Solar Photooxidation of Pesticides in Dilute Hydrogen Peroxide

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Dilute hydrogen peroxide (HOOH, 5–100 μM) initiates photooxidation of thiolcarbamate, chlorophenoxy acid, organophosphorus, *N*-methylcarbamate, cyclodiene, and other classes of commercial pesticides in both sunlight and near-ultraviolet (UV) light. Levels of photodecomposition in 100 μM HOOH were increased by factors of 1.5 to >25 with the greatest rate enhancements for compounds with low direct photolysis rates (and weak absorption at 290 nm). Hydroxyl free radicals (HO·) were major reactants in the system as demonstrated by isomer distributions for the hydroxylation of nitrobenzene and by the quenching of nitrobenzene oxidation with added methanol. HO· mechanisms were proposed to account for the photoinduced epoxidation and rearrangement of aldrin to dieldrin and photoaldrin, respectively. HOOH also initiated photochemical sulfur oxidation, aromatic ring hydroxylation, N-dealkylation, and oxidations at saturated carbons of the herbicides molinate and thiobencarb. Hydrogen peroxide promoted photooxidation reactions at concentrations that occur naturally in agricultural irrigation water and other surface waters.

The photodecomposition of pesticides and other man-made pollutants in the aquatic environment occurs in both direct and indirect photochemical processes. Indirect photolysis reactions have been demonstrated, for example, in studies of aldrin (Ross and Crosby, 1975a), methoxychlor (Zepp et al., 1976), (2,4-dichlorophenoxy)acetic acid (Wolfe et al., 1976), and molinate (Soderquist et al., 1977). The underlying mechanisms for natural aquatic photosensitization, however, are not well understood.

Energy transfer photosensitization, the basis for much organic photochemistry, is believed to be of little importance due to energy limitations of sunlight (Zepp et al., 1976). Photochemically generated singlet molecular oxygen (Zepp et al., 1977), free radicals (Mill et al., 1980), organic hydroperoxides (Larson et al., 1981), and hydrogen peroxide (Draper and Crosby, 1983a; Cooper and Zika, 1983) have been characterized and quantitated in natural waters, suggesting alternative mechanisms for indirect photolysis. Superoxide radical anion and solvated electrons, formed during photooxidation of aromatic compounds in near-UV light (Draper and Crosby, 1983b), may also act as environmental reagents.

Concentrated hydrogen peroxide irradiated under intense UV light has been investigated as a treatment for refractory pollutants and the disinfection of water, but little is known of the reactivity of this oxidant at high dilution in sunlight. This study examines the chemical and near-UV photochemical reactivity of organic pesticides in dilute hydrogen peroxide. The photooxidation products were characterized for some of the substrates to determine the scope of chemical transformations occurring.

MATERIALS AND METHODS

Chemicals. Pesticides were obtained from the following sources: aldrin and dieldrin from the U.S. Environmental Protection Agency (Research Triangle Park, NC); carbofuran from FMC Corp. (Middleport, NY); disulfoton from Mobay Chemical Corp. (Kansas City, MO); drepamon 70% emulsifiable concentrate (purified by Florisil column chromatography) from Montedison S.P.A. (Milano, Italy); (4-chloro-2-methylphenoxy)acetic acid (MCPA) from the Dow Chemical Co. (Midland, MI); methyl parathion, ethyl parathion, and molinate from Stauffer Chemical Co. (Mountain View, CA); propanil from Rohm and Haas Co. (Philadelphia, PA); technical thiobencarb (purified by reduced-pressure distillation) from Chevron Chemical Co. (Richmond, CA). The pesticides studied were >97% pure by temperature-programmed gas–liquid chromatography (GLC) analysis or the supplier's specifications. Uniformly ring-labeled [^{14}C]thiobencarb (15 mCi/g, 3.8 mCi/mM; Chevron Chemical Co.) was isolated in >99.5% radiochemical purity by thin-layer chromatography (TLC) on silica gel plates after two developments in benzene (Pack, 1977).

Reagent-grade 30% hydrogen peroxide (Mallinckrodt, Inc.) was used exclusively. This product contained a stabilizer, but no extraneous absorptions were observed in its ultraviolet absorption spectrum, nor were contaminants otherwise detected. All solvents were pesticide analytical grade or redistilled reagent grade. Premixed scintillation cocktail and a [^{14}C]toluene standard were obtained commercially. Ethereal diazomethane was prepared by alkaline hydrolysis of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide in a distillation apparatus designed for this purpose (Aldrich Chemical Co.) and the reagent obtained was stored at −5 °C.

Apparatus and Chromatography. GLC analyses were carried out with a Varian Model 2400 instrument fitted with a hydrogen flame ionization detector (FID) with the following operating conditions: injector temperature, 275 °C; detector temperature, 310 °C; hydrogen flow rate, 30 mL/min; air flow rate, 200 mL/min; nitrogen carrier gas flow rate, 38 mL/min. For pesticide analyses the FID instrument was equipped with a 1.5 m × 3 mm (i.d.) glass column packed with Gas-Chrom Q (60–80 mesh) coated with 3% OV-17 with the following oven temperatures: molinate and MCPA methyl ester, 160 °C; carbofuran and drepamon, 185 °C; propanil, 195 °C; thiobencarb, 200 °C; methyl parathion and ethyl parathion, 205 °C. Nitroanisoles were separated on a 4 m × 3 mm (i.d.) stainless steel column packed with Gas-Chrom Q (60–80 mesh) coated with 4% OV-17. The column temperature was programmed from 140 °C at 10 °C/min with the nitroanisoles eluting at the following temperatures: meta isomer, 206 °C; ortho isomer, 213 °C; para isomer, 218 °C.

