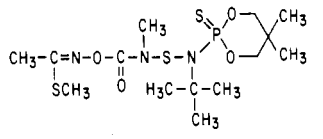
# Multiphase Photodegradation of Methyl *N*-[[[[[(1,1-Dimethylethyl)(5,5-dimethyl-2-thioxo-1,3,2-dioxaphosphorinan-2-yl)-amino]thio]methylamino]carbonyl]oxy]ethanimidothioate

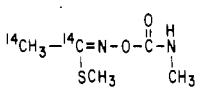
K. Thomas Koshy,* Michael D. Burdick,[1] and Dean W. Knuth

The photolysis of methyl *N*-[[[[[(1,1-dimethylethyl)(5,5-dimethyl-2-thioxo-1,3,2-dioxaphosphorinan-2-yl)amino]thio]methylamino]carbonyl]oxy]ethanimidothioate (I) was conducted in aqueous solution through which $CO_2$-free air was bubbled and in the solid state as a thin film on glass beads under a 3000-Å light. The compound underwent rapid and extensive degradation in both systems. The half-lives were approximately 4.5 h in solution and 1 h in the solid state. Methomyl (II), thiophosphoramide (III), bis(methomyl) sulfide (IV), and bis(methomyl) disulfide (V) were identified as intermediate photolysis products. A cyclic oxophosphoramide (VI) was also seen by TLC–autoradiography and by GC/MS. Finely powdered I was also photolyzed in a chamber sealed with a quartz cover plate under a stream of $CO_2$-free air. The volatiles trapped in cold benzene or water were identified by GC and GC/MS to be acetonitrile and acetone. Other volatiles were $CO_2$, methyl mercaptan, and $SO_2$. There were some volatiles present in low concentrations that were not identified. Nonvolatile compounds were identified as II–VI.

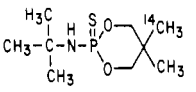
Methyl *N*-[[[[[(1,1-dimethylethyl)(5,5-dimethyl-2-thioxo-1,3,2-dioxaphosphorinan-2-yl)amino]thio]methylamino]carbonyl]oxy]ethanimidothioate (I) is an experimental compound that has shown good activity for control of various lepidopterous pests in several agronomic and horticultural crops (Dutton et al., 1981). The structure of I shows that the carbamate portion is methomyl (II), which is joined by a sulfur bridge to a cyclic thiophosphoramide (III). This combination has resulted in a compound with good biological activity and considerably lower mammalian toxicity than II or other related compounds. Photolysis of I was undertaken as part of determining its environmental fate. There is no published information for the photolysis of II and related commercially available pesticides.



U-56,295 (I)



Methomyl (II)



Thiophosphoramide (III)

## EXPERIMENTAL SECTION

**Equipment.** A Rayonet RPR-208 photochemical reactor with 8 RUL-3000 Å UV lamps (Southern New England Ultraviolet Co., Middletown, CT) was used for the solution photolysis. The average energy output at the center of the assembly was $1.13 \times 10^4$ ergs/(cm$^2$ s) ($1.13 \times 10^3$ $\mu$W/cm$^2$) when measured with a UVX-30 sensor at 297 nm (Ultra-Violet Products, Inc., San Gabriel, CA). A single RUL 3000-Å lamp module which provided $2.6 \times 10^3$ ergs/(cm$^2$ s) ($2.6 \times 10^2$ $\mu$W/cm$^2$) at the sample surface was used for the solid-state photolysis. High-performance liquid chromatography (HPLC) employed an LDC Constametric III pump and UV III detector with an accessory zinc lamp and power supply which monitored the absorbance at 214 nm (Laboratory Data Control, Riviera Beach, FL). The HPLC column packing material was $C_{18}$-bonded microparticulate silica (Zorbax ODS, 0.46 × 25 cm, E. I. DuPont de Nemours & Co., Wilmington, DE). Injections were made either manually through a loop injector (Model CV-6-HPax 3000 psig, Valco Instruments Co., Houston, TX) or through an automatic injector (Model WISP 710B, Waters Associates, Inc., Milford, MA). The mobile phase was $CH_3CN$–$H_2O$ in the ratio of 65:35 at a flow rate of 1.25 mL/min. A 10-mV dual-pen recorder (Model A25, Varian Instruments, Palo Alto, CA) in conjunction with an integrator (Model 3390A, Hewlett-Packard, Palo Alto, CA) was used to determine the peak height or area responses.

