identified photoproducts are shown in Fig. 1.

According to Kormali et al. (2004) fenitrothion is photodegraded very slowly in absence of catalysts. It is effectively photodecomposed upon photolysis with near visible and UV light, in presence of either $PW_{12}^{-3}O_{40}$ or TiO_2, fenitrothion disappeared within 30–40 min in the presence of $PW_{12}^{-3}O_{40}$, whereas less than 20 min are required in the presence of TiO_2 (Kormali et al., 2004).

3.2. Photodecomposition of ^{14}C-fenitrothion on silica gel chromatoplates

Table 4 shows photodecomposition of fenitrothion on silica gel chromatoplates when exposed to UV light or sunlight. The half-life of the insecticide was calculated to be approximately 15 min with UV and around one week when exposured to sunlight. The Carboxyfenitrothion, fenitrooxon, carboxyfenitrooxon and 3-methyl-4-nitro-phenol represented the main products in each case and a small amount of 3-carboxy-4-nitrophenol was also formed during the exposure of fenitrothion to sunlight (Fig. 1). On the other hand, fenitrothion was found to suffer no change on silica gel plates when kept in the dark within two weeks. Addison (1981) reported on the photolysis of fenitrothion by UV radiation (200–400 nm) from a xenon lamp in the vapour phase (10–15 mg/50–1 reaction chamber) at 85–90 °C and computed the disappearance half life to be 61 ± 11 min and 24 ± 3 min in the absence or presence of ozone (0.7–0.9 ± 1 mg/m^3), respectively (Addison, 1981). The vapour phase photolysis of fenitrothion at 313 nm UV radiations was also studied where 3-methyl-4-nitrophenol and an unidentified product were detected as primary photoproducts (Brewer et al., 1974). In the dark, at room temperature, the hydrolysis of fenitrothion proceeded very slowly (Greenhalgh et al., 1980).

3.3. ^{14}C-Fenitrothion on glass, quartz and plastic

Solid fenitrothion on glass, quartz and plastic surfaces is readily decomposed after exposure to sunlight for two weeks.

According to Fukushima and Katagi, 2006, silica gel provides a photo reactive environment of fenitrothion where a number of unknown polar products were obtained. Simple aliphatic organic solvents, inert surfaces such as glass, octadecylsilane and poly (tetrafluoroethylene) and reactive silica gel were not appropriate for a model surface of a plant (Fukushima and Katagi, 2006).

Table 5
Distribution of ^{14}C-fenitrothion at different time after application to beans leaves

Fraction	Recovery of applied ^{14}C-fenitrothion %			
	Days after application			
	1	3	6	12
Surface wash	43	10	7	2
Methanol extract	25	20	15	12
Residues	2	1.5	1.3	0.8
Total	70	31.5	23.3	14.8

Table 6
Photodegradation products formed on bean leaves treated with ^{14}C-fenitrothion on exposure to sunlight

photoproduct	% of recovered radiocarbon as indicated products			
	Days after application			
	1	3	6	12
Fenitrothion [I]	40	4.5	3	0.3
Fenitrooxon [II]	1.1	1.5	0.5	0.1
3-Methyl- 4-nitrophenol [III]	Detected by colour			
Carboxyfenitrothion [IV]	0.3	0.5	0.5	0.1
3-Carboxy-4-nitrophenol [VI]	Detected by colour			
Unknown (origin)	1.6	3.5	3	1.5
Total	43	10	7	2

Table 4
Photodecomposition of ^{14}C-fenitrothion on silica gel chromatoplates irradiated with UV light and exposed to sunlight

