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Ecological Research Series

CHEMICAL AND PHOTOCHEMICAL TRANSFORMATION OF SELECTED PESTICIDES IN AQUATIC SYSTEMS



**Environmental Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Athens, Georgia 30601**

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This report has been assigned to the ECOLOGICAL RESEARCH series. This series describes research on the effects of pollution on humans, plant and animal species, and materials. Problems are assessed for their long- and short-term influences. Investigations include formation, transport, and pathway studies to determine the fate of pollutants and their effects. This work provides the technical basis for setting standards to minimize undesirable changes in living organisms in the aquatic, terrestrial, and atmospheric environments.

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CHEMICAL AND PHOTOCHEMICAL TRANSFORMATION OF
SELECTED PESTICIDES IN AQUATIC SYSTEMS

by

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SECTION I

INTRODUCTION

Lack of data on the fate and impact of pesticides in freshwater systems prompted Environmental Protection Agency researchers in 1971 to select 10 representative materials (Figure 1) for detailed study. One of the needs highlighted at that time was for more reliable data on the rates, routes, and products of transformation. Subsequently, Paris and Lewis¹ comprehensively reviewed the literature on microbial, chemical, and photochemical transformations of these materials and have since completed microbial studies with them.

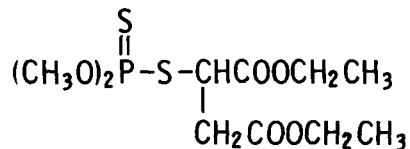
This report describes laboratory research on the chemical and photochemical behavior of the selected chemicals under conditions expected in aquatic ecosystems. Polychlorinated biphenyls (PCB's) were not included in these studies. The results are offered not as a statement of what is important in the environment but rather as a first approximation of what is LIKELY TO BE important and should be considered. In this sense, the results are complementary to other EPA studies concerning toxicology, microbiology, or other aspects of the environmental transport and transformation of these materials.

A major objective has been to obtain rate data that can be used as a yardstick for assessing the relative importance of various chemical and photochemical transformations of the selected pesticides. Products and mechanisms of a reaction were studied in detail when it appeared that the reaction might be significant under environmental conditions. These studies were pursued for several reasons. First, products must be known because of their potential environmental impact, in order to define the reaction mechanism, and frequently in order to measure the rate. Second, information about reaction mechanisms is required if reasonable predictions are to be made concerning the effect of water quality parameters on reaction rates or products, likelihood and nature of catalysis, effect of temperature, etc. Knowledge of the reaction mechanisms is also required to predict the probable rate and products of transformation of related compounds.

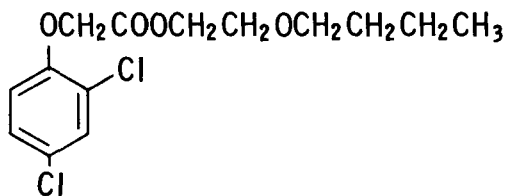
A second objective of the project was to synthesize the transformation products and make them available to others for analytical, toxicological, and other studies.

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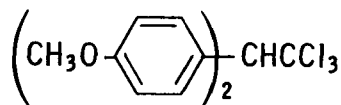
- 1 Paris, D. F., and D. L. Lewis. Residue Reviews. 45:95, 1973.



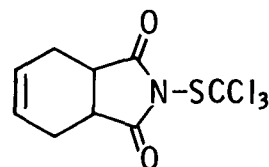
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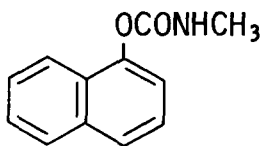
BUTOXYETHYL ESTER OF 2,4-D



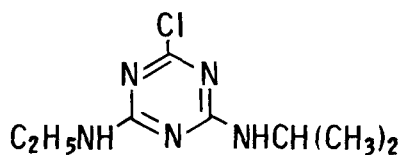
METHOXYCHLOR



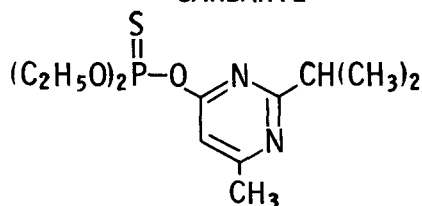
CAPTAN



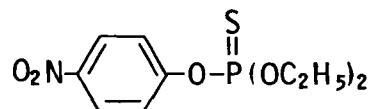
CARBARYL



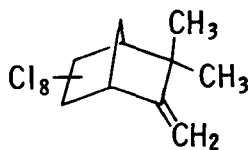
ATRAZINE



DIAZINON

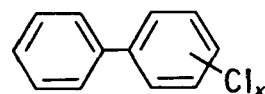


PARATHION



TOXAPHENE

A mixture of polychlorobicyclic terpenes with chlorinated camphene predominating. (Structural formula is representative.)



POLYCHLORINATED BIPHENYLS

A mixture of chlorinated biphenyls; $x = 1, 2, \dots 10$

Figure 1. Ten representative materials selected for study by the U.S. EPA

SECTION II

SUMMARY

This report presents the results of laboratory studies to quantitatively predict chemical and photochemical transformation rates and products of pesticides in water. It includes a general discussion of relevant transformation processes and associated kinetic expressions. The processes treated in most detail are hydrolysis, direct photolysis, and reaction with singlet oxygen. Implications of other processes such as oxidation and sensitized photolysis are also discussed.

Results of detailed studies are included for the pesticides malathion, carbaryl, methoxychlor, captan, and 2,4-D esters. The measured rate constants and half-lives indicate that chemical and/or photochemical processes of these compounds are likely to be important in the aquatic environment.

Less extensive data are presented for the pesticides atrazine, diazinon, parathion, and toxaphene, along with a discussion of available literature data.

SECTION III

CONCLUSIONS

- 1 Chemical degradation of malathion is likely to be the major pathway for its transformation in basic natural waters (pH greater than 7). The products are a mixture of malathion acids, fumaric acid and its ethyl esters, and 0,0-diethylphosphorodithioic acid. Photolysis of malathion by sunlight is too slow to compete with chemical degradation in pure water.
- 2 Hydrolysis of 2,4-D esters to 2,4-D is very rapid in basic water but is slow in acidic water. Hydrolysis rates of 2,4-D esters depend greatly upon ester structure; esters possessing ether linkages near the carboxyl group generally hydrolyze more rapidly than hydrocarbon chain esters. Photolysis of 2,4-D esters in pure water is a slow process (half-life for the butoxyethyl ester is about 14 days), but it can be important in acidic natural waters. The major photoproducts are chlorohydroxyphenoxy-acetic acid esters and 2,4-dichlorophenol.
- 3 Hydrolysis of methoxychlor is very slow and is pH-independent under reaction conditions that are usually found in aquatic environments; the half-life is greater than 200 days at 25°C. Photolysis of methoxychlor in pure water is also very slow; the half-life is greater than 300 hours of summer sunlight. However, sensitized photolysis may be rapid in natural waters.
- 4 Captan hydrolyzes very rapidly in water with a maximum half-life of one-half day. The hydrolysis products are 4-cyclohexene-1,2-dicarboximide, sulfur, carbon dioxide, and hydrochloric acid. Photolysis in pure water is too slow to compete with hydrolysis, but in a river-water sample, sensitized photooxidation of captan was very rapid. One of the products of photooxidation by singlet oxygen was found to be N-[(trichloromethyl)thio]-3-cyclohexene-4-hydroperoxy-1,2-dicarboximide. The imide derived from captan hydrolysis is also rapidly photooxidized by singlet oxygen. Abiotic transformations of captan are likely to be the predominant processes in aquatic environments.
- 5 Hydrolysis of carbaryl is fast in basic waters but slow in acidic waters. Hydrolysis half-lives range from 1.3 days at pH 8 to 4.4 months at pH 6. Products of hydrolysis are 1-naphthol, methylamine, and carbon dioxide. Direct

photolysis of carbaryl is pH-independent in the pH 5 to 7 range and may be important in acidic water; the minimum photolysis half-life is about four days in the central United States (latitude 40°N).