Gas-liquid chromatography (GC) was performed with a Mikrotek MT 220 GC equipped with $H_2$ flame ionization and $H_2$ flame photometric detectors (Tracor, Inc., Austin, TX). The GC column for the low molecular weight volatile compounds was a 120 × 0.3 cm i.d. glass tube packed with 100–120-mesh Porapak Q (Waters Associates, Inc., Milford, MA) which was operated at 110 °C. The column for the thiophosphoramide (III) and its oxygen analogue (VI) was a 120 × 0.3 cm i.d. glass tube packed with 3% HIEFF 8 BP on 100–120-mesh Gas-Chrom Q. This column was operated at 145 °C. The carrier gas was $N_2$ in both cases.

Photolysis of the aqueous solution of I was performed in a 2-L cylindrical flask as shown in Figure 1. The flask was mounted in the center of the RPR-208 reactor. Solid-state photolysis was performed in a reactor made from a cut off battery jar with two $^1/_4$-in side arms fused on opposite sides (Figure 2). One of the RUL 3000-Å light modules from the RPR-208 reactor was clamped horizontally about 3.5 in. above the bottom of the reaction chamber.

**Procedures.** (*A*) *Coatings of Glass Beads.* The glass beads were 170–230-mesh size from Applied Sciences Laboratories, Ann Arbor, MI. They were cleaned and coated with I, II, or III according to a previously reported procedure (Koshy et al., 1975). The concentration of I on the beads was about 1 mg/g.

(*B*) *Photolysis in Solution.* The photolysis of I in solution was carried out with saturated aqueous solutions

The Upjohn Company, Agricultural Division, Kalamazoo, Michigan 49001.

[1]Present address: Biochemistry Department, Michigan State University, East Lansing, MI.

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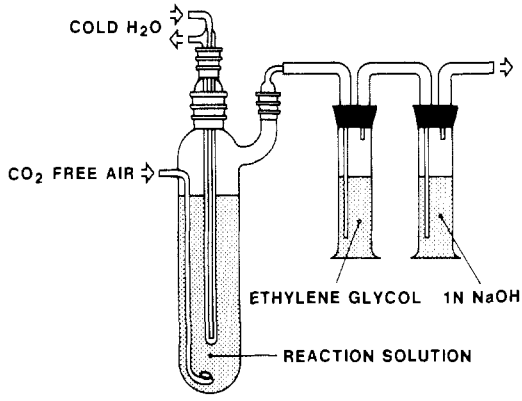



**Figure 1.** Reaction setup for the solution photolysis of compound I, methomyl (II), and the thiophosphoramide (III).

(≃0.4 μg/mL) or with saturated aqueous solutions fortified with radiolabeled I. The label was with $^{14}C$ at either the methomyl ([$^{14}C$]METH-I) or the thiophosphoramide ([$^{14}C$]TPA-I) end of the molecule. The positions of the label are indicated in the structures of II and III shown earlier.

Two liters of the solution was poured into the reaction vessel. One milliliter of the $^{14}C$-labeled I (3–4 μCi/mL, 120 μg/mL in $CH_3CN$) was then added and mixed. Carbon dioxide free air was bubbled through the solution at the rate of 25–30 mL/min. Water was passed through the cold finger at a rate which maintained the solution temperature at 27 ± 2 °C. Three 100-mL aliquots were taken as control samples before before starting the reaction. The effluent air was scrubbed with 50 mL of ethylene glycol to trap radioactive volatile organics and then with 50 mL of 1 N NaOH to trap $^{14}CO_2$. Fifty-milliliter samples were taken at hourly intervals for the first 4 h and thereafter once every 2 h for 32 h. The samples were extracted with 65 mL of $CH_2Cl_2$, evaporated under vacuum, and reconstituted in exactly 2 mL of $CH_3CN$. The extracts were analyzed by HPLC. The extracted aqueous phase was also dried by rotary evaporation and taken up in 2 mL of distilled water. Exactly 250 μL of the $CH_3CN$ extract and the entire concentrated aqueous residue were mixed separately with 15 mL of Diotol and the amounts of radioactivity determined in a scintillation spectrophotometer. An internal standard method was used to correct for quenching. One-milliliter aliquots from the NaOH and ethylene glycol traps were also counted. Five hundred milliliters of the reaction mixture remaining after 32 h of photolysis was extracted with about 100 mL of $CH_2Cl_2$, evaporated to dryness, and then taken up with 2 mL of $CHCl_3$. Approximately 25 μL of this solution was spotted on TLC plates and developed with hexane–ethyl acetate, 1:1 or 7:3. An autoradiogram of the resulting chromatogram was taken, and then the plate was scraped in 5-mm increments into scintillation vials for counting. The initial pH of the solution was 6.2 and dropped to 4.8 after 32 h. A control experiment was conducted with a saturated solution of I without irradation. Hydrolysis of I under control conditions was negligible.