For electron capture (EC) GLC a Varian Model 1400 instrument with a tritium foil detector was used with the following operating conditions: injector temperature, 245 °C; detector temperature, 210 °C; column temperature, 195 °C; nitrogen carrier gas flow rate, 30 mL/min. This in-

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strument was equipped with a 2.5 m × 3 mm (i.d.) glass column packed with 5% SE-30 liquid phase on Gas-Chrom Q (60–80 mesh). Quantitative analyses by GLC utilized absolute calibration by peak height against standards unless otherwise noted.

Mass spectra (electron impact, 70 eV) were recorded with a Finnigan Model 3000 spectrometer with sample introduction by GLC using the 3% OV-17 column and helium carrier gas (10 mL/min) or by solid probe. A Packard Tri-Carb liquid scintillation spectrometer was used for radiometric assays, and autoradiograms were produced with a Berthold radioactive scanner and a dot recorder.

TLC utilized precoated silica gel chromatoplates (0.25-mm silica gel 60 F-254, Scientific Products) developed with benzene–methanol (9:1 v/v, solvent A) or 1-butanol–acetic acid–water (4:1:1 v/v/v, solvent B) in chromatography tanks without liners.

Photooxidation Reactions and Analytical Procedures. *Preparation of Solutions.* The pesticide or chemical probe was added to distilled water without a carrier solvent, and the resulting suspensions were stirred vigorously in sealed flasks for up to 48 h. Solutions were filtered through a fritted glass funnel and dispensed from separatory funnels. Aldrin solutions were obtained by percolating distilled water [prepurified with XAD-4 macroreticular resin (Rohm and Haas Co.)] through a bed of 5-mm glass beads coated with the insecticide (1.5 μg of aldrin/g of glass beads); the effluent solution was collected at the rate of ~1 L/h. Micromolar solutions of hydrogen peroxide were obtained by dilution of a 10.0 mM stock solution.

Nitrobenzene Hydroxylation. Nitrobenzene solutions were irradiated in a large-scale photoreactor by using six F40BL fluorescent UV lamps (maximal energy output at ~360 nm) with an energy cutoff of ~285 nm. The total radiant energy in the center of the chamber (external to the reaction vessel) was 390 $\mu W/cm^2$ and increased to 785 $\mu W/cm^2$ halfway from the center to the lamp surface. The photolysis solutions in borosilicate glass flasks did not exceed 30 °C. The nitrobenzene solutions (0.50 or 7.0 mM) containing 100 μM hydrogen peroxide were irradiated for 18 h with and without 0.5 M methanol. Initial nitrobenzene concentrations were determined spectrophotometrically (λ_{max} = 269 nm, ϵ = 7800 L mol^{-1} cm^{-1}). The photolysate (100 mL) was adjusted to pH 12.5 with 5 N sodium hydroxide, and neutral and basic substances were extracted with methylene chloride (2 × 10 mL) and discarded. The aqueous layer was acidified to pH 2 with concentrated hydrochloric acid and further extracted with methylene chloride (3 × 50 mL) to isolate the phenolic products. The pooled extract was concentrated, derivatized with ethereal diazomethane at 0 °C for 40 h, and reduced in volume to 1.0 mL for determination of the nitroanisoles by GLC. The extraction of each nitrophenol isomer was quantitative and determinations were precise with standard deviations of ~5%.

Photoreactivity of Pesticides. Pesticide solutions were irradiated in sunlight (October, Davis, CA) in sealed borosilicate flasks for up to 250 h with or without added hydrogen peroxide (100 μM). Dark controls were maintained at similar temperatures to monitor chemical oxidation and hydrolysis of the substrates. Water samples (50 mL) were extracted with methylene chloride (2 × 5 mL), and pesticide residues in the combined solvent extracts were determined by GLC. A modified procedure was used in the analysis of MCPA solutions. Water samples (50 mL) were acidified by addition of 3 drops of concentrated hydrochloric acid prior to solvent extraction, and the extract obtained was concentrated, derivatized with ethereal diazomethane for 1 h, concentrated under a stream of dry nitrogen to drive off unreacted methylating reagent, and adjusted to 5.0 mL for GLC analysis. Recoveries determined for each pesticide were 95–100%.

Aldrin Photooxidation. Aldrin solutions (<35 μg/L or 95 nM) were irradiated in 5, 30, and 100 μM hydrogen peroxide in the previously described laboratory photoreactor in sealed flasks. Aldrin-containing water samples (100 mL) were withdrawn by pipet and extracted by agitation with hexane (20 mL) for 20 min on a mechanical shaker. Aldrin was determined directly by EC-GLC analysis of the hexane extract. Aldrin's photoproducts, photoaldrin, dieldrin, and photodieldrin (Ross and Crosby, 1975a), also were determined by EC-GLC after reduction of the extract volume to 5.0 mL.