- 6 These studies indicate that atrazine is very stable to hydrolysis and direct photolysis in aquatic systems. Literature data indicate that half-lives at pH 3 and pH 11 (25°C) are 66 days and 81 days, respectively. Photochemical screening studies using uv light of wavelengths > 280 nm indicated that the photolysis rate of atrazine is at least ten times slower than that of carbaryl.
- 7 Hydrolysis of diazinon is very slow at pH values normally found in lakes and rivers (minimum half-life of one month at 20°C). Hydrolysis is more rapid in acidic water (pH 5-7) than in basic water (pH 7-9). Photolysis in pure water is also a slow process; under high-intensity uv light (> 280 nm) the photolysis rate was about eight times slower than that of carbaryl.
- 8 Data in the literature indicate that parathion hydrolyzes slowly in pure water at pH values and temperature found in the aquatic environment. The pH-independent hydrolysis half-life in the pH 5 to 9 range is 243 days (20°C). Photolysis in pure water was about ten times slower than carbaryl when Pyrex-filtered (> 280 nm) light from a mercury lamp was employed as light source.
- 9 The hydrolysis and direct photolysis of toxaphene is extremely slow in water, even at temperatures and uv light intensities that are much greater than those in the environment.
- 10 Malathion, 2,4-D esters, methoxychlor, carbaryl, atrazine, diazinon, parathion, and toxaphene are not readily oxidized by singlet oxygen.
- 11 Oxidation of malathion, 2,4-D esters, methoxychlor, and toxaphene by molecular oxygen in water is too slow to have environmental significance.

SECTION IV
RECOMMENDATIONS

- 1 The indirect (or "sensitized") photolysis of pollutants in natural waters should be studied in more detail. These studies should include (1) elucidation of the products formed by sensitized photolysis in natural waters; (2) characterization of the materials in natural waters that are responsible for sensitized photolysis; (3) determination of the rates and mechanisms of sensitized photolysis.
- 2 Studies should be carried out to delineate sediment-associated hydrolysis processes. These should include a quantitative evaluation of its contribution and characterization of the products.
- 3 The role of oxidative processes in natural waters should be determined. Oxidizing agents should be identified, and rates of oxidation with known pollutants should be measured and products characterized. These studies should include an investigation of light-initiated autooxidation of pollutants on plant and soil surfaces.

SECTION V

BACKGROUND

CHEMICAL

Hydrolysis

No pesticide review article is considered complete without a section on the chemical degradation of pesticides. These sections generally contain fragmentary information, often contradictory, describing the persistence of a pesticide under given reaction conditions. For example, a known amount of pesticide might be added to water at an elevated temperature and its persistence monitored. While such studies have some limited value, this type of information will not allow extrapolation of the observed chemical behavior to other reaction conditions. Also in many cases the products of degradation and the persistence of these products, even if identified, are not known.

There are several common pathways of chemical degradation under environmental conditions which are apparent from an examination of the pesticide literature. These are nucleophilic substitution, elimination, oxidation, reduction, and autooxidation reactions. The term "hydrolysis" is loosely used to describe reactions in which a bond of the molecule is cleaved and a new bond is formed with the oxygen atom of a water molecule.

Hydrolytic reactions are generally mediated by acid and/or base. The extent to which these catalytic effects come into play is dependent on the type of reaction and the chemical structure of the compound.

Temperature effects vary for different reaction pathways and the magnitude of these effects vary with chemical structure. In fact, temperature may affect not only the rate of the reaction, but the products as well (see Section VIII).

pH-rate profiles (Figure 2) are useful in understanding and evaluating contributions of acid, alkaline, and neutral hydrolysis. For purposes of example, pH-rate profiles of carboxyl ester hydrolysis are discussed. However, similar pH-rate profiles are applicable to phosphate esters, amides, carbamates, and other compounds labile to hydrolysis.

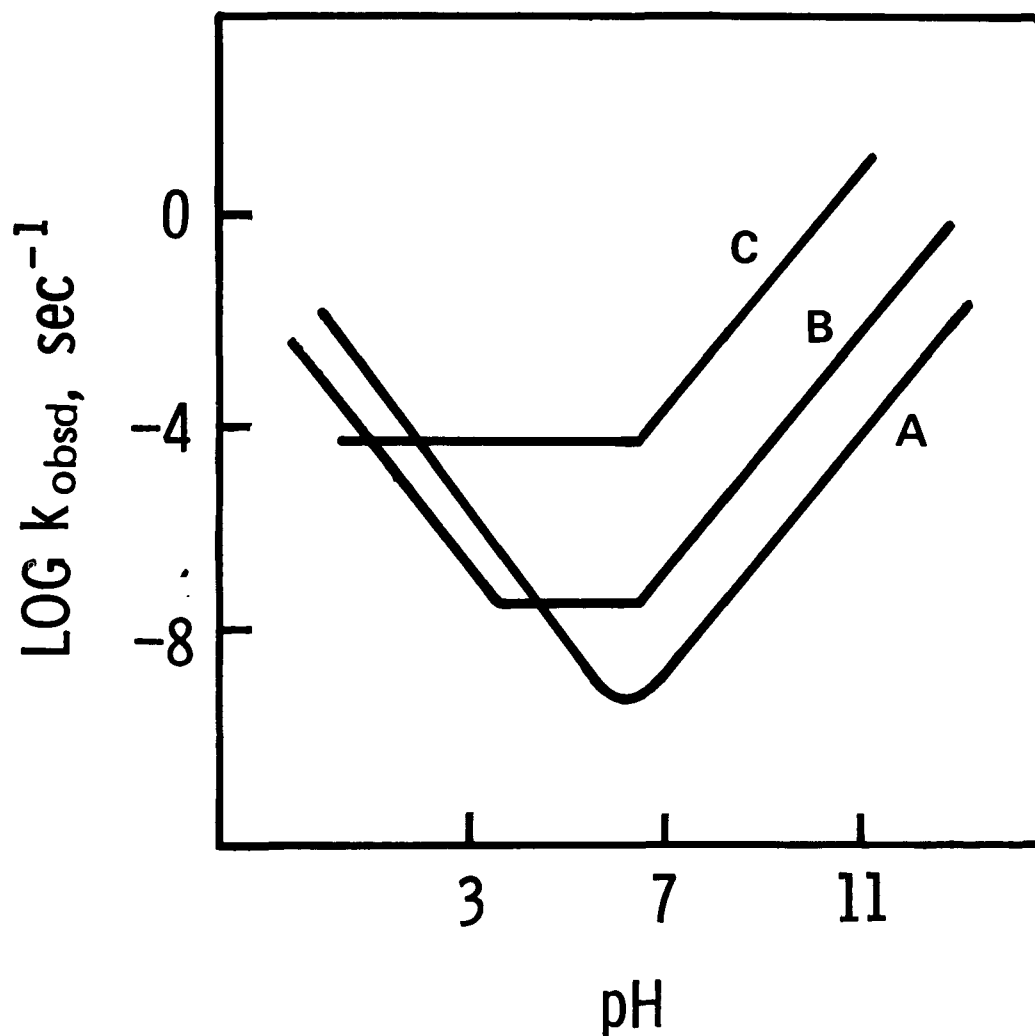
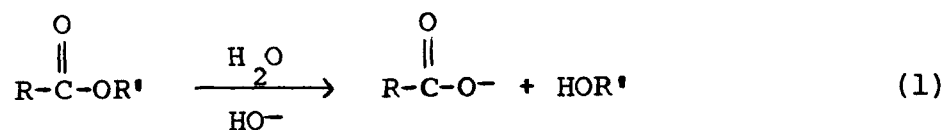


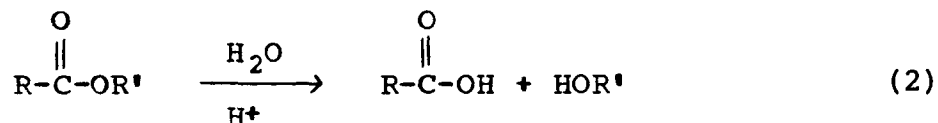
Figure 2. Typical pH-rate profile for the hydrolysis of pesticides containing ester moieties: A, less reactive; B, ester of intermediate reactivity; C, highly reactive ester.