(*C*) *Photolysis on Glass Beads.* Five grams of the coated beads was placed in the reaction chamber (Figure 2), covered with a quartz plate (Quartz Scientific, Inc., Fairport Harbor, OH), and clamped to form an airtight seal. $CO_2$-free air was passed through the chamber and then in series through 5 mL of ice-cold water, 5 mL of cold ethanol, 25 mL of ethylene glycol, and 25 mL of 1 N NaOH to trap volatile water solubles, organic solubles, and $^{14}CO_2$, respectively. Samples of the beads were taken periodically to determine radioactivity distribution. For each sampling 250 mg of the beads was extracted with 5 mL of $CH_3CN$. Exactly 500 μL of the $CH_3CN$ extract, 100 μL of the water and ethanol, and 250 μL the NaOH and ethylene glycol from the various traps were sampled and the radioactivity of each determined in 15 mL of Diotol. The $CH_3CN$ extract was also analyzed by HPLC for concentrations of I and other photoproducts and by GLC for compounds III and VI on the HIEFF 8BP column using the flame photometric detector. The water trap was analyzed by GC and GC/MS for volatile products on the Porapak Q column.

(*D*) *Powder Photolysis.* Photolysis of powdered I, II, and III was conducted in order to generate more of the photolytic products and also to ascertain their origin. About 5 g of finely powdered I, II, or III was placed in the reaction chamber. Tapered tubes containing 2 mL each of cold water and benzene immersed in an ice water bath as shown in Figure 2 were used as traps in the trials with unlabeled compound; water, ethanol, NaOH, and ethylene glycol traps were used in the radioactive studies. Sampling and analysis of the traps were the same as described under Section C. One hundred milligrams of the photolyzed powder was dissolved in 100 mL of $CH_3CN$ and analyzed by HPLC for I and the intermediary photolysis products. Radiolabeled studies were performed by adding a similar reaction chamber containing the labeled compound in series to the first so that the effluents from both chambers were collected in the same traps. About 100 μg (10 mCi/mM) of the compound being studied was photolyzed. Some of the photolyzed labeled material was used for TLC–autoradiograms.

## RESULTS AND DISCUSSION

Figure 3 shows the UV absorbance spectra of I, II, and III and Figure 4 shows the energy spectrum of the Rayonet-RUL 3000-Å lamp. Since the compounds have prac-

