

# Hydrogen Peroxide and Hydroxyl Radical: Intermediates in Indirect Photolysis Reactions in Water

William M. Draper\*<sup>1</sup> and Donald G. Crosby

Thiobencarb (I) photodecomposes slowly to thiobencarb S-oxide (II) in aqueous solutions exposed to sunlight. The rate of photodecomposition of I in water was greatly increased by addition of small amounts of hydrogen peroxide, tryptophan, or methylene blue. In these solutions, 2-hydroxythiobencarb (III), 3-hydroxythiobencarb (V), II, and *N*-monoethylthiobencarb (IV) were isolated as photooxidation products of I; the distributions of these products were similar in each case. Thiobencarb did not undergo reaction with photochemically generated, singlet molecular oxygen but was oxidized by hydroxyl radical (Fenton's reagent) to III, V, and II. The free radical photooxidation of I in aqueous acetone was unique; II and IV were among the photoproducts but the phenols, III and V, were absent. These results demonstrate the involvement and common intermediacy of hydrogen peroxide and hydroxyl radical in indirect photolysis reactions in aqueous solutions of hydrogen peroxide, tryptophan, and methylene blue.

The photochemical transformation of xenobiotics in pure water occurs only by a direct photolysis mechanism in which the compound absorbs the incident radiation directly (Zepp and Cline, 1977). There is much interest in indirect photolysis processes which occur in water. In these reactions, an additional solute is needed to act as a chromophore and, somehow, to transfer absorbed energy or generate an active oxidizing species.

Photosensitized oxidations involving singlet molecular oxygen are well-known. Pioneering work was carried out primarily in nonpolar, organic solvents, presumably for practical reasons—acceptor molecules are highly soluble in nonpolar solvents and, due to the enhanced lifetime of the oxidant,  $^1\Delta_g$  O<sub>2</sub>, organic solvents were preferred to water for singlet oxygenation reactions. Similar mechanisms are often assumed to rationalize photosensitized oxidations occurring in water, in spite of the unique properties of this solvent.

The present work is a comparative study of photochemical transformations occurring in water containing various organic and inorganic additives. The photoproduct distribution of the probe molecule, thiobencarb, was described qualitatively for each system in order to delineate the scope of reactivity and thereby postulate reaction mechanisms. Thiobencarb's reactions with singlet molecular oxygen and hydroxyl radicals were defined similarly. A major goal of the investigation was to assess the relative importance of these two oxidants in indirect photooxidations in water.

## EXPERIMENTAL SECTION

**Chemicals.** Reagent-grade 30% hydrogen peroxide (Mallinkrodt, Inc.) was used exclusively. This product contains a stabilizer, but no extraneous absorptions were observed when compared to the published ultraviolet spectrum (Heidt, 1967), nor were contaminants otherwise detected. Methylene blue (U.S.P. crystals) and tryptophan (greater than 99% pure) were obtained from Aldrich Chemical Co. All solvents were pesticide analytical grade or reagent grade which had been redistilled in a glass still. Other chemicals were reagent grade.

Thiobencarb [*S*-(4-chlorobenzyl) *N,N*-diethyl-1-carbamothioate, I] was purified by vacuum distillation of tech-

nical material (95.5%) provided by Chevron Chemical Co. (Richmond, Ca.). The clear, colorless oil collected was homogeneous to TLC and was found to be greater than 98.5% pure by temperature-programmed GLC: MS (GC/MS, 70 eV) *m/e* 100 (base, C<sub>5</sub>H<sub>10</sub>NO), 72 (48%, C<sub>3</sub>H<sub>6</sub>NO), 125 (17%, C<sub>7</sub>H<sub>6</sub>Cl), 257 (<5%, M<sup>+</sup>); MS (solid probe, 40 eV) *m/e* 100 (base), 72 (95%), 125 (74%), 257 (M<sup>+</sup>, 41%), 259 (M + 2, 16%); IR 3040, 2980, 2950, 1650 (CO), 1500, 1420, 1250 cm<sup>-1</sup>; NMR (CDCl<sub>3</sub>)  $\delta$  7.23 (s, 4.3, phenyl), 4.05 (s, 2, -SCH<sub>2</sub>-), 3.35 (q, 4, NCH<sub>2</sub>CH<sub>3</sub>, *J* = 7 Hz), 1.14 (t, 6.6, CH<sub>3</sub>, *J* = 7 Hz).