The hydrolytic behavior of carboxylic esters in the pH range 4 to 8 varies with the hydrolytic reactivity of the ester (for a more complete discussion, see reference 1). The overall reaction for alkaline hydrolysis is



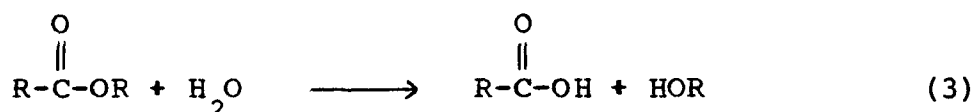
How readily the ester is converted to the acid is dependent on the structure of the substituents R and R' and the pH of the water.

Acid hydrolysis generally requires more stringent reaction conditions. The overall reaction is



This reaction occurs by a pathway in which acid is not consumed and is termed an acid catalyzed reaction.

Esters can also undergo hydrolysis by reaction with water in the absence of acid or base:



This reaction is most significant in the cases of more reactive esters.

The overall rate expression for the disappearance of the ester is given by

$$-\frac{dE}{dt} = k_{\text{H}^+}[\text{RCOOR}'][\text{H}^+] + k_{\text{H}_2\text{O}}[\text{RCOOR}'] + k_{\text{OH}^-}[\text{RCOOR}'][\text{OH}^-] \quad (4)$$

where k_{H^+} , $k_{\text{H}_2\text{O}}$, and k_{OH^-} are the rate constants for acid, neutral, and alkaline degradation, respectively¹.

Because most natural waters have considerable buffering capacity and pollutant concentrations are low, the effective concentration of acid or base does not change during the reaction. Pseudo-first-order kinetics are observed and the observed first-order rate constant is given by

$$k_{\text{obsd}} = k_{\text{H}^+}[\text{H}] + k_{\text{H}_2\text{O}} + k_{\text{OH}^-}[\text{OH}] \quad (5)$$

and the half-life expression² is

$$t_{1/2} = \frac{0.693}{k_{\text{H}^+}[\text{H}^+] + k_{\text{H}_2\text{O}} + k_{\text{OH}^-}[\text{OH}^-]} \quad (6)$$

Figure 2 is a plot of pH vs. $\log k_{\text{obsd}}$ for the reaction of three different esters based on literature data. For ester A the neutral hydrolysis contribution is negligible and the profile consists of two straight lines with a slope of minus one (-1) for acid catalysis and plus one (+1) for alkaline reaction which intersect at the rate minimum. At this minimum the rate of acid and base hydrolysis are equal.

More reactive esters give a pH-rate profile illustrated by curve B. In this case, the minimum is indicated by a line with a slope of 0 which is attributed to hydrolysis by water.

For very reactive esters, no minimum is observed because the reaction with water makes the reaction pH independent at acid pH's (curve C).

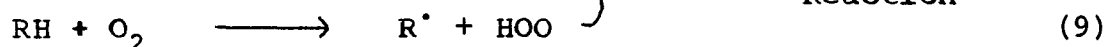
Oxidation-Reduction

The definition of oxidation-reduction is not adequately explained in terms of gain or loss of oxygen. It is customary to define these reactions in terms of electron loss (oxidation), electron gain (reduction)³, and half-cell reactions. However, there may be little relation between what is shown in the half-cell reactions and what actually occurs when two reagents are mixed.

An understanding of the oxidation-reduction reaction requires knowledge of whether electrons or atoms are transferred, how many electrons are involved, any intermediates formed, and rate constants for the reactions involved.

Oxidation-reduction reactions have received environmental interest, but it has been from a thermodynamic point of view. Work is needed to evaluate oxidation-reduction reactions of pollutants under conditions common to aquatic ecosystems and to determine their contribution as a degradative pathway.

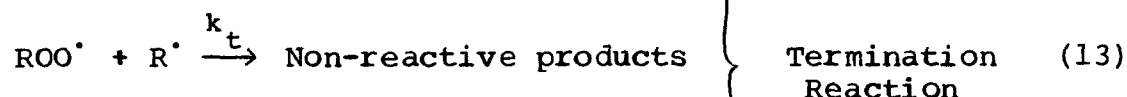
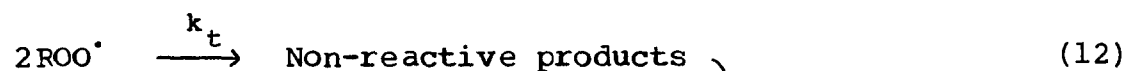
Another oxidative pathway which is potentially important for pollutant degradation is autooxidation. Autooxidation is defined by Pryor⁴ as the slow oxidation of an organic compound by oxygen. Examples of autooxidation include air drying of paints and varnishes, and deterioration of rubbers and plastics. The general reaction scheme for autooxidation is given below. There are three parts to the reaction: initiation (steps 7-9), propagation (steps 10 and 11), and termination (steps 12, 13, and 14).



Initiation
Reaction



Propagation
Reaction



Termination
Reaction

Autooxidation involves free radicals and the reaction may be initiated (steps 7-8) by peroxides, metal salts, or any other free radical source A-B to give a pollutant-derived free radical, R^\cdot . In the absence of a free radical source, the reactions are initiated by slow reaction of oxygen with pollutants (equation 9). The slow build-up of free radical initiators, A-B, can occur by such pathways as photolysis or thermolysis.

The propagation steps (10 and 11) involve reaction of the pollutant-derived free radical with molecular oxygen (step 10) which gives a peroxy radical. The peroxy radical reacts with the pollutant (step 11) to give a peroxide and regenerate R^\cdot .

There are three possible termination reactions (steps 12-14). At moderately high oxygen pressures which exist in aerobic waters and low pollutant concentrations, step 12 is the most likely termination step. Under these conditions and making a steady-state assumption, the rate of radical initiation (R_i) may be expressed as

$$R_i = 2 k_t [ROO^\cdot]^2$$

where k_t is the termination rate constant. The rate of disappearance of pollutant (RH) is given by:

$$-\frac{d(RH)}{dt} = k_2[RH][ROO^\bullet] = \frac{k_2[RH] (Ri)^{\frac{1}{2}}}{[2 k_t]^{\frac{1}{2}}} \quad (16)$$

This equation shows that the overall rate of disappearance is proportional to the pollutant concentration and the square root of the free radical initiation rate.

Extrapolation of autooxidation kinetic data to the environment is complicated by lack of data on concentrations of free radical initiators that are present under environmental conditions. Rate constants for steps 10, 11, and 12 are readily available in the literature.⁴ For example, for the organic compound tetralin, k_1 ($6.7 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$) and k_t ($2 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$) approach diffusion control. However, k_2 ($13 \text{ M}^{-1} \text{ sec}^{-1}$) is slow and the magnitude varies with organic structure.

Another complicating factor is the presence of naturally occurring anti-antioxidants, compounds like phenols and aromatic amines⁵ with readily extractable hydrogen atoms. These compounds react with R^\bullet to form non-reactive free radicals and halt the chain propagation steps (10 and 11).

The impact of autooxidation on the degradation of pollutants in the environment has not been evaluated. Reports in the literature indicate that autooxidation of pesticides does occur. These investigations, however, deal with pesticide degradation in thin films on soils, plants, and glass.

PHOTOCHEMICAL

Direct Photolysis

Numerous studies concerning pesticide photodecomposition via direct absorption of light have appeared in the literature. A great majority of these studies were concerned with products derived from such direct photolysis. A review of this work is well beyond the scope of this report. Moreover, several excellent review articles have already been published⁶⁻¹⁴.