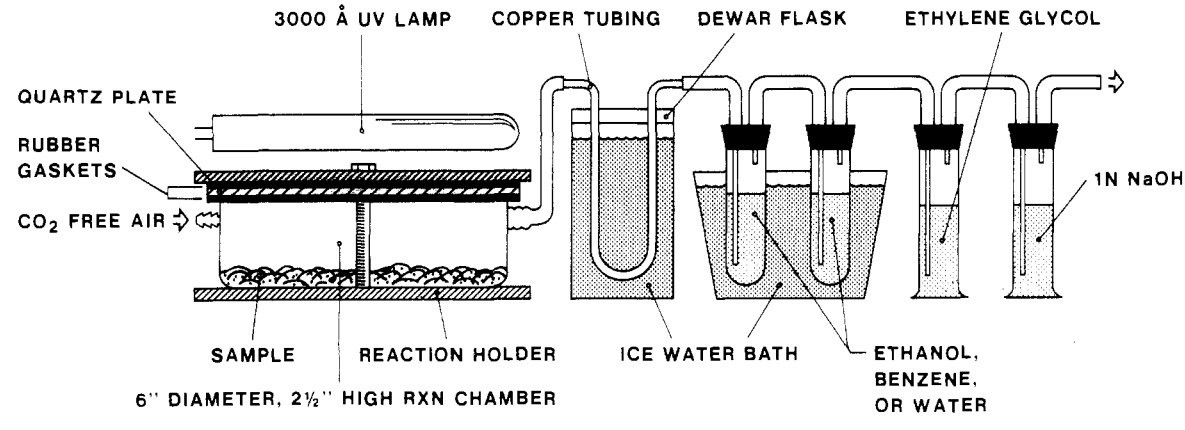



**Figure 2.** Reaction setup for the solid-state photolysis of compound I, methomyl (II), and the thiophosphoramide (III).

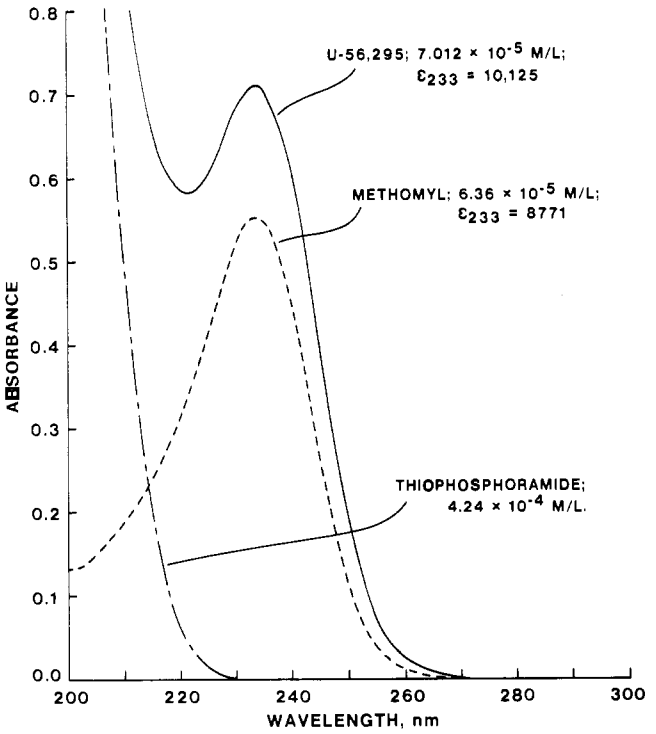
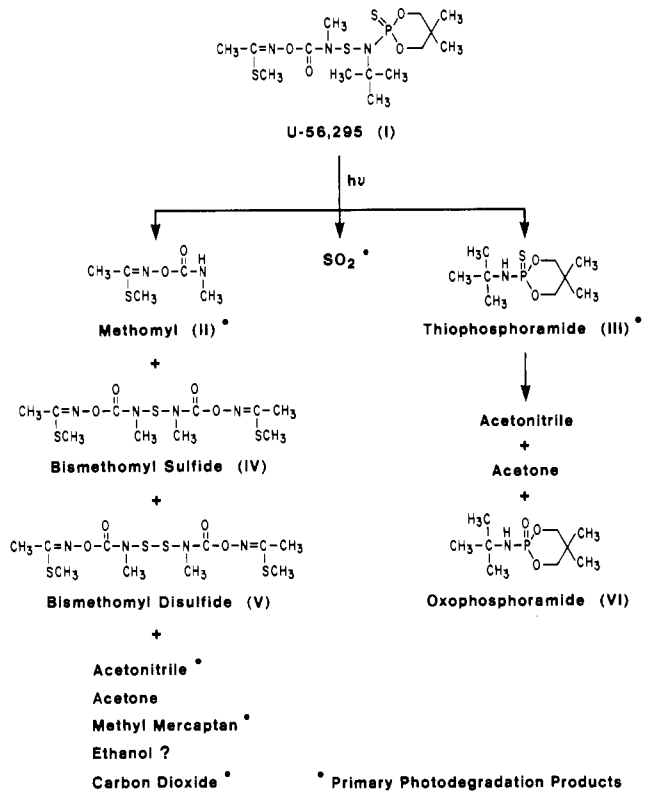



**Figure 3.** Ultraviolet absorbance spectra of compound (I), methomyl (II), and the thiophosphoramide (III).

Scheme I. Postulated Photodegradation Pathway of I




tically no absorbance at 3000 Å, they were not suspected to be susceptible to photolysis, but this assumption proved to be wrong for I and II.