Molinate Photooxidation. Molinate solutions (20 mg/L, 120 μM) were irradiated with 1 or 2 equiv of hydrogen peroxide in an immersion-type photoreactor equipped with a single FS40 fluorescent UV lamp (Crosby and Tang, 1969). The photolysis solutions were held at 23 °C by refrigeration and were not sealed, allowing aeration and a limited amount of volatilization of the herbicide and aqueous solvent. Molinate and its photooxidation product, 1-[(ethylsulfinyl)carbonyl]hexahydro-1*H*-azipine (2-oxomolinate), were determined by GLC (Soderquist et al., 1977). The photooxidation products of molinate also were characterized by TLC (specifically for the semiquantitative determination of molinate *S*-oxide) and GLC-coupled mass spectrometry (GLC–MS). Water samples (500 mL) were extracted with methylene chloride (2 × 30 mL), and the organic extract was concentrated to 1 mL for application to chromatoplates (developed in solvent A) or GLC–MS analysis. Hydrogen peroxide concentrations were monitored by redox titration. Samples of the photolysate (10 mL) were combined with 10 mL of freshly prepared, deoxygenated 4 M potassium iodide and the solution was titrated with 1.00 mM sodium thiosulfate; a soluble starch indicator aided in detecting the end point.

Thiobencarb Photooxidation. Aqueous [^{14}C]thiobencarb solutions (2 × 10^6 dpm/L, 10 mg/L) containing 30 or 100 μM hydrogen peroxide were irradiated under conditions described for aldrin. Solutions of the labeled herbicide were prepared with low specific activity [^{14}C]thiobencarb (8 μCi of labeled material diluted in 70 mg of unlabeled thiobencarb). For radiometric assays 1-L water samples were extracted with methylene chloride (4 × 50 mL) and the pooled extract was dried (Na_2SO_4) and concentrated to 1.0 mL. Concentrated extracts (60–100 μL) were separated by TLC on silica gel plates developed in solvent A, and the photoproducts were visualized by phenol- and sulfur-specific spray reagents (Draper and Crosby, 1981), quenching of UV light, and autoradiography. Adsorbed bands were transferred directly to 12 mL of precounted scintillation fluid for analysis. Radioactivity in water samples and extract concentrations was determined by counting 2-mL and 25-μL volumes, respectively. At the termination of the experiment, extracted water samples were pooled to give a 3-L composite sample, adjusted to pH 2, and extracted with chloroform (4 × 100 μL). The aqueous layer was neutralized and concentrated to dryness for analysis by TLC–autoradiography (silica gel, solvent B). Counting efficiencies for radioassays were determined by fortification with [^{14}C]toluene.

Thiobencarb also was irradiated in polishing pond water from a treatment facility (Woodland, CA). The pond water was sterilized by boiling for ~1 h, filtered through glass

Table I. Photochemical Hydroxylation of Nitrobenzene in Dilute Hydrogen Peroxide Solutions[a]

nitrobenzene concn, M	isomer distribution ortho	meta	para	% inhibition with 0.5 M methanol[b]
5.0×10^{-4}	50	29.5	20.5	99
7.0×10^{-3}	44	34.5	22	69

[a] Phenolic products were determined after 18 h of irradiation in the laboratory photoreactor of 100 μM peroxide solutions. [b] Decrease in the total yield of phenols (ortho, meta, and para) due to quenching with methanol.

wool, and cooled in an ice bath. Preparation of [^{14}C]-thiobencarb solutions, irradiation, and radioassay procedures were similar to those described for peroxide experiments except that these samples (1) required centrifugation to separate emulsions formed on extraction and (2) were aerated initially and after sampling by sparging with purified oxygen (~5 min at 50 mL/min). A dark control was maintained to monitor nonphotochemical degradation of the herbicide.

RESULTS

Nitrobenzene Hydroxylation. Nitrobenzene underwent aromatic ring hydroxylation in hydrogen peroxide solutions irradiated in near-UV light but not in oxidant-containing solutions in the dark. After 18 h the yield of nitrophenols reached 10 μM in 0.50 and 7.0 mM nitrobenzene solutions, representing 2.0 and 0.14% conversion of the substrate, respectively. Analysis of the nitrobenzene indicated no phenolic contaminants prior to irradiation. The distribution of nitrophenol isomers (Table I) indicated preferential hydroxylation in the ortho position since random addition to the aromatic ring would result in an isomer distribution of 40% ortho:40% meta:20% para. Methanol quenched the photochemical hydroxylation of nitrobenzene in dilute peroxide solutions (Table I), but quantitative inhibition of the reaction (i.e., >99%) required [methanol]:[nitrobenzene] ratios exceeding 10^3.