Our review of the pesticide literature indicated that little has been published about the rates of direct photolysis under sunlight. Generally, information of this type can be obtained only by careful inspection of the Experimental sections of papers. Since rate data are essential to the modeling of pollutant dynamics in the environment, one of the

principal goals of this project was to obtain data that can be used to predict direct photolysis rates under a variety of environmental conditions.

The simplest way to determine direct photolysis rates is irradiation of the pollutant by sunlight in an uncovered reaction vessel. However, kinetic data obtained in this way should not be extrapolated from one location to another, because the intensity of solar ultraviolet radiation at the earth's surface, particularly in the 300-320 nm region, is a function of latitude, season, and elevation¹⁵. All of the pesticides included in this study absorb sunlight most strongly in the ultraviolet region. In the following section, we will discuss a simple technique that employs laboratory data to calculate direct photolysis rates. Other discussions of direct photolysis kinetics in solution¹⁶ or the atmosphere¹⁷ provide a good background for this section.

Scientists realized long ago that only light which is absorbed can effect chemical change in a system; this basic law of photochemistry was first enunciated by Grotthus, then Draper, back in the early Nineteenth Century. The average photoreaction rate, $(-d[P]/dt)_\lambda$, at wavelength λ in a completely mixed water body is directly proportional to the amount of light absorbed in a unit volume per unit time. The latter is defined by Lamberts law (equation 17) where α_λ is the absorbance of a one-centimeter thick layer of the water body and ℓ is the pathlength of the light.

$$\text{Fraction Absorbed} = 1 - 10^{-\alpha_\lambda \ell} \quad (17)$$

Underwater sunlight intensity on a horizontal plane is derived from two sources, light intensity directly obtained from the sun ($I_{d\lambda}$) and the diffuse light intensity obtained from the sky ($I_{s\lambda}$)^{15,17}. The average rate of light absorption ($I_{a\lambda}$) for a water layer of depth D is defined by equation 18

$$I_{a\lambda} = \frac{I_{d\lambda} (1 - 10^{-\alpha_\lambda \ell_d}) + I_{s\lambda} (1 - 10^{-\alpha_\lambda \ell_s})}{D} \quad (18)$$

where ℓ_d and ℓ_s are the average pathlengths for direct and sky radiation respectively.

Under most natural conditions, a pollutant absorbs only a fraction of the light absorbed by a water body. This fraction is expressed by the ratio $\epsilon_\lambda[P]/\alpha_\lambda$ where ϵ_λ is the molar extinction coefficient of the pesticide at wavelength λ in units of 1000 cm²/mole and $[P]$ is the pollutant concentration.

The average rate of light absorption by a pollutant ($I'_{a\lambda}$) is defined by equations 19 and 20

$$I'_{a\lambda} = I_{a\lambda} \frac{\epsilon_{\lambda} [P]}{j\alpha_{\lambda}} \quad (19)$$

$$I'_{a\lambda} = k_{a\lambda} [P] \quad (20)$$

where $k_{a\lambda} = I_{a\lambda}\epsilon_{\lambda}/j\alpha_{\lambda}$ and j is a constant that converts $[P]$ into units that are compatible with the intensity units (j equals 6.02×10^{20} when $[P]$ is expressed as moles/liter).

The equation for $k_{a\lambda}$ simplifies under two circumstances:

- If $\alpha_{\lambda}l_d$ and $\alpha_{\lambda}l_s$ are both > 2 , then essentially all the sunlight responsible for photolysis is absorbed and $k_{a\lambda}$ can be expressed by equation 21

$$k_{a\lambda} = \frac{[I_{d\lambda} + I_{s\lambda}] \epsilon_{\lambda}}{jD\alpha_{\lambda}} \quad (21)$$

- If $\alpha_{\lambda}l_d$ and $\alpha_{\lambda}l_s$ are both < 0.02 , e.g., near the surface of a water body, then the fraction of light absorbed (equation 17) becomes approximately equal to $2.303 \alpha_{\lambda}l$ and $k_{a\lambda}$ is defined by equation 22

$$k_{a\lambda} = \frac{2.303 \epsilon_{\lambda} [I_{d\lambda}l_d + I_{s\lambda}l_s]}{jD} \quad (22)$$

Note that the value of $k_{a\lambda}$ in this case is independent of the nature of the water body.

Equation 22 can be re-expressed as

$$k_{a\lambda} = \frac{2.303 \epsilon_{\lambda} Z_{\lambda}}{j} \quad (23)$$

where Z_{λ} is defined as

$$Z_{\lambda} = \frac{[I_{d\lambda}l_d + I_{s\lambda}l_s]}{D} \quad (24)$$

The pathlengths, ℓ_d and ℓ_s , can be expressed in terms of D by equations 25 and 26

$$\ell_d = \frac{Dn}{\sqrt{n^2 - \sin^2 z}} \quad (25)$$

$$\ell_s = 1.2D \quad (26)$$

where n is the refractive index of water and z is the angle that the sun makes with the sky zenith, i.e., the "solar zenith angle." Values of Z_λ for the mid-part of the four seasons in the central United States (latitude 40°N) are included in Table 1. All values pertain to midday solar radiation at sea level. For most wavelengths (330 to 500 nm) the Z_λ values are expressed in photons $\text{cm}^{-2} \text{sec}^{-1}$ averaged over 10 nm intervals. The values of 297.5 to 320 nm are averaged over 2.5 nm intervals and the 323.1 nm value represents 323.125 ± 1.875 nm. Midsummer values of Z_λ for three latitudes (0°, 40°, 70°N) are listed in Table 2. Data for the 297.5 to 380 nm regions were taken from Bener's report¹⁵; we calculated the other data by computer using data and procedures described by Leighton¹⁷. The values take into account reflection of sunlight at the water's surface.¹⁸

Usually, only a fraction of the light absorbed by a compound results in photoreaction. This fraction, or quantum yield for reaction (ϕ), can be determined by laboratory experiments employing monochromatic light. The direct photolysis rate of a pesticide is also proportional to its quantum yield for reaction.

The complete photolysis rate expression is shown in equation 27

$$-\frac{d[P]}{dt} = \phi \sum k_{a\lambda} [P] \quad (27)$$

where $(-d[P]/dt)$ is the observed photolysis rate and $\sum k_{a\lambda}$ is the sunlight absorption rate summed over all the wavelengths of sunlight that are absorbed by the pollutant. Maximum direct photolysis rates of the pesticides were calculated using equation 22 to calculate $k_{a\lambda}$ values. The latter were calculated using the ultraviolet absorption spectra of the pesticides and tables of Z_λ values. We have also expressed our data in terms of photolysis half-lives, $t_{1/2}$ (equation 28)