Thiobencarb sulfoxide [(4-chlorobenzyl)sulfinyl]-carbonyl-*N,N*-diethylamine, II] was synthesized by oxidation of I with 1 equiv of 3-chloroperoxybenzoic acid in chloroform, followed by purification on a Florisil column (Casida et al., 1975). The product was homogeneous to TLC: MS (solid probe, 70 eV) *m/e* 100 (base, C<sub>5</sub>H<sub>10</sub>NO), 72 (62%, C<sub>3</sub>H<sub>6</sub>NO), 125 (37%, C<sub>7</sub>H<sub>6</sub>Cl), no M<sup>+</sup>; MS (solid probe, 40 eV) *m/e* 100 (base), 72 (56%), 125 (24%).

**Diazotized Sulfanilic Acid.** Sodium sulfanilate (10 g, 51 mM), 50 mL of 10% aqueous potassium hydroxide, and 40 mL of 10% sodium nitrite were combined in a three-neck flask fitted with an ice bath and a magnetic stirrer. The solution was treated dropwise with 24 mL of 8 M hydrochloric acid, resulting in the precipitation of the product which was collected by filtration and washed with cold water, ethanol, and ether (Randerath, 1964). The explosive salt was stored at -5 °C.

**Methods.** Thin-layer chromatography (TLC) was performed on precoated silica gel plates containing a phosphor (0.25 mm × 20 cm, silica gel 60 F-254, Scientific Products, Inc.). Solvent systems utilized were benzene-methanol (90:10 v/v, solvent A); benzene-ethanol-acetic acid (40:1:2 v/v/v, solvent B; Ishikawa et al., 1976, benzene-methanol-formic acid (100:20:1 v/v/v, solvent C). Compounds were visualized on chromatoplates by quenching of 254-nm light, by adsorption of iodine vapor, and with specific chromogenic reagents. Sulfur-containing compounds were detected with palladium chloride (Blinn, 1964) and phenolic materials by their reaction with Pauly's reagent prepared immediately prior to use by addition of 50 mg of diazotized sulfanilic acid to 10 mL of 10% aqueous sodium carbonate (Randerath, 1964).

All analyses by gas-liquid chromatography (GLC) were carried out with a Varian Model 2400 chromatograph fitted with a hydrogen flame ionization detector. Two 3 mm i.d. glass columns were used; a 1.0-m column packed with 3% OV-17 on 60-80-mesh Gas-Chrom Q and a 1.5-m column of Chromosorb 102. Gas flow rates were 37 mL/min nitrogen carrier, 30 mL/min hydrogen, and 200 mL/min air.

Department of Environmental Toxicology, University of California, Davis, California 95616.

<sup>1</sup>Present address: Department of Animal, Dairy and Veterinary Sciences, Utah State University, Logan, UT 84322.

The injection port and detector were operated at 275 and 310 °C, respectively.

Mass spectra (electron impact, 70 eV) were determined on a Finnigan Model 3000 gas chromatograph peak identifier equipped with a gas-liquid chromatograph (1.5 m × 3 mm i.d. glass column; 3% OV-17 on 60–80-mesh Gas-Chrom Q; 10 mL/min He flow rate). A Du Pont Model 492 mass spectrometer interfaced to a Finnigan Incos data system was utilized for "soft" ionization spectra (electron impact, 40 eV). Some compounds were introduced directly to the mass spectrometers by solid probe; compound II is thermally unstable. Proton NMR spectra were obtained with a Varian Model EM-390 60-MHz instrument; samples were dissolved in deuterated chloroform containing tetramethylsilane as an internal standard.

**Solution Preparation.** Thiobencarb (12 µL/L) was introduced directly into demineralized water, stirred for 48 h, and filtered through a medium-porosity fritted glass funnel. Oxidant fortification at the micromolar level was accomplished accurately by dilution of a 10.0 mM hydrogen peroxide stock solution.