Photoreactivity of Pesticides. The direct photolysis rates of pesticides were highly dependent upon near-UV extinction coefficients. Molinate and thiobencarb were relatively stable in mid-October sunlight (Table II), but compounds with more efficient chromophores (i.e., methyl parathion and ethyl parathion) photodegraded rapidly. First-order direct photolysis half-lives were estimated from the parent material remaining after 125 h of treatment or, in the case of molinate, after 245 h. Logarithms of half-lives thus obtained showed a negative correlation (correlation coefficient = −0.97) with the logarithms of molar absorptivities at 290 nm (Figure 1). Disulfoton was considerably more reactive than predicted, possibly due to autoxidation. Direct photolysis half-lives for mid-October

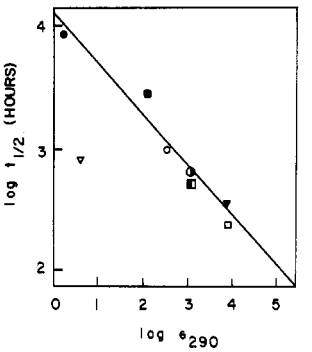

Figure 1. Relationship between direct photolysis half-lives and 290-nm molar extinction coefficients for molinate (●), disulfoton (▽), thiobencarb (■), carbofuran (○), MCPA (◑), propanil (◧), ethyl parathion (▼), and methyl parathion (□). Regression line is based on all pesticides except disulfoton.

in Davis, CA, were approximated by the empirically derived expression

$$t_{1/2} = e^{-1.01(\log \epsilon_{290}) + 9.47} \text{ h}$$

This relationship implies not only that the spectral overlap with sunlight is proportional to a single absorbance value but also that pesticides exhibit approximately equivalent reaction quantum yields. This correlation has a number of serious limitations in terms of predictive value in its present form. The data apply only to a single latitude for mid-October sunlight and are based on a limited number of compounds. An experimental design incorporating diverse chemical classes and controlling for hydrolysis is needed to thoroughly evaluate the utility of this regression equation.

Low concentrations of hydrogen peroxide were ineffective in oxidizing these pesticides in the dark (Table II). Disulfoton, an organophosphorus insecticide with an electron-rich (ethylthio)ethyl moiety, was most reactive to chemical oxidation with ~35% of the compound consumed after 245 h of treatment with 100 μM hydrogen peroxide.

Traces of hydrogen peroxide significantly increased the photolysis rate of each pesticide in sunlight (Table II). This effect applied to all compounds tested but was most striking for pesticides with low direct photolysis rates. Molinate, for example, photooxidized rapidly in dilute peroxide solutions. MCPA was highly reactive with 90% of the herbicide reacting in 125 h, and carbofuran also appeared exceptionally reactive on a molar basis.

Photooxidation of Aldrin. Direct photolysis rates were low for aldrin in the laboratory photoreactor. After 12 h of irradiation 1% conversion to dieldrin and 3% conversion to photoaldrin were detected. Aldrin's photostability in near-UV light (Ross and Crosby, 1975a) is anticipated since the insecticide does not absorb appreciably above 250 nm.

Table II. Photodecomposition of Pesticides in Water and Dilute Hydrogen Peroxide[a]

pesticide	concn, μm	ϵ_{290},[b] L mol^{-1} cm^{-1}	% remaining after 125 h light	dark, HOOH	light, HOOH	% remaining after 245 h light	dark, HOOH	light, HOOH
molinate	63	1.63	100	97	65	98	95	46
disulfoton	13	3.42	89	82	46	71	65	16
thiobencarb	46	110	97	81	40	97	86	15
carbofuran	97	487	91	90	47	86	95	29
MCPA	45	883[c]	84	89	7	83	98	1.5
propanil	68	902	88	89	41	86	87	19
ethyl parathion	30	5810[c,d]	77	82	47	65	84	28
methyl parathion	79	6290	67	88	42	44	76	20

[a] Solutions irradiated in October sunlight (Davis, CA) with or without 100 μM hydrogen peroxide. [b] Extinction coefficients determined for methanol solutions. [c] Gore et al. (1971). [d] Hexane solution.

Table III. Photodecomposition of Aldrin in Hydrogen Peroxide Solutions[a]

hydrogen peroxide concn, μM	aldrin concn, μg/L		
	initial	light	dark[b]
0	6.8	5.0	4.9
5	7.3	1.5	4.9
30	7.6	nd[c]	4.8
100	7.3	nd	4.8

[a] After 12 h of irradiation in the laboratory photoreactor. [b] Dark control. [c] Not detected.

Table IV. Photooxidation Products of Aldrin in 5 μM Hydrogen Peroxide[a]

time of irradiation, h	aldrin, μg/L	dieldrin, μg/L	photoaldrin, μg/L	unknown,[b] μg/L
0	31	0.25	nd[c]	0.66
2	25	0.84	0.91	4.1
5	17	1.5	1.6	15
15	6.0	2.4	2.1	11
15, dark[d]	21	0.36	nd	0.95

[a] Irradiated in sealed containers in the laboratory photoreactor; values represent the average of two determinations. [b] Considered to have the same detector response per mass as aldrin. [c] Not detected. [d] Dark control.

Hydrogen peroxide accelerated the photodecomposition of aldrin (Table III), so much so that in order to monitor photoproduct formation it was necessary to limit the peroxide concentration to 5 μM. Free radical photooxidation products of aldrin included dieldrin, photoaldrin, and an unidentified product with GLC retention time intermediate between those of dieldrin and photoaldrin (Table IV). The unknown, which may be a hydroperoxide (Crosby, 1972) or its decomposition product, was the major photoproduct assuming an EC detector response equivalent to that for aldrin.