$$t_{1/2} = \frac{0.693}{\phi \sum k_{a\lambda}} \quad (28)$$

Table 1. Z_{λ} VALUES FOR LATITUDE 40°N

PHOTONS (CM-2 SEC-1 2.5 NM-1)				
	SP	SU	FA	WIN
297.5	0.274E+12	0.716E+12	0.949E+11	0.000E+00
300.0	0.120E+13	0.240E+13	0.524E+12	0.733E+11
302.5	0.419E+13	0.723E+13	0.223E+13	0.368E+12
305.0	0.121E+14	0.181E+14	0.670E+13	0.170E+13
307.5	0.223E+14	0.305E+14	0.135E+14	0.450E+13
310.0	0.372E+14	0.495E+14	0.200E+14	0.854E+13
312.5	0.584E+14	0.717E+14	0.371E+14	0.177E+14
315.0	0.780E+14	0.933E+14	0.494E+14	0.271E+14
317.5	0.992E+14	0.115E+15	0.641E+14	0.362E+14
320.0	0.117E+15	0.135E+15	0.800E+14	0.498E+14
PHOTONS (CM-2 SEC-1 3.75 NM-1)				
323.1	0.221E+15	0.252E+15	0.144E+15	0.906E+14
PHOTONS (CM-2 SEC-1 10 NM-1)				
330.0	0.761E+15	0.846E+15	0.500E+15	0.342E+15
340.0	0.880E+15	0.963E+15	0.604E+15	0.420E+15
350.0	0.942E+15	0.103E+16	0.645E+15	0.449E+15
360.0	0.101E+16	0.110E+16	0.687E+15	0.479E+15
370.0	0.112E+16	0.122E+16	0.754E+15	0.520E+15
380.0	0.124E+16	0.135E+16	0.822E+15	0.562E+15
390.0	0.149E+16	0.161E+16	0.100E+16	0.805E+15
400.0	0.213E+16	0.231E+16	0.156E+16	0.116E+16
410.0	0.280E+16	0.302E+16	0.206E+16	0.154E+16
420.0	0.288E+16	0.310E+16	0.212E+16	0.159E+16
430.0	0.277E+16	0.298E+16	0.205E+16	0.154E+16
440.0	0.327E+16	0.351E+16	0.244E+16	0.184E+16
450.0	0.368E+16	0.394E+16	0.275E+16	0.208E+16
460.0	0.371E+16	0.398E+16	0.279E+16	0.211E+16
470.0	0.384E+16	0.411E+16	0.289E+16	0.219E+16
480.0	0.392E+16	0.420E+16	0.296E+16	0.225E+16
490.0	0.371E+16	0.396E+16	0.281E+16	0.213E+16
500.0	0.378E+16	0.404E+16	0.287E+16	0.218E+16
525.0	0.398E+16	0.426E+16	0.305E+16	0.232E+16
550.0	0.413E+16	0.442E+16	0.318E+16	0.241E+16
575.0	0.417E+16	0.446E+16	0.322E+16	0.243E+16
600.0	0.421E+16	0.450E+16	0.326E+16	0.247E+16
625.0	0.422E+16	0.450E+16	0.329E+16	0.252E+16
650.0	0.424E+16	0.451E+16	0.332E+16	0.256E+16
675.0	0.423E+16	0.448E+16	0.333E+16	0.259E+16
700.0	0.419E+16	0.443E+16	0.330E+16	0.258E+16
750.0	0.401E+16	0.423E+16	0.318E+16	0.250E+16
800.0	0.385E+16	0.405E+16	0.306E+16	0.242E+16

Table 2. Z_{λ} VALUES FOR THE SUMMER SEASON

	0	40	70
297.5	0.161E+13	0.716E+12	0.307E+11
300.0	0.422E+13	0.240E+13	0.233E+12
302.5	0.109E+14	0.723E+13	0.121E+13
305.0	0.244E+14	0.181E+14	0.417E+13
307.5	0.384E+14	0.305E+14	0.923E+13
310.0	0.587E+14	0.495E+14	0.157E+14
312.5	0.806E+14	0.717E+14	0.307E+14
315.0	0.101E+15	0.933E+14	0.436E+14
317.5	0.124E+15	0.115E+15	0.571E+14
320.0	0.143E+15	0.135E+15	0.731E+14
323.1	0.263E+15	0.252E+15	0.134E+15
330.0	0.858E+15	0.846E+15	0.497E+15
340.0	0.963E+15	0.963E+15	0.604E+15
350.0	0.103E+16	0.103E+16	0.645E+15
360.0	0.110E+16	0.110E+16	0.687E+15
370.0	0.122E+16	0.122E+16	0.754E+15
380.0	0.135E+16	0.135E+16	0.822E+15
390.0	0.161E+16	0.161E+16	0.108E+16
400.0	0.231E+16	0.231E+16	0.156E+16
410.0	0.302E+16	0.302E+16	0.206E+16
420.0	0.310E+16	0.310E+16	0.212E+16
430.0	0.298E+16	0.298E+16	0.205E+16
440.0	0.351E+16	0.351E+16	0.244E+16
450.0	0.394E+16	0.394E+16	0.275E+16
460.0	0.398E+16	0.398E+16	0.279E+16
470.0	0.411E+16	0.411E+16	0.288E+16
480.0	0.420E+16	0.420E+16	0.296E+16
490.0	0.397E+16	0.396E+16	0.280E+16
500.0	0.405E+16	0.404E+16	0.286E+16
525.0	0.427E+16	0.426E+16	0.303E+16
550.0	0.445E+16	0.442E+16	0.315E+16
575.0	0.450E+16	0.446E+16	0.318E+16
600.0	0.454E+16	0.450E+16	0.322E+16
625.0	0.453E+16	0.450E+16	0.326E+16
650.0	0.453E+16	0.451E+16	0.330E+16
675.0	0.450E+16	0.448E+16	0.331E+16
700.0	0.444E+16	0.443E+16	0.330E+16
750.0	0.424E+16	0.423E+16	0.318E+16
800.0	0.405E+16	0.405E+16	0.306E+16

As previously noted, all of the pesticides included in our study absorb sunlight most strongly in the uv regions. The short-wavelength intensity of solar uv light (297.5 to 320 nm) is strongly influenced by both the solar zenith angle, z , and the atmospheric ozone content (O_3). Ozone absorption causes a sharp decrease in intensity at wavelengths < 320 nm (Figure 3). Both Z_λ and (O_3) depend upon season and latitude^{15,17,19}.