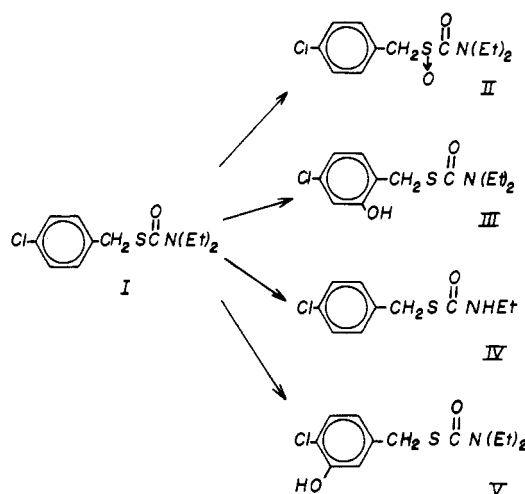
**Photoproduct Structure Determination.** Photooxidation products of thiobencarb were determined initially in a preparative scale experiment. A 2-L aqueous thiobencarb solution (20 mg/L) containing 100 µM hydrogen peroxide was irradiated in sunlight for 96 h (Davis, CA; 38° 30' N; 20-m elevation; August). The solution was extracted with three 100-mL portions of dichloromethane and the concentrated extract was resolved by preparative TLC. Bands were detected by the previously described methods, desorbed from the silica gel with acetone, and further characterized by mass spectrometry.

**Comparative Photodecomposition.** One-liter thiobencarb solutions were prepared containing one of the following: 100 µM hydrogen peroxide; 340 mM acetone; 134 µM methylene blue; 490 µM tryptophan. These solutions and a control were exposed to sunlight (August) in sealed borosilicate flasks; equivalent control solutions were maintained at the same temperature in the dark. The consumption of thiobencarb in each treatment was monitored. Fifty-milliliter water samples were withdrawn, extracted with 2 × 5 mL of dichloromethane, and the extract analyzed by GLC using the OV-17 column operating at 195 °C. The extraction efficiency exceeded 97%.

The photolysate remaining after the thiobencarb concentration had declined by 50–60% was extracted with three 50-mL volumes of dichloromethane; the combined extract was reduced to 1 mL on a rotary evaporator and a portion subjected to semiquantitative analysis by TLC. The acetone-sensitized photolysis was analyzed after 6 h (650 mL remaining) while other treatments were terminated after 240 h with 450 mL remaining. Photoproducts were identified by retardation factors and specific chromogenic reactions.

**Oxidation by Fenton's Reagent.** Ferrous sulfate heptahydrate granules (16.7 mg, 60 µM) were added to a rapidly stirring thiobencarb solution (1 L) containing 30 µM hydrogen peroxide and allowed to react for 15 min. The oxidation was repeated by readdition of oxidant, followed by iron. Oxidation products in the 800-mL water sample were analyzed as above.

**Reactions with Singlet Molecular Oxygen.** A methanolic solution of thiobencarb (10 mg/100 mL) and eosin (10 mg/100 mL) was irradiated for 24 h in a large-scale laboratory photoreactor fitted with F 40 BL fluorescent lamps (Crosby and Wong, 1973). The herbicide concentration was measured periodically by direct analysis of the photolysate by GLC. For verification that singlet



**Figure 1.** Products of the free radical photooxidation of thiobencarb.

oxygen was being generated, 2,5-dimethylfuran (mg/mL) was used as an acceptor in a second experiment under identical conditions; the disappearance of 2,5-dimethylfuran was measured by using the porous polymer GLC column operating at 220 °C.

## RESULTS AND DISCUSSION

**Products of Free Radical Photooxidation.** Thiobencarb photodegrades rapidly in the presence of hydrogen peroxide, exhibiting a half-life of 41 h. The probe, however, is relatively stable in purified water exposed to sunlight and in oxidant solutions maintained in the dark; under these conditions, less than 10% of the parent compound was altered after 100 h of treatment.