Aldrin concentrations dropped by approximately 25% in 12 h with or without added oxidant in dark controls (Table III) due to adsorption of the pesticide on glass surfaces; approximately 30% of the lost material was recovered on rinsing the glassware with hexane. Adsorption occurred even in homogeneous solutions well below aldrin's solubility limit [20 μg/L at 20 °C (Gunther et al., 1968)].

Molinate Photooxidation. Molinate dissipated slowly in hydrogen peroxide solutions held in the dark (Figures 2 and 3), and after 165 h, 90 and 80% of the herbicide remained in solutions treated with 1 and 2 equiv of peroxide, respectively. In the dark major losses were probably due to volatilization (Soderquist et al., 1977), however, and oxidation products were not detected. In concentrated peroxide solutions (10^{-2} M or greater) molinate oxidation proceeded more rapidly with molinate *S*-oxide and 2-oxomolinate formed as products.

The photodecomposition of molinate was initiated by hydrogen peroxide as noted above. In the laboratory photoreactor the half-life of the herbicide was 180 h with 1 equiv of hydrogen peroxide and 120 h with 2 equiv of oxidant. The major photooxidation products were 2-oxomolinate (Figures 2 and 3) and molinate *S*-oxide representing approximately 20 and 5%, respectively, of molinate undergoing reaction. The sulfoxide product was estimated by the TLC spot area. Two additional isomers of 2-oxomolinate were detected by temperature-programmed GLC–MS. One isomer eluted before 2-oxomolinate (OV-17 liquid phase) and the second, a minor product, eluted immediately after. The isomers were identified by their mass spectra, which lacked the hexahydroazipine

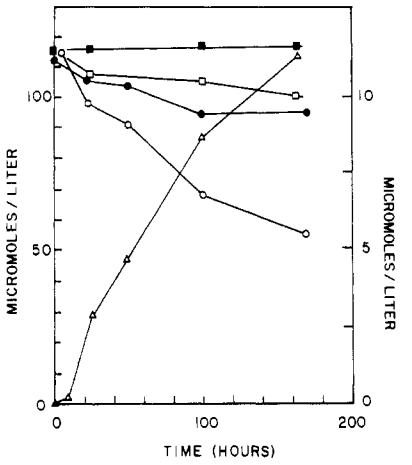

Figure 2. Photodecomposition of molinate (○) and hydrogen peroxide (□) in an equimolar solution (scale to the left) and the formation of 2-oxomolinate [(△) scale to the right]. Filled symbols represent a dark control.

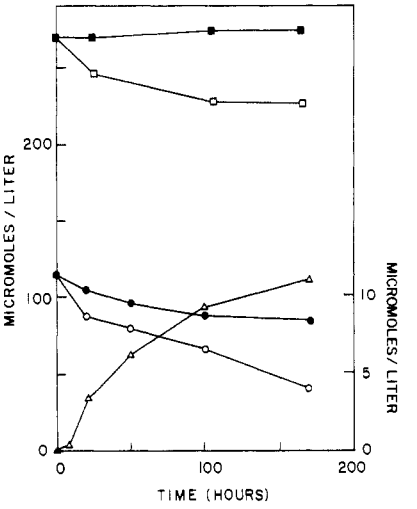

Figure 3. Photodecomposition of molinate [(○) scale to the left] with 2 equiv of hydrogen peroxide [(□) scale to the left] and the formation of 2-oxomolinate [(△) scale to the right]. Filled symbols represent a dark control.

isocyanate ion (*m/e* 126), the base peak for molinate, and gave oxygenated hexahydroazipine isocyanate ions (*m/e* 140) as base fragments and weak molecular ions (*m/e* 201).

The photodecomposition of hydrogen peroxide in molinate solutions was rapid initially but declined with continued irradiation (Figures 2 and 3). Kinetics were greater than first-order based on semilog plots of peroxide concentration with time. In the dark, however, hydrogen peroxide levels remained relatively constant. The efficiency of molinate photooxidation (Δ[molinate]/Δ[hydrogen peroxide]) was relatively low during the first 25 h of treatment with ratios of 0.7 (2 equiv of peroxide) and 1.2 (1 equiv of peroxide). Over the next 140 h, however, the overall oxidation efficiency (for the total 165-h period) increased with ratios of 2.8 and 0.9 with 1 and 2 equiv of oxidant, respectively.

Thiobencarb Photooxidation. Thiobencarb photodecomposed slowly in distilled water, yielding thiobencarb *S*-oxide and unextractable products. The sulfoxide and other photoproducts were identified previously in studies using near-UV light (Ross, 1974) and UV light (Ishikawa et al., 1977). The rate of thiobencarb photodecomposition was accelerated in dilute hydrogen peroxide (Figure 4) with the majority of photoproduct incorporated, ^{14}C radiolabel being unextractable. After 47 h of irradia-