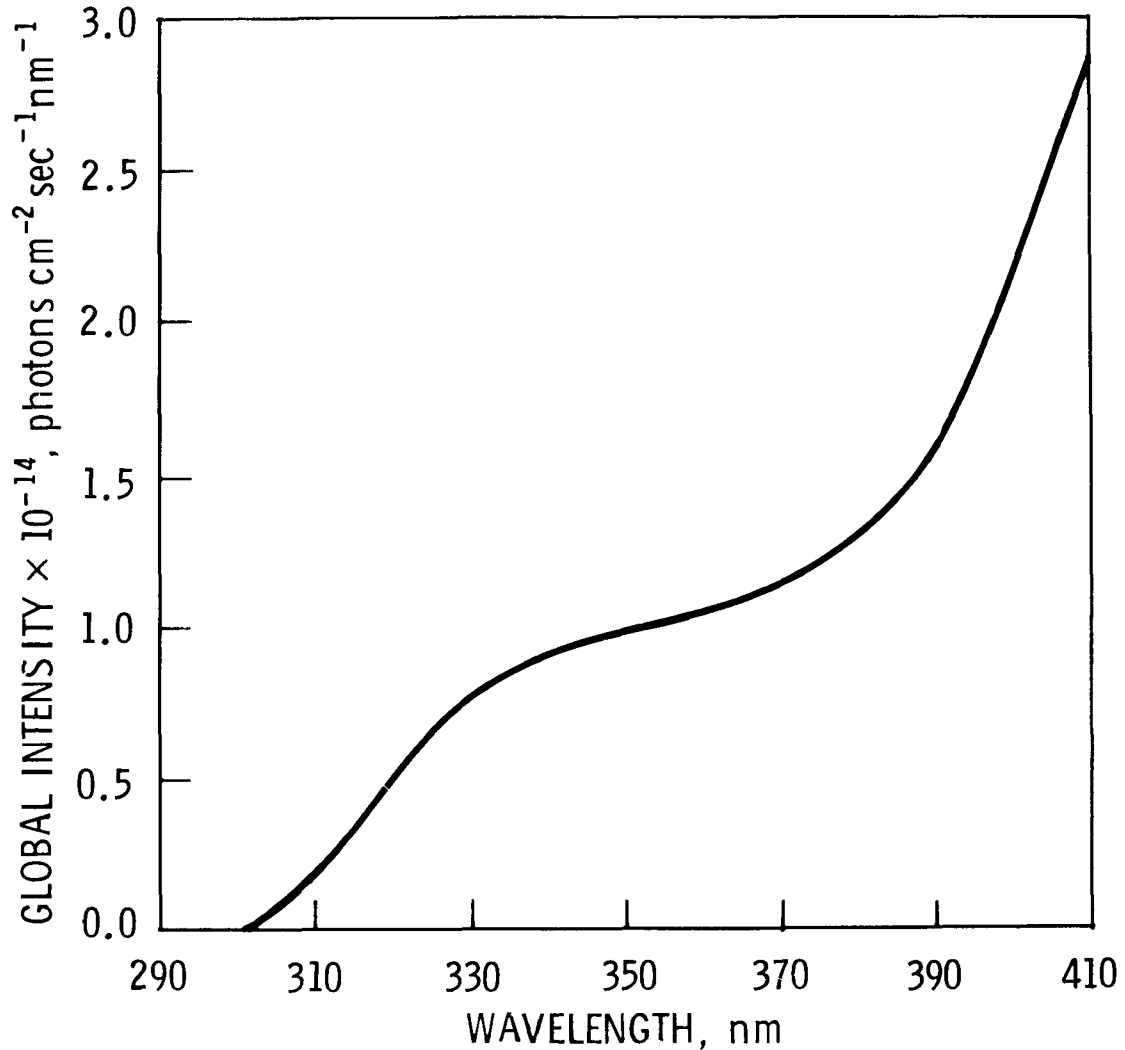


Figure 3. Midday solar irradiance for summer, latitude 40°N

The long wavelength portion of solar uv light (330-390 nm) is unaffected by (O_3), but depends only on variations in z . Seasonal variations of Z_λ values for several latitudes are shown in Figures 4 and 5. Note that seasonal variations of the short-wavelength Z_λ values (Figure 4), because they are influenced by (O_3), are much more pronounced than variations

in the 330-390 nm region (Figure 5). Generally, the amplitude of the seasonal variation of Z_λ becomes larger and the magnitude of Z_λ smaller with increasing Northern latitude, especially with Z_λ values for wavelengths < 320 nm. The following conclusions can be derived from Figures 3-5.

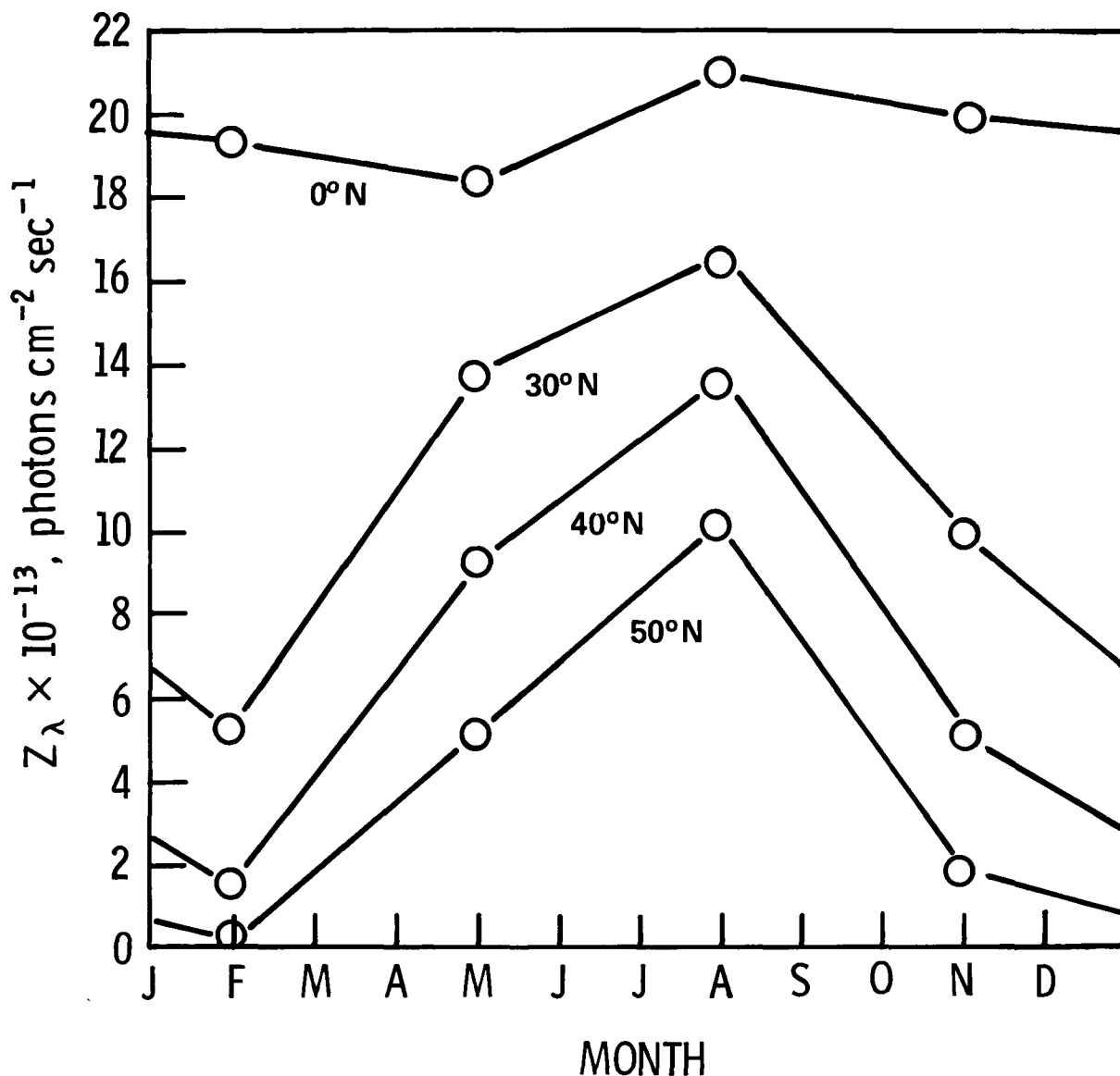


Figure 4. Dependence of short-wavelength solar uv irradiance upon season and latitude

- Direct photolysis rates of pollutants that absorb sunlight most strongly at wavelengths < 320 nm vary considerably from one season to another. Maximum photolysis rates, however, generally occur during the

seasons (spring and summer) of greatest pesticide use.

- Direct photolysis rates generally decrease with increasing Northern latitude. During the summer, however, there is less than a two-fold difference in rates between the equator and latitude 50°N.