Figure 5 shows liquid chromatograms of a synthetic mixture of I and the suspected degradation products and also of an extract of a solution of I that was photolyzed for 68 h (see Scheme I for structures). The HPLC system can detect II, IV, and V at 12 ng on column and III at 120 ng on column.

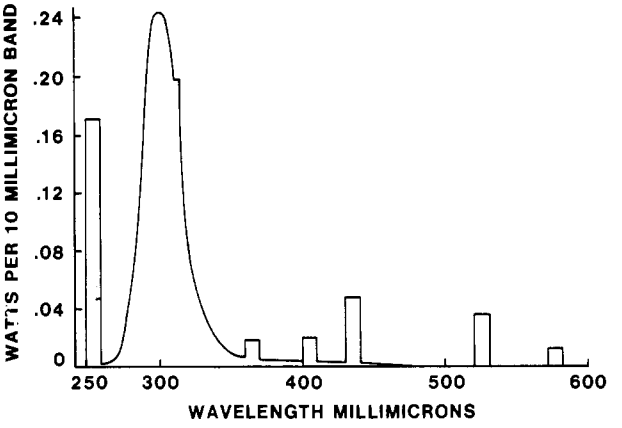



**Figure 4.** Energy spectrum of the Rayonet-RUL 3000-Å lamp.

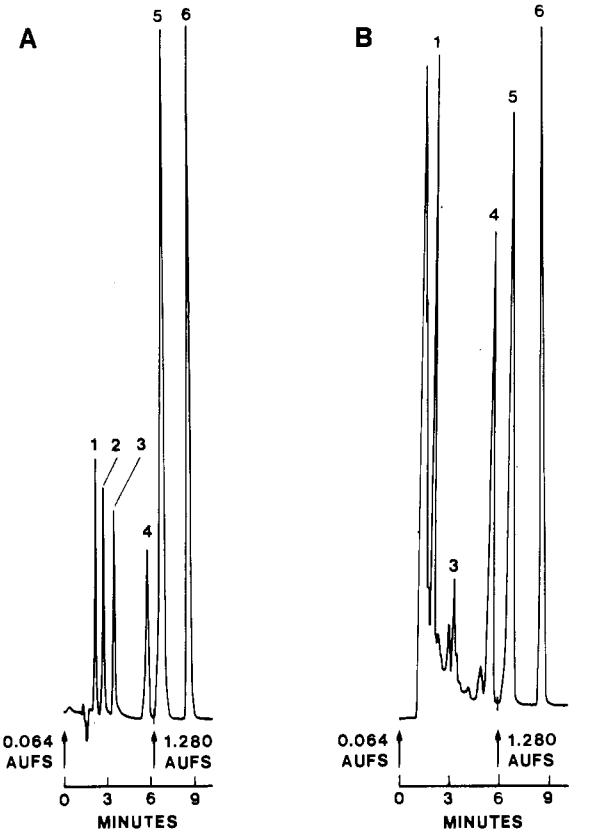



**Figure 5.** High-performance liquid chromatogram of compound I and degradation compounds. (A) A synthetic mixture. Key: 1, methomyl; 2, bis(methomyl) sulfide; 3, bis(methomyl) disulfide; 4, thiophosphoramide; 5, compound I; 6, naphthalene (internal standard). The concentrations were 3.17, 3.15, 3.16, 25, 1000, and 40 μg/mL, respectively. (B) Extract from a solution of I photolyzed for 68 h.