The preparative-scale photooxidation experiment yielded four extractable photooxidation products (Figure 1): II; *S*-(2-hydroxy-4-chlorobenzyl) *N,N*-diethyl-1-carbamothioate (III) [MS (solid probe, 70 eV) *m/e* 100 (base, C<sub>5</sub>H<sub>10</sub>NO), 72 (55%, C<sub>3</sub>H<sub>6</sub>NO or C<sub>4</sub>H<sub>10</sub>N), 141 (11%, C<sub>7</sub>H<sub>6</sub>ClO), 273 (M<sup>+</sup>, <2%); MS (solid probe, 40 eV) *m/e* 100 (base), 72 (65%), 273 (25%), 141 (24%)]; *S*-(4-chlorobenzyl) *N*-ethyl-1-carbamothioate (IV) [MS (solid probe, 40 eV) *m/e* 125 (base, C<sub>7</sub>H<sub>8</sub>Cl), 72 (31%, C<sub>3</sub>H<sub>6</sub>NO), 158 (28%, C<sub>7</sub>H<sub>7</sub>ClS), 229 (M<sup>+</sup>, 18%)]; *S*-(3-hydroxy-4-chlorobenzyl) *N,N*-diethyl-1-carbamothioate (V) [MS (solid probe, 70 eV) *m/e* 100 (base, C<sub>5</sub>H<sub>10</sub>NO), 72 (86%, C<sub>3</sub>H<sub>6</sub>NO or C<sub>4</sub>H<sub>10</sub>N), 141 (18%, C<sub>7</sub>H<sub>6</sub>ClO), 273 (M<sup>+</sup>, 3%); MS (solid probe, 40 eV) *m/e* 100 (base), 72 (91%), 141 (68%), 274 (45.5%)].

Thiobencarb's phenolic products, III and V, were readily identified by mass spectrometry; each exhibited an abundant molecular ion in 40-eV spectra in addition to the characteristic hydroxychlorotropilium ion, *m/e* 141. Phenolic structures were confirmed by chromogenic reactions with Pauly's reagent (Table I). III and V were differentiated by comparison to retardation factors published for the former compound using solvents B and C (Ishikawa et al., 1976). Where intramolecular H bonding is possible, ortho-substituted molecules exhibit exceptional mobility when subjected to liquid-solid chromatography (Karger et al., 1973).

Hydroxyl radical is responsible for free radical photooxidations occurring in aqueous peroxide. Hydrogen peroxide exhibits weak absorption in the actinic portion of the spectrum; photon absorption results directly in homolysis of the weak peroxygen bond (Volman, 1963). The phenolic products of thiobencarb result from hydroxyl attack at the aromatic nucleus; addition yielding the hydroxycyclohexadienyl radical is the favored mechanism

Table I. Photooxidation Products of Thiobencarb in Aqueous Hydrogen Peroxide: Their Retardation Factors and Chromogenic Reactions

compd	retardation factors			chromogenic reactions	
	solvent A	solvent B	solvent C	PdCl <sub>2</sub> reagent	Pauly's reagent
I	0.67	0.55	0.70	yellow	NR <sup>a</sup>
III	0.61	0.52	0.64	grey	+ <sup>b</sup>
IV	0.55	0.40	0.58	yellow	NR
V	0.39	0.26	0.43	yellow	+
II	0.31	0.14	0.34	peach	NR

<sup>a</sup> No reaction. <sup>b</sup> Reaction yielding a brown-colored complex.

(Fendler and Gasowski, 1968) although initial electron transfer cannot be ruled out (Snook and Hamilton, 1974).

The formation of II and IV is also rationalized by free radical mechanisms. The nonbonded electrons of thiobencarb's sulfur are readily abstracted as are the  $\alpha$ -hydrogens of the *N*-ethyl substituents. The free radicals formed by I yield isolable products by disproportionation and coupling reactions with other free radicals including ground-state, diradical oxygen.

Although the thin-layer analysis was semiquantitative, hydroxyl attack at the aromatic ring appeared to predominate while significantly lesser amounts of the *N*-deethyl analogue were present.