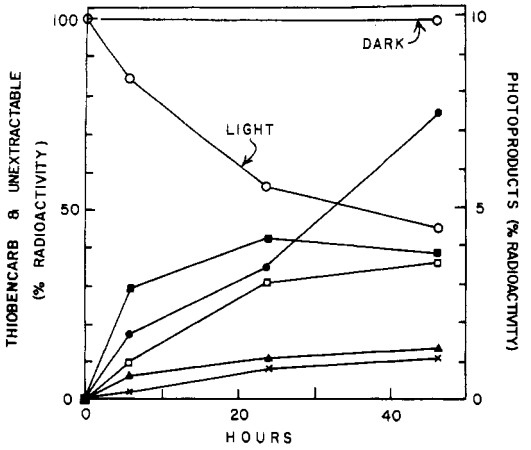

Figure 4. [^{14}C]Thiobencarb photooxidation in aqueous hydrogen peroxide. Thiobencarb (○) and unextractable radioactivity (□) are plotted according to the scale on the left of the figure, and the extractable photoproducts, 2-hydroxythiobencarb (●), 3-hydroxythiobencarb (■), thiobencarb *S*-oxide (▲), and *N*-monoethylthiobencarb (×), utilize the scale to the right.

tion in 100 μM hydrogen peroxide, radiocarbon from the ring-labeled herbicide was distributed as follows: unreacted thiobencarb, 46%; extractable photooxidation products, 19%; unextractable products, 36%. The organosoluble photoproducts included 2- and 3-hydroxythiobencarb, thiobencarb *S*-oxide, and *N*-monoethylthiobencarb (Figure 4) (Draper and Crosby, 1981). Minor amounts of 4-chlorobenzaldehyde (detected by GLC), 4-chlorobenzyl alcohol, and minor polar products (<1%) with R_f values between 0 and 0.3 (solvent A) also were present.

Efforts to characterize thiobencarb's previously reported, unextractable transformation products (Ishikawa et al., 1977) were unsuccessful. Acidic photoproducts (~1%), isolated by reextracting the acidified photolysate, consisted of 4-chlorobenzoic acid (R_f 0.78, solvent B) and an unidentified product (R_f 0.69). Chromatographic separation of residual radioactivity in the aqueous layer revealed a complex mixture distributed from the origin to R_f 0.7 (solvent B). A band corresponding to 4-chloro-α-toluenesulfonic acid (R_f 0.51) was present in this fraction. We speculate that these polar products are hydroxylated toluenesulfonic and benzoic acids, ring-cleavage products, and possibly polymerized phenols (Ishikawa et al., 1977).

Dissolved substances in natural water accelerated the photodecomposition of thiobencarb and, as in other systems, the bulk of the photoproduct-incorporated label was unextractable (Figure 5). Thiobencarb *S*-oxide (major), 4-chlorobenzoic acid, and 2-hydroxythiobencarb were detected, but these photoproducts accounted for only about 10% of the herbicide undergoing photodecomposition. The vast majority of the photoproduct-incorporated label (>50%) was unextractable. The mass balance for products in the pond water sample was approximately 65%, considerably lower than in studies with peroxide. This may have been due, in part, to volatilization of *p*-chlorobenzaldehyde (Ishikawa et al., 1977).

DISCUSSION

Hydroxyl Radicals as Reactants. Irradiation of hydrogen peroxide in UV light is an established source for hydroxyl free radicals (Dorfman and Adams, 1973), and the present study establishes that similar activation occurs in near-UV light or sunlight. Hydrogen peroxide is photochemically unstable in near-UV light (Figures 2 and 3). The distribution of nitrophenol isomers formed on photooxidation of 0.5 mM nitrobenzene in these peroxide

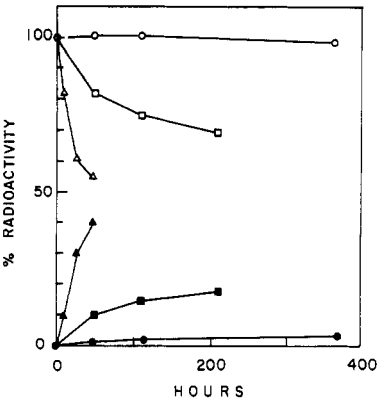

Figure 5. Photodecomposition of [^{14}C]thiobencarb in water (○), sterilized settling pond water (□), and 100 μM hydrogen peroxide (△). Filled symbols indicate the accumulation of unextractable photooxidation products.

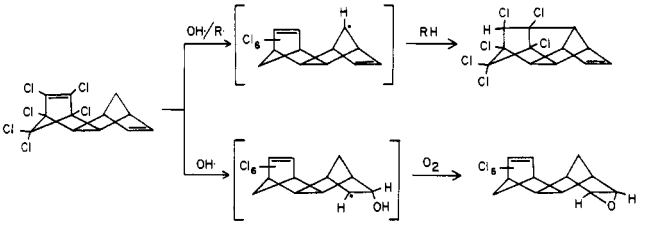

Figure 6. Proposed mechanisms for peroxide-initiated photodecomposition of aldrin. R· represents substrate-derived radicals.

solutions (Table I) is in good agreement with that from the reaction of HO· generated in γ-irradiated pure water (Fendler and Gasowski, 1968). Other studies of the reactions of HO· produced on radiolysis of aqueous nitrobenzene indicate slightly higher yields of *p*-nitrophenol at the expense of the meta isomer (Eberhardt and Yoshida, 1973). Isomer distributions for this reaction vary with pH, dissolved oxygen concentration, solvent, and dissolved metal ion concentration, and in the present study the experimental conditions of Fendler and Gasowski (1968) were matched. There were minor differences in the isomer distributions obtained in 7 mM nitrobenzene (with the radiolysis study of Fendler and Gasowski), possiby due to reactions of nitrobenzene-derived radicals with the probe.