Figure 6 shows the decline curves for the photolysis of I in solution and in the solid state as a thin film. The half-lives in the two systems are about 4.5 and 1 h, respectively. Irradiation of a saturated aqueous solution of I produced II–VI (Scheme I). Compounds II, IV, and V were detected by HPLC. Compound III was identified by GC/MS (model LKB 9000, LKB Producter AB Stockholm, Broma, Sweden). The oxophosphoramide (VI) was identified by TLC–autoradiography on silica gel $GF_{254}$, 250-μm plates in the [$^{14}$C]TPA-I aqueous study and later confirmed by GC/MS on a 3% HIEFF 8BP column in the powder photolysis of I and III. Its concentration was always low (≤1%). This compound was, however, the major metabolite of I in soil metabolism studies (Johnson and Cox, 1982).

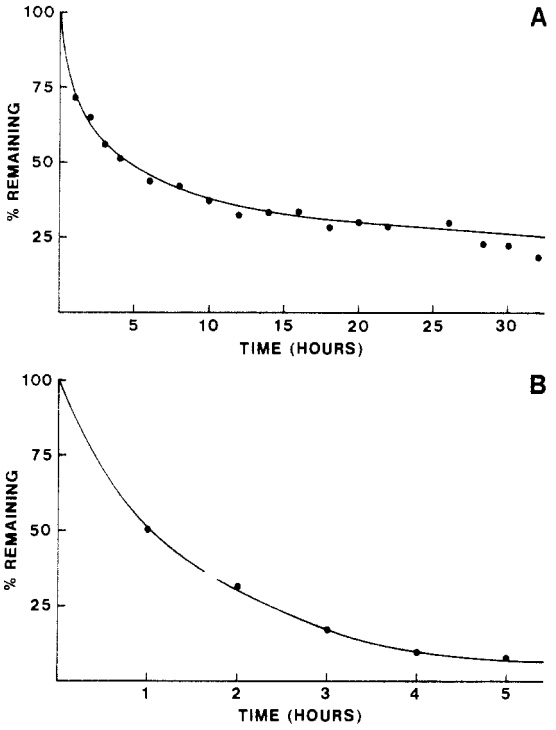



**Figure 6.** Decline curves for the photolysis of (A) I in solution and (B) I in the solid state as a thin film.

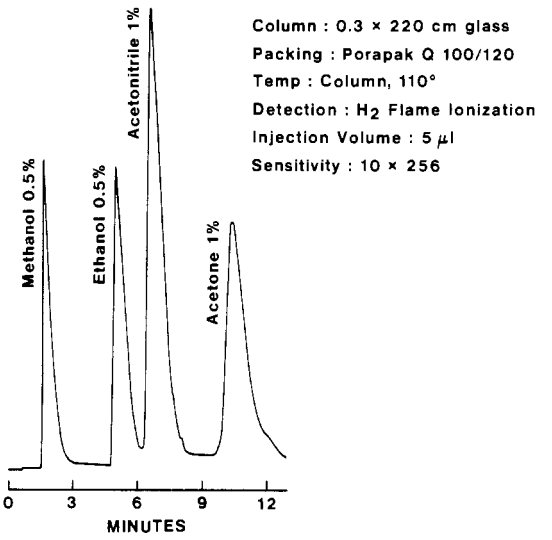



**Figure 7.** Gas–liquid chromatogram of a synthetic mixture of the volatile photoproducts of I and II on the Porapak Q column.

There was no substantial buildup of any of the identified solid-state products in the solution photolysis. There was a linear increase of radioactivity in the traps during the 32-h aqueous photolysis from both the [$^{14}$C]METH-I and [$^{14}$C]TPA-I studies. In one study with [$^{14}$C]METH-I in solution, after 6 h of irradiation, 67.5% of the radioactivity was organic soluble, 1.8% was unextractable, 3.6% was volatile organics, and 1% was $CO_2$, accounting for a total of 74% of the original radioactivity. It was later found that there was some loss of radioactivity during evaporation of the organic extract and of the water. None of the previously identified methomyl type of photoproducts were seen in the photolysis of I as a thin film on glass beads, suggesting that these intermediate compounds are susceptible to rapid degradation. Small quantities of III (<0.5% of the starting material) were detected.