Photoproduct	% of recovered radiocarbon as indicated products (irradiated UV)				% of recovered radiocarbon as indicated products (exposed to sunlight)			
	Irradiation time (min)				Days after application			
	15	30	60	90	1	3	7	15
Fenitrothion [I]	50	40	25	18	80	70	50	30
Fenitrooxon [II]	6	5	3.5	2.5	2	4	6	8
3-Methyl-4-nitrophenol [III]	Detected by colour				Detected by colour			
Carboxyfenitrothion [IV]	2.5	4.0	2.3	1.2	1.0	3	5	6
Carboxyfenitrooxon [V]	0.5	1.0	0.7	0.1	1.2	1.5	2	2.1
3-Carboxy-4-nitrophenol [VI]	Detected by colour				Detected by colour			
Unknown (origin)	15.0	10.0	8.0	6.5	10. 5	6.9	7.5	11.0
Total	74	60	39.5	28.3	94.7	85.4	70.5	57.1

Table 7
Effect of carbaryl and deltamethrin on the photodecomposition of ^{14}C-fenitrothion exposed to sunlight in solution and on silica gel

Pesticide chemical	% of recovered radiocarbon as indicated products													
	I		II		III		IV		V		Origin		Total	
	A	B	A	B	A	B	A	B	A	B	A	B	A	B
Fenitrothion	54	70	10	4	Detected by colour		5	3	2	3	10	7	81	87
Fenitrothion + carbaryl	46	60	5	3			3	1.5	3	2	15	12	72	78.5
Fenitrothion + deltamethrin	40	45	5	5			5	4	2	2	20	18	72	74

A = spotted on silica gel.
B = in solution.
I = fenitrothion.
II = fenitrooxon.
III = 3-methyl-4-nitrophenol.
IV = carboxyfenitrothion.
V = caroxyfenitrooxon.

3.4. Exposure of ^{14}C-fenitrothion deposition on bean leaves to sunlight

As shown in Table 5 the radiocarbon applied was rapidly lost from leaf surfaces. The surface wash after different time intervals contained a relatively small percentage of applied radioactivity. The main metabolites were identified by TLC using the authentic compounds e.g., carboxyfenitrothion, fenitrooxon, 3-methyl-4-nitrophenol and 3-carboxy-4-nitrophenol. The relative amounts of these products are shown in Table 6.

Epicuticular waxes of fruits and vegetables can affect the photodegradation rate and photoproducts that are formed. Pesticides decay rates can be increased, decreased or unchanged by waxes (Cabras et al., 1997; Pirisi et al., 1998, 2001).

3.5. Effect of carbaryl and deltamethrin on ^{14}C-fenitrothion photodecomposition

The nature and percentage of photodegradation products of fenitrothion in presence and absence of carbaryl and deltamethrin on silica gel and in solution are illustrated in Table 7. The obtained data show that carbaryl slightly accelerates the photodecomposition of fenitrothion in comparison with the insecticide alone. On the other hand, deltamethrin also accelerates the photolysis of the insecticide and increases the formation of oxon and origin product on silica gel and in solution.

It seems that certain of these interactions occur on plant foliage exposed to sunlight (Okowa et al., 1974).

Fenitrothion deposits on leaf surfaces underwent oxidation of P=S to P=O, oxidation of m-methyl to carboxyl and P–O-aryl cleavage as happens on silica gel chromatoplates. Contact between various pesticide chemicals occurs in the environment either directly due to application of mixture of compounds or indirectly due to contamination of soil with other insecticides. Therefore, there is a possibility of a photo sensitizing pesticide chemical altering the persistence of fenitrothion residues on treated crops and in the environment.

It should be stressed that some photolysis products obtained in the present study e.g., Oxon and 3-methyl-4-nitrophenol and carboxyfenitrothion were reported in other studies (Okowa et al., 1974; Mikami et al., 1985; Durand et al., 1992, 1994; Castillo et al., 1997; Sakellarides et al., 2003; Kormali et al., 2004). On the other hand, the previously reported denitration products and the S-methyl isomers of fenitrothion (Barcelo et al., 1993; Durand et al., 1994; Sakellarides et al., 2003) could not be detected.

It seems that, under tropical conditions, fenitrothion suffers oxidation of the methyl group in solution (water, acetone) to a considerable extent under the influence of UV or sunlight (25–28%). Under the experimental conditions used, the percentage of fenitooxon and carboxyfenitrothion is also relatively high.

It can be stated that oxidation processes dominate in photolysis of fenitrothion under tropical conditions

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