The inhibitory effect of methanol on nitrobenzene photooxidation provides further evidence for the reaction of HO· (Table I). The concentration dependency observed for the competitive oxidation of the substrate is consistent with bimolecular rate constants for HO·, i.e., $k = 10^9$–10^{10} M^{-1} s^{-1} for addition to aromatic nuclei (Walling, 1975) and 4×10^8 M^{-1} s^{-1} for α-hydrogen abstraction from methanol.

Photooxidation Mechanisms. Hydroxyl radical reactions in water are known to include radical addition, hydrogen abstraction, and electron transfer (Dorfman and Adams, 1973), and evidence for each of these processes was obtained in the determination of photooxidation products in this study.

Hydrogen Abstraction. The photochemical rearrangement of aldrin to photoaldrin may involve H· abstraction from the bridgehead methylene (Figure 6). The intermediate sp^2-hybridized radical readily cyclizes to the half-cage product since the unshared electron interacts with the π-bond of the adjacent ring. Hydrogens of the tertiary carbons, however, are less reactive since aldrin cannot accommodate planar radical intermediates at these carbons. Hydrogens in the α-positions of the hexahydroazipine ring of molinate also are readily abstracted (Figure 7), accounting for the high yield of 2-oxomolinate. The low yields of 3- and 4-oxomolinate indicate HO· attack to

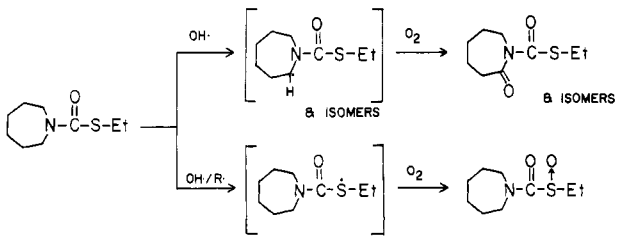

Figure 7. Proposed reaction scheme for the free radical photooxidation of molinate.

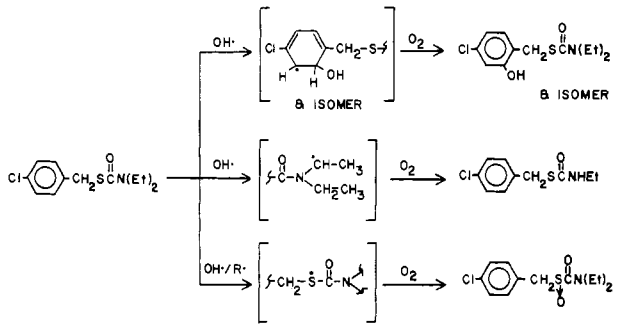

Figure 8. Mechanisms for the free radical photooxidation of thiobencarb.

a lesser degree on the β- and γ-hydrogens as well. The ketone (or amide) photooxidation products represent a more typical fate for secondary carbons than the carbon skeleton rearrangement observed in the case of aldrin. Introduction of the keto function probably involves combination of the carbon-centered radical with ground-state diradical oxygen to give peroxyl radical intermediates. Heteroatom dealkylation, a minor reaction of thiobencarb (Figure 8), also is rationalized by H· abstraction in the favored α-position and may involve the undetected acetamide as an intermediate.

Electron Transfer. Electron transfer reactions are proposed to initiate sulfur oxidation observed in the thiolcarbamates, molinate and thiobencarb (Figures 7 and 8). Sulfoxide formation, like introduction of the keto group, may result from radical coupling with dissolved oxygen. In the case of thiobencarb the *S*-oxide was detected as a minor photooxidation product (Figure 4), although this may be due to the sulfoxide's chemical and photochemical reactivity. Alkyl sulfoxides, for example, react with HO· with resulting cleavage of the carbon–sulfur linkage (Lagercrantz and Forschult, 1969).

Radical Addition. Hydroxyl free radicals react rapidly at unsaturated carbons, usually by radical addition. Hydroxyl addition to aromatic nuclei yields hydroxycyclohexadienyl radicals (Figure 8), which are oxidized by molecular oxygen to the isolated phenols. Addition to the aromatic ring is the preferred mechanism for aryl hydroxylation (Fendler and Gasowski, 1968), although initial oxidation of the aromatic ring to a radical cation cannot be ruled out. The differential stability of the phenolic products is demonstrated by the relative concentrations of 2- and 3-hydroxythiobencarb over time (Figure 4); the 2-isomer is considerably more stable than the transitory 3-isomer. Photodechlorination of the aromatic ring of thiobencarb was apparently unimportant in near-UV irradiated peroxide solutions and neither the unsubstituted nor 4-hydroxy derivatives were detected.

Addition of HO· to aldrin's unsubstituted double bond (Figure 6) probably precedes epoxide formation. While the epoxidation of olefins does not appear to be a general reaction of HO·, a previous report of the conversion of aldrin to dieldrin by Fenton's reagent (Marshall and Wilkinson, 1970) and our studies indicate that HO· does initiate this reaction in certain olefins.