Most of the data on the photoproducts were obtained from the photolysis of finely powdered I. When the powder was analyzed by HPLC after 68 h of photolysis, there was 86% of residual I, 0.54% of II, and 5.4% of III. Trace amounts of IV and V were also detected. The identities of all solid compounds were confirmed by TLC separation of a solution of the photolyzed powder and by analysis of the concentrated extract by direct probe mass spectrometry against authentic standards. The TLC separation was on silica gel $GF_{254}$ plates using 7:3 ethyl acetate–hexane as the mobile phase. Among the volatile photoproducts, acetonitrile was detected by GC in the water or benzene trap within 1 h. Acetonitrile was the major volatile product and seemed to build up with time. Acetone was generated within a few hours but in much smaller amounts. Ethanol was also seen but only in trace amounts. The identity of acetonitrile, ethanol, and acetone was confirmed by GC/MS. These compounds were seen at higher concentrations from II than from I. Figure 7 shows a chromatogram of a standard mixture of the low molecular weight volatiles by GC on the Porapak Q column. Methyl mercaptan was detected within an hour from I and II by a color reaction with 5,5′-dithiobis(2-nitrobenzoic acid) as described by Prescott (1966) and is thus considered to be a primary photoproduct. Carbon dioxide and $SO_2$ were detected by precipitation tests with $BaCl_2$ from the aqueous traps. Dissolved $SO_2$ was first oxidized to $H_2SO_4$ with a few drops of 30% $H_2O_2$ prior to precipitation with $BaCl_2$.

Results from the powder photolysis of II and III gave clues to the reaction pathway of I and the source of the volatile products. Compound II was highly susceptible to photolysis, producing the same volatile organics as from I. The thiophosphoramide (III) was much more stable to photolysis than I or II. After 100 h of photolysis of [$^{14}$C]III, 96% of the compound remained intact. There was about 1.2% VI. The water, ethanol, NaOH, and ethylene glycol traps contained 1.6, 0.3, 1.0, and 0.1% of the radioactivity, respectively. Acetonitrile was one of the products detected by GC for photolysis of III, but unlike the case of I or II, its concentration did not increase with time. Trace amounts of acetone and $CO_2$ were also detected.

From the results of the photolysis of I, II, and III, Scheme I is created to crudely represent the reaction pathway. This is recognized to be an oversimplified version since other reactions were taking place simultaneously as exemplified by the formation of $CH_3CN$ and $CH_3SH$ within 1 h during the powder photolysis of I. It is also recognized that there are unidentified photoproducts as judged by the progressive discoloration and strong odor generated during photolysis. The odor is more than likely to be due to only $CH_3SH$ and $SO_2$. No $SO_2$ was detected from the photolysis of II or III (except the small amount formed in the conversion of III to VI), suggesting that cleavage of I takes place at one or both sides of the sulfur bridge. Since comparatively higher concentrations of the disulfide (V) than of the sulfide (IV) are always produced during photolysis of I, the cleavage occurs more on the thiophosphoramide side of the molecule than the methomyl side. Since II readily breaks down to $CH_3CN$, $(CH_3)_2C{=}O$, $C_2H_5OH$, and $CH_3SH$, it is likely that $CH_3NH_2$ would also be a photoproduct. Efforts to detect it as the heptafluoramide by electron capture gas chromatography were not successful. Methanol and ethanol were detected, but their presence was not reproducible.

The primary photoproducts of I in powder form are II, III, $SO_2$, $CH_3CN$, $CH_3SH$ and $CO_2$. The secondary ones are IV–VI, acetone, ethanol, and possibly other unidentified compounds. During powder photolysis it was noticed that the underside of the quartz cover plate always became cloudy or covered with a yellowish film. The GC/MS of

a solution of this film on a 3% OV-1 column (3-mm i.d. × 2 ft) gave five peaks with fragmentation patterns and weak molecular ions characteristic of straight-chain hydrocarbons. No further effort was made to characterize these compounds.

From an environmental safety point of view, the photolysis of I poses no danger. As a thin film, the compound rapidly photolyzed without producing detectable amounts of any other photolyte other than $CO_2$.

ACKNOWLEDGMENT

We thank Dr. D. B. Johnson of the Upjohn Company for the synthesis and supply of [$^{14}$C]METH-I and [$^{14}$C]-TPA-I. We thank Dr. S. J. Nelson and F. E. Dutton for supplies of all the other unlabeled compounds.