**Oxidation by Fenton's Reagent.** The combination of hydrogen peroxide and a ferrous salt, Fenton's reagent, is an established technique for generating hydroxyl radicals (Walling, 1975). Thiobencarb levels dropped from 12.5 to 7.4 mg/L after the first treatment with Fenton's reagent and to 3.7 mg/L after the second. As before, the hydroxylated products, III and V, predominated with sulf-oxidation being a significant route of oxidation as well. *N*-Dealkylation yielding IV, however, was not detected in this system. This discrepancy in product distribution with the photochemical system described previously may be due to the secondary redox reactions of iron (Walling, 1975). For example, the reduction of organic radicals by ferrous ion is extremely rapid. With the exception of compound IV, identical products resulted from oxidation of I with Fenton's reagent or photooxidation of I in dilute aqueous hydrogen peroxide. These data suggest that hydroxyl radical is the active oxidizing species in both systems.

**Comparative Photodecomposition.** The photochemical stability of thiobencarb in pure water is depicted in Figure 2. The presence of methylene blue, tryptophan, acetone, or hydrogen peroxide, as was noted earlier, significantly altered the probe's photochemical stability. Each represents an example of indirect photodecomposition. The photooxidation products isolated from solutions containing methylene blue or tryptophan were II, III, IV, and V. Here, *N*-dealkylation was a relatively minor process.

Photooxidation of tryptophan or methylene blue yields hydrogen peroxide. Peroxide formation in irradiated tryptophan solutions has been demonstrated (McCormick et al., 1976; Draper, 1977) and superoxide shown to be its precursor (McCormick and Thomason, 1978). Tryptophan is not unique, however, as superoxide radical anion is generated by a variety of organic compounds exposed to light (Draper, 1979). The intermediacy of hydrogen peroxide in these photochemical systems accounts for the similarity in their reactivities. Product distributions are summarized in Table II.

Photodegradation products in 2% acetone indicate free radical reactions not attributable to hydroxyl radical. As

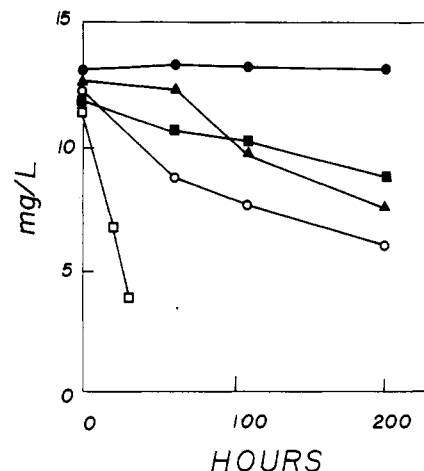


Figure 2. Thiobencarb photodegradation in water (●), aqueous tryptophan (▲), aqueous methylene blue (■), aqueous hydrogen peroxide (○), and aqueous acetone (□).

Table II. Product Distributions in Photochemical and Thermal Oxidation Systems

compd	photochemical reactions					thermal reactions, Fenton's reagent
	pure water	ace- tone	hydrogen peroxide	methyl- ene blue	trypto- phan	
I	+	+	+	+	+	+
II	tr <sup>a</sup>	+	+	+	+	+
III	ND <sup>b</sup>	ND	+	+	+	+
IV	ND	+	+	+	+	ND
V	ND	ND	+	+	+	+

<sup>a</sup> Trace. <sup>b</sup> Not detected.

in the other systems, electron transfer and hydrogen abstraction resulting in the formation of II and IV occurred, but the phenolic products were absent. The acetone-sensitized experiment was duplicated in solutions sparged with purified oxygen or nitrogen. In deoxygenated solutions the rate of photodecomposition of the probe was 40% greater. The diminution of free radical reactions in the presence of oxygen is frequently observed due to pre-termination reactions. II and IV were not detected in deoxygenated solutions and three sulfur-containing photo-products predominated: *R*<sub>f</sub> 0.53, *R*<sub>f</sub> 0.48, and *R*<sub>f</sub> 0.44 (solvent A). Acetone may generate free radicals photochemically by  $\alpha$  cleavage, or acetone's triplet state diradical may abstract hydrogen, yielding ketyl radicals (Cowan and Drisko, 1976).