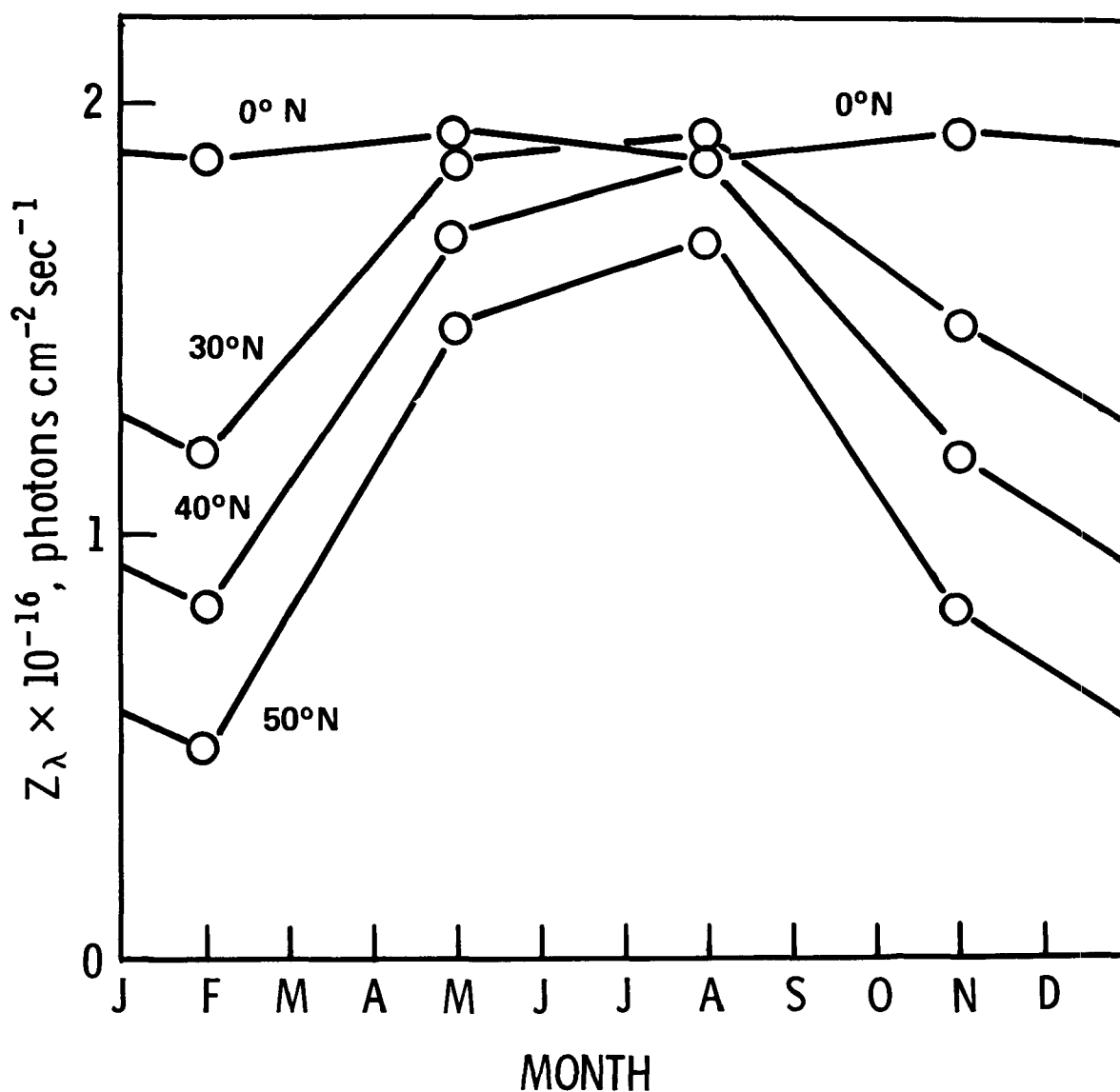


Figure 5. Dependence of long-wavelength solar uv irradiance upon season and latitude

Other factors also influence direct photolysis rates of pesticides. Ultraviolet intensity is decreased somewhat by clouds, but even on an overcast day the midday ultraviolet

intensity is attenuated only by a factor of two²⁰. Reflection of sunlight from the surface of a water body also decreases its intensity, but the fraction of sunlight reflected is less than 0.1 during most of the day¹⁵.

One of the most important determinants of direct photolysis rates is the penetration of ultraviolet light into the water. Inland surface waters generally contain varying amounts of dissolved organic or humic materials that are derived primarily from decayed vegetation. As shown in Figure 6, these dissolved organics can have an appreciable effect upon the penetration of ultraviolet light. The term $2/\alpha$ in Figure 6 is the depth at which 99% of direct sunlight at $z = 0^\circ$ is absorbed. In rivers such as the Suwannee River in north Florida, direct photolysis, on the average, is very slow, since it occurs at depths not greater than a few centimeters. This is certainly not the case in all inland surface waters. For example, ultraviolet light penetrates to much greater depths in the Savannah River (Figure 6). Light scattering by suspended particles in turbid natural waters can also markedly attenuate ultraviolet penetration.²¹

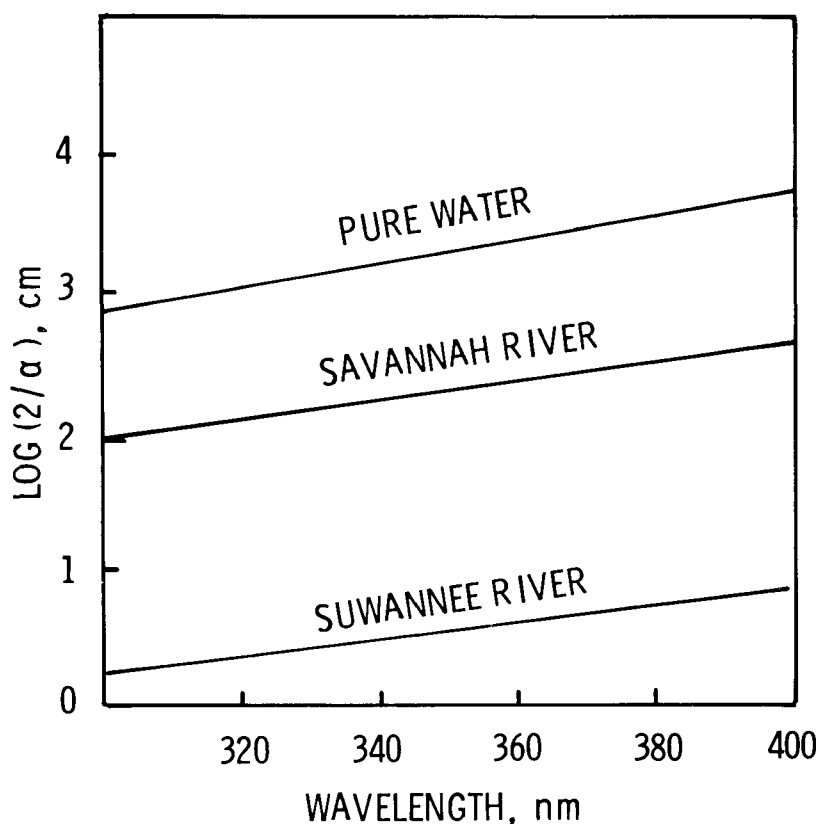


Figure 6. Penetration of ultraviolet light into two natural waters and pure water

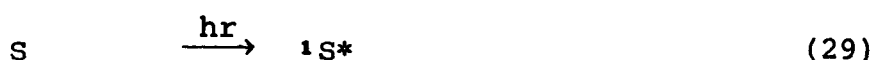
Some scientists have found that highly insoluble chlorinated pesticides such as DDT and dieldrin concentrate in slicks that occur on the surface of natural waters.²²⁻²⁴ This phenomenon obviously accelerates the overall photolysis rates of the pesticides. Unfortunately, there are insufficient data to assess its general importance at the present time. It is likely that the more water-soluble pesticides such as carbaryl and malathion will not concentrate in surface slicks to a great extent.

In conclusion, the above discussion demonstrates that the direct photolysis of pesticides should obey a first-order rate law and be directly proportional to the quantum yields for reaction and the sunlight absorption rates. Near the surface of water bodies, the latter are independent of the nature of the water body and can be calculated from the ultraviolet absorption spectra of the pollutants and tables of solar radiation data. Direct photolysis rates can be calculated for different locations and seasons. Photolysis rates in natural waters are strongly dependent upon absorption and scattering of ultraviolet light by materials in the water.

Sensitized Photolysis

Several studies have shown that the photodecomposition of pesticides can be accelerated by the presence of other organic compounds that absorb light more strongly than the pesticides themselves²⁵. Such acceleration, generally referred to as photosensitization, can occur on solid surfaces such as plant leaves,²⁶ or in natural waters.^{27,28}

Perusal of the literature suggests that several mechanisms may account for pesticide photosensitization. One mechanism involves light absorption by a sensitizer S (eq 29), followed by energy transfer from the sensitizer to the pesticide P (eq 31)²⁹.



Although light absorption initially puts the sensitizer into its first excited singlet state, ${}^1S^*$, energy transfer most often occurs from its first excited triplet state, ${}^3S^*$ (eq 30). It should be noted that physical chemists usually restrict the term "photosensitization" to energy transfer phenomena.