Free Radical Chain Processes. The stoichiometry of the molinate–peroxide photodecomposition demonstrates that free radical chain processes occur (Figure 2), i.e., the maximum oxidation efficiency predicted from photolysis of hydrogen peroxide is 2.0, but efficiencies greater than 4 were observed in the late stages of the photodecomposition. The reactive 3- and 4-position carbon-centered radicals of the hexahydroazipine ring or peroxyl and alkoxy radicals derived from them may, for example, oxidize the sulfur atom of molinate. Potential chain carrying steps are suggested in Figures 6–8 by the inclusion of substrate-derived radicals (R·) as reactants.

Photochemical Reactivity of Pesticides. The photochemical decomposition of thiolcarbamate and phenoxy herbicides, organophosphorous and *N*-methylcarbamate insecticides, and other pesticides was greatly accelerated in dilute hydrogen peroxide (Table II). The rate enhancements were most pronounced for compounds with low direct photolysis rates (and low extinction coefficients in the near-UV) although none of the substrates was refractory. In 100 μM hydrogen peroxide the photodecomposition occurring (percent material reacting) in 245 h was increased by >25-fold for molinate and thiobencarb. Added oxidant, however, resulted in only a 1.5–2-fold increase in the photodecomposition of methyl and ethyl parathion, insecticides that photodegrade relatively rapidly in distilled water. The susceptibility of this diverse group of pesticides is not surprising in view of the high reactivity of hydroxyl radicals, for which many reaction rate constants are available (Dorfman and Adams, 1973; Pitts et al., 1976). It is anticipated that pesticides and pollutants of many other chemical classes, even those considered refractory to biooxidation and chemical treatment, will show similar reactivity in this system.

Photosensitization in Natural Water. Several lines of evidence suggest that low steady-state levels of hydrogen peroxide initiate photooxidation of chemicals in natural water. The photodecomposition of aldrin, for example, is rapid in 5 μM hydrogen peroxide solutions (Table IV). Comparable and higher oxidant levels are found in sunlight-irradiated natural water (Draper and Crosby, 1983a; Cooper and Zika, 1983). Furthermore, the photooxidation-promoting substances, tryptophan and tyrosine, have been isolated from agricultural irrigation water (Ross and Crosby, 1975b). The photooxidation reactions induced by these amino acids and other aromatic compounds result from their ability to generate superoxide radical anion and hydrogen peroxide in sunlight (Draper and Crosby, 1981, 1983b). The photochemical generation of HO· in lake and river waters (Mill et al., 1980) provides further evidence for hydrogen peroxide's role, although other oxidants (i.e., hydroperoxides) and nitrate ions (Kotzias et al., 1982) also yield this radical upon photodecomposition.

The photooxidation of [^{14}C]thiobencarb in peroxide solutions and in sterilized pond water showed similarities (Figure 5). The bulk of the photoproduct-incorporated radiolabel in both cases was not extracted with organic solvent, but unfortunately, these major fractions also remained uncharacterized. The distribution of organosoluble photoproducts, 35% of the herbicide reacting in peroxide-containing solutions and 10% in pond water, showed differences, however. Phenolic products predominated in peroxide solutions (Figure 4), but in natural water thiobencarb *S*-oxide was the major isolable photoproduct. Due to the poor mass balance realized in this study of natural water, mechanistic interpretations are not possible. The

experiment serves only to demonstrate the potential for indirect photolysis processes in natural water. It is known that eutrophic water samples of the type studied under similar experimental conditions generate hydrogen peroxide at levels as high as 30 μM (Draper and Crosby, 1983a). Photochemically generated singlet molecular oxygen is not involved, however, since thiobencarb does not react with this oxidant (Draper and Crosby, 1981).

Hydrogen peroxide and the extremely reactive hydroxyl radical initiate free radical photooxidation of xenobiotics in natural water. Chemical phenomena observed in distilled water containing realistic levels of a natural reagent, however, are not necessarily valid models for reactions in natural water. Aqueous carbonate ions and humic materials will be significant HO· scavengers in natural water (Hoigné and Bader, 1979). Secondary radical species from the oxidation of carbonate ions and dissolved organic and inorganic matter thus provides an abundant source for more selective (and less reactive) free radicals that may ultimately consume trace micropollutants.

CONCLUSION

Hydrogen peroxide is photochemically unstable in near-UV light or sunlight and photodecomposes with the formation of reactive hydroxyl free radicals. At high dilution in sunlight hydrogen peroxide effectively initiates the photooxidation of pesticides. The photoinduced reactions of peroxide are most dramatic for substrates with low direct photolysis rates and occur at oxidant concentrations equivalent to those found in sunlight-irradiated natural water.

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Registry No. Aldrin, 309-00-2; dieldrin, 60-57-1; photoaldrin, 13350-71-5; molinate, 2212-67-1; thiobencarb, 28249-77-6; carbofuran, 1563-66-2; disulfoton, 298-04-4; drepamon, 36756-79-3; (4-chloro-2-methylphenoxy)acetic acid, 94-74-6; methyl parathion, 298-00-0; ethyl parathion, 56-38-2; propanil, 709-98-8; hydrogen peroxide, 7722-84-1.

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