**Reactions with Singlet Molecular Oxygen.** Methanolic eosin is a desirable system for the photochemical generation of singlet oxygen for several reasons: eosin's triplet energy (43–46 kcal/mol; Gollnick, 1968) is similar to the energy of the <sup>1</sup> $\Sigma_g^+$  excited state of molecular oxygen (37 kcal/mol), allowing efficient energy transfer; this triplet energy is low, improving the specificity of the system; the longevity of the excited molecule in methanol exceeds that in water, enhancing the oxidation of acceptor molecules ( $\tau$  for <sup>1</sup> $\Delta_g$  O<sub>2</sub> is 2  $\mu$ s in water and 7  $\mu$ s in methanol; Merkel and Kearns, 1972).

When thiobencarb was exposed to singlet oxygen in methanolic eosin solutions, no reaction of the probe occurred during 24 h of exposure to light. Thiobencarb levels did not decrease nor were photooxidation products formed; the sensitive, thin-layer analysis employed could have detected less than 2% conversion to a sulfur-containing photoproduct. That singlet oxygen was being generated in these experiments was demonstrated by the rapid consumption of dimethylfuran; its half-life was less than

4 min and the material was not detectable after 15 min of irradiation. In methanol, dimethylfuran reacts with singlet dioxygen to form an ozonide-like peroxide which undergoes solvolysis to form a hydroperoxide (Foote and Wexler, 1964).

Photochemical oxidations taking place in aqueous solutions of organic dyes, so-called sensitizers, are frequently attributed to the presence of singlet oxygen (Acher and Dunkelblum, 1979; Larson and Stabler, 1978). Thiobencarb, however, is a very poor singlet oxygen acceptor. This might be anticipated as singlet oxygen is known to be a relatively selective oxidant, reacting primarily with sulfides and certain olefins. In similar experiments, phosphorodithioates (malathion), phosphorothioates (ethyl and methyl parathion), and other thiocarbamates (molinat and drepamon) proved unreactive to photochemically generated singlet oxygen (Draper, 1979). Of the agricultural chemicals examined, only disulfoton reacted with singlet oxygen due to the presence of an ethylthioethyl sulfide moiety.

#### CONCLUSION

Free radical reactions are of major importance in indirect photolysis processes in water. The photooxidations observed in aqueous hydrogen peroxide, methylene blue, and tryptophan are similar to those produced by Fenton's reagent, supporting the view that hydrogen peroxide and hydroxyl radicals are the active oxidizing species in each of these systems. Thiobencarb is not oxidized by singlet molecular oxygen.

This work emphasizes the differences between sensitized photooxidations in organic media and those in water. A triplet dye, for example, may exhibit only singlet oxygen reactions in a low dielectric medium, while in water free radical reactions, due to the formation of peroxide, become important. Many photooxidation reactions previously ascribed to the presence of singlet oxygen in water may be due to hydroxyl radical. A requirement for oxygen or the demonstrated reactivity with a known singlet oxygen

acceptor will not distinguish these mechanisms.

#### ACKNOWLEDGMENT

The authors thank Professors Lloyd L. Ingraham and Aloys Tappel for their comments on the manuscript.