Several studies have demonstrated that triplet energy transfer (eq 31) occurs efficiently only when the triplet state energy of the sensitizer is greater than or equal to that of the energy acceptor.²⁹ Our studies of the photosensitized decomposition of phenylmercury compounds³⁰ have demonstrated that large decreases in quantum yield occur when sensitizers with insufficient triplet state energies are employed. Since the triplet state energies of pesticides are important determinants of the efficiency of triplet energy transfer, we have listed approximate triplet state energies of some pesticides and their hydrolysis products in Table 3. Classical studies by Lewis and Kasha³⁴ established that most benzene derivatives have triplet state energies in the 75-85 kcal mole⁻¹ range. The data in Table 3 indicate, as expected, that most of the pesticides included in this study have triplet energies > 75 kcal. Notable exceptions are the nitrobenzene derivatives, parathion and p-nitrophenol, the naphthalene derivatives, carbaryl and 1-naphthol, and 1,1-diphenylethylene derivatives, DDE and the DDE analog of methoxychlor. The relatively low triplet energies of these compounds indicate that a wide range of sensitizers can transfer energy to them. On the other hand, the high triplet state energies of pesticides such as DDT-type compounds and 2,4-D derivatives indicate that their photodecomposition by an energy transfer mechanism can only occur when high energy sensitizers, such as acetone³⁰, are employed. Various naturally occurring compounds, such as some amino acids and some common aromatic formulation components, such as xylenes, have sufficiently high triplet energies to transfer energy to all of the pesticides listed in Table 3^{34,35}. The sunlight absorption rates of these high-energy sensitizers are low, however, and the quantum yields for energy transfer photosensitization are sharply reduced by the presence of competing energy acceptors such as oxygen.

Several studies in the literature indicate that mechanisms other than energy transfer are also responsible for photosensitized decomposition. Ivie and Casida²⁶ found that there was no good correlation between the effectiveness of several sensitizers and their triplet state energies. Moreover, Plimmer and Kearney³⁶ and Rosen and co-workers³⁷ have reported that chloroaniline decomposition is photosensitized by benzophenone and riboflavin. Since the triplet energies of benzophenone (68 kcal mole⁻¹) and riboflavin (47 kcal mole⁻¹) are lower than those of anilines (> 75 kcal mole⁻¹)³⁴, mechanism(s) other than energy transfer must account for these observations.

Another likely mechanism for photosensitization involves chemical reaction between the electronically excited sensitizer and the pesticide (eq 33)

Table 3. TRIPLET STATE ENERGIES OF SEVERAL PESTICIDES

Pesticide or Hydrolysis Product	Triplet Energy ^{a,b} Kcal/mole ⁻¹
DDT	79 ^{c,e}
Methoxychlor	80 ^{c,f}
DDE	54 ^d
DDE Analog-Methoxychlor	53 ^d
Parathion	58
Diazinon	76
Carbaryl	60
2,4-D Butoxyethyl ester	77 ^{c,f}
p-Nitrophenol	58
1-Naphthol	60

^aExcept where noted, calculated from λ_{\max} of highest energy band in phosphorescence spectrum.

^bExcept where noted, taken from phosphorescence data reported by Winefordner³¹.

^cCalculated from onset of phosphorescence.

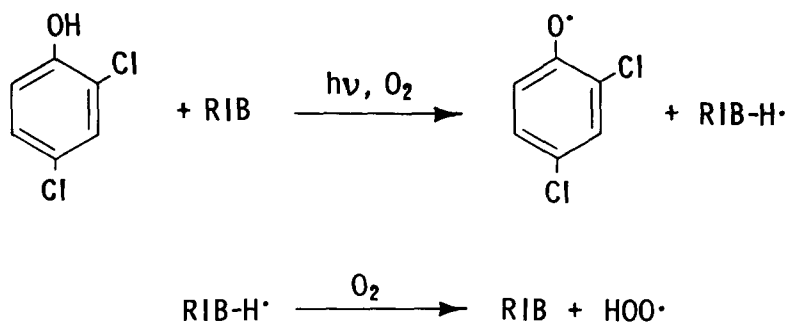
^dReference 32.

^eReference 33.

^fMeasured in collaboration with Dr. R. Hautala, University of Georgia.

Of the variety of reactions that can occur, hydrogen atom transfer from pesticide to sensitizer is one of the most general. In the presence of oxygen, this reaction often leads to oxidation of the pesticide by a free radical mechanism. The effectiveness of rotenone as a sensitizer²⁶ is probably related to the fact that it is a substituted phenyl ketone; photoexcited phenyl ketones are known to be efficient hydrogen-atom abstractors³⁸. Riboflavin, a widely used pesticide photosensitizer, is also a good hydrogen abstractor in the excited state³⁹. The riboflavin-sensitized oxidation of 2,4-dichlorophenol apparently involves hydrogen abstraction⁴⁰ (Figure 7) as products due to coupling of free radicals are obtained.

Formation of ground-state or excited-state complexes⁴¹ between naturally occurring substances and pesticides can also lead to accelerated pesticide photodecomposition. The enhanced sunlight photolysis rate of DDT observed in the presence of high concentrations of amines has been attributed to formation of excited-state charge-transfer complexes⁴². Light-induced decomposition of dissolved pesticides in the aquatic environment is not likely to occur via ground-state amine-pesticide complexes; the weak complexes that amines form with chlorinated hydrocarbons⁴³ are completely dissociated at low concentrations. Numerous studies in the chemical literature have provided examples of photoreactions mediated by excited-state complexes, or "exciplexes."^{41,44} Compounds

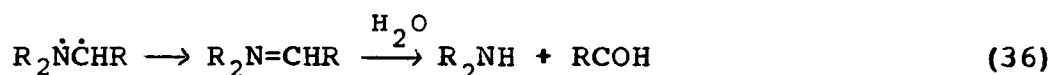
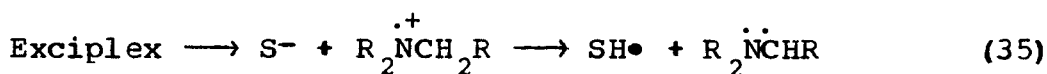
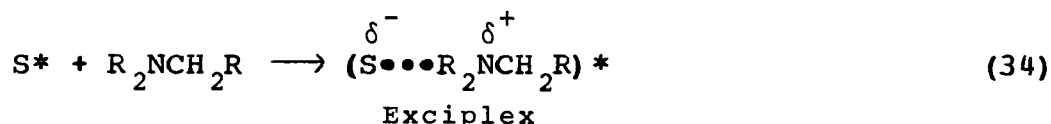


RIB = riboflavin

J. Plimmer and U. Klingebiel, *Science*, 174, 407 (1971).

Figure 7. Mechanisms for the riboflavin-sensitized oxidation of 2,4-dichlorophenol

containing alkylamino groups are particularly prone to photoreact by this pathway⁴⁵ (eq 34-36); oxidation of the amine and reduction of the sensitizer occurs via electron transfer within the exciplex.



Ketones, such as benzophenone, and aromatic compounds, such as naphthalene derivatives, are known to be photoreduced by amines.

Because all aquatic environments contain dissolved molecular oxygen, autooxidation, initiated by photochemical decomposition of free radical initiators, may also be involved in the light-induced decomposition of pesticides in natural waters. Autooxidation was discussed in detail in an earlier section of this report. Autooxidation could be initiated by photoinduced hydrogen-abstraction reactions (eq 37), similar to those previously discussed.



The above discussion demonstrates that a variety of pathways are available for the light-induced decomposition of pesticides. Thus, the direct photolysis half-life can be regarded only as a minimum estimate of the photoreactivity of a pesticide under environmental conditions. Studies discussed later in this report demonstrate that photolysis half-lives for pesticides in natural waters are sometimes much shorter than direct photolysis half-lives.

Photooxygenation Involving Singlet Oxygen

One other general mechanism for photosensitized oxidation of pesticides deserves separate consideration. Singlet molecular oxygen⁴⁶ can be generated by energy transfer from sunlight-absorbing substances in water bodies (Figure 8). In Figure 8, SENS and SENS* represent some singlet oxygen photosensitizer in its ground and electronically excited state, ³O₂ and ¹O₂ represent oxygen in its triplet ground

state and first excited singlet state, and P represents a reactive pesticide.