**Registry No.** I, 72542-56-4; II, 16752-77-5; III, 72542-64-4; IV, 59669-26-0; V, 68789-90-2; VI, 944-23-0.

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Received for review July 6, 1982. Accepted February 18, 1983.

# Application of a High-Performance Liquid Chromatographic System with an On-Line Infrared Detector to the Residue Analysis of Permethrin

Euphemia Papadopoulou-Mourkidou,*[1] Yutaka Iwata, and Francis A. Gunther

The first application of a high-performance liquid chromatographic system (HPLC) with an on-line infrared (IR) detector for pesticide residue analysis is reported. The system was applied to the residue analysis of permethrin in lettuce which was field-treated with an emulsifiable concentrate formulation. Permethrin residues were extracted with acetone, the extract was liquid–liquid partitioned with hexane and $CH_3CN$, and the coextracted chlorophyll was removed with charcoal. The extract was then concentrated, filtered through a silica gel Sep-PAK, and analyzed by HPLC on a 5-μm Partisil column which was eluted with a solvent mixture composed of 3% 1-tetradecene, 70% $CH_2Cl_2$, and 27% cyclohexane. Under these conditions the cis and trans isomers of permethrin were separated and quantified. With the IR detector operated at 5.8 μm and 0.025 absorbance unit full scale, a minimum detectable level of 0.2 μg/g was obtained based on a 20-μL injection volume and a concentration factor of 0.2 mL/100 g of fresh lettuce. A tandem ultraviolet detector operated at 254 nm was also used as a second on-line detection system.

Permethrin [(3-phenoxyphenyl)methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate] was the first pyrethroid insecticide developed which was appropriate for field use (Elliott et al., 1978). Residue analyses for permethrin have been conducted principally by gas chromatography (GC) with electron-capture detection. GC analyses for permethrin residues in extracts prepared from plant and animal tissues, soil, and water have been reported (Bélanger and Hamilton, 1979; Chapman and Harris, 1978, 1979; Chiba, 1978; Estesen et al., 1979; Fujie and Fullmer, 1978; Oehler, 1979; Reichel et al., 1981; Siegel et al., 1980; Williams, 1976; Williams and Brown, 1979). The use of high-performance liquid chromatography (HPLC) with an ultraviolet (UV) detector has been reported only by Kikta and Shierling (1978) for the analysis of permethrin in extracts from plant deposits.

An HPLC–infrared (IR) system reported for the analysis of pyrethroid and carbamate insecticides in formulations and technical-grade materials (Papadopoulou-Mourkidou et al., 1980, 1981a,b) has now been used for residue analysis with permethrin serving as a test compound. This report represents the first application of such a system to pesticide residue analysis.

Department of Entomology, University of California, Riverside, Riverside, California 92521.
[1]Present address: Department of Agricultural Chemistry, Aristotelion University, Thessaloniki, Greece.

EXPERIMENTAL SECTION

**Materials.** Analytical standards of *cis*- and *trans*-permethrin (99%) and Pounce 3.2 EC formulation [0.38 kg of active ingredient (AI)/L] were obtained from FMC Corp. HPLC solvents were purchased from J. T. Baker Chemical Co. 1-Tetradecene was obtained from Aldrich Chemical Co., Inc. Acetone, $CH_2Cl_2$, hexane, $CH_3CN$, and cyclohexane were used for residue extractions, and sample preparations were of reagent grade and were redistilled prior to use.

A 250 × 4.6 mm i.d. analytical column packed with 5-μm Partisil and a 50 × 4.6 mm i.d. guard column packed with 35–50-μm HC Pellosil were obtained from Whatman. Other chromatographic materials used were Celite 545 (AW) (Supelco, Inc.), Norit A acid-washed charcoal (Phanstiehl Laboratories, Inc.), silica gel Sep-PAK (Waters Associates), attaclay, and anhydrous $Na_2SO_4$.

**Instrumentation.** The liquid chromatographic system (Waters Associates) consisted of two Model 6000A pumps controlled by a Model 660 solvent programmer. A Rheodyne 7125 valve-type injector equipped with 10-, 20-, or 200-μL loops was used.

A Rheodyne 7000A valve with a guard column in the loop was inserted between the injector and the analytical

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