#### LITERATURE CITED

- Acher, A. J.; Dunkelblum, E. *J. Agric. Food Chem.* **1979**, *27*, 1164.  
 Blinn, R. C. *J. Assoc. Off. Anal. Chem.* **1964**, *47*, 641.  
 Casida, J. E.; Kimmel, E. C.; Ohkawa, H.; Ohkawa, R. *Pestic. Biochem. Physiol.* **1975**, *5*, 1.  
 Cowan, D. O.; Drisko, R. L. "Elements of Organic Photochemistry"; Plenum: New York, 1976; p 75.  
 Crosby, D. G.; Wong, A. S. *J. Agric. Food Chem.* **1973**, *21*, 1052.  
 Draper, W. M. M.S. Thesis, University of California, Davis, CA, 1977.  
 Draper, W. M. Ph.D. Dissertation, University of California, Davis, CA, 1979.  
 Fendler, J. H.; Gasowski, G. L. *J. Org. Chem.* **1968**, *33*, 1865.  
 Foote, C. S.; Wexler, S. *J. Am. Chem. Soc.* **1964**, *86*, 3879.  
 Gollnick, K. *Adv. Photochem.* **1968**, *6*, 1.  
 Heidt, L. *J. Sol. Energy* **1967**, *11*, 123.  
 Ishikawa, K.; Nakamura, Y.; Kuwatsuka, S. *Nippon Noyaku Gakkaishi* **1976**, *1*, 49.  
 Karger, B. L.; Snyder, L. R.; Horvath, C. "An Introduction to Separation Science"; Wiley: New York, 1973; p 391.  
 Larson, R. A.; Stabler, P. P. *J. Environ. Sci. Health, Part A* **1978**, *A13*, 545.  
 McCormick, J. P.; Fischer, J. R.; Pachlatko, J. P.; Eisenstark, A. *Science (Washington, D.C.)* **1976**, *191*, 468.  
 McCormick, J. P.; Thomason, T. *J. Am. Chem. Soc.* **1978**, *100*, 312.  
 Merkel, P. B.; Kearns, D. R. *J. Am. Chem. Soc.* **1972**, *94*, 7244.  
 Randerath, K. "Thin-Layer Chromatography"; Academic Press: New York, 1964.  
 Snook, M. E.; Hamilton, G. A. *J. Am. Chem. Soc.* **1974**, *96*, 860.  
 Volman, D. H. *Adv. Photochem.* **1963**, *1*, 43.  
 Walling, C. *Acc. Chem. Res.* **1975**, *8*, 125.  
 Zepp, R. G.; Cline, D. M. *Environ. Sci. Technol.* **1977**, *11*, 359.

Received for review August 15, 1980. Accepted March 27, 1981. The research was supported in part by the California Rice Research Foundation.

## Pyrethroid Photochemistry: (*S*)- $\alpha$ -Cyano-3-phenoxybenzyl *cis*-(1*R*,3*R*,1'*R* or *S*)-3-(1',2'-Dibromo-2',2'-dihaloethyl)-2,2-dimethylcyclopropanecarboxylates

Luis O. Ruzo\* and John E. Casida

The *cis*-(1*R*,3*R*,1'*R* or *S*)-3-(1',2'-dibromo-2',2'-dihaloethyl)-2,2-dimethylcyclopropanecarboxylates, tralomethrin and tralocythrin (Roussel-Uclaf, proposed common names), readily debrominate when solutions or thin films are irradiated at 360 nm or by sunlight. Debromination results from homolytic cleavage of a carbon-bromine bond, followed by collapse of the resulting trihaloethyl radical to the dihaloalkene. Effects of various hydrogen donors and of triethylamine on the reaction rate and product distribution suggest that bromine is not produced from a concerted process. Dehydrobromination, 1*R*,*cis*  $\rightarrow$  1*RS*,*cis*,*trans* isomerization, and ester cleavage are also significant photochemical reactions of tralomethrin and tralocythrin in the solid phase whereas only the first two of these processes are important with irradiated solutions. The reactions of tralomethrin in solution are sensitized by triplet donors but the excited state responsible for debromination is not established.

The photochemical reactions of tralomethrin and tralocythrin (Figure 1) are of interest because these *cis*-(1*R*,3*R*,1'*RS*)-3-(1',2'-dibromo-2',2'-dihaloethyl)-2,2-di-

methylcyclopropanecarboxylates have remarkably high insecticidal potency (Ackermann et al., 1980; Roussel-Uclaf, 1978). Photoreactions of polyhalogenated alkyls usually involve dehydrohalogenation and reductive dehalogenation (Sammes, 1973). Photodehalogenation of vicinal dihalides yields alkenes by extrusion of two halogen atoms (Chapman et al., 1976; Huyser and DeMott, 1963) or molecular halogen (Yuan and Wijnen, 1980). The

\* Pesticide Chemistry and Toxicology Laboratory, Department of Entomological Sciences, University of California, Berkeley, California 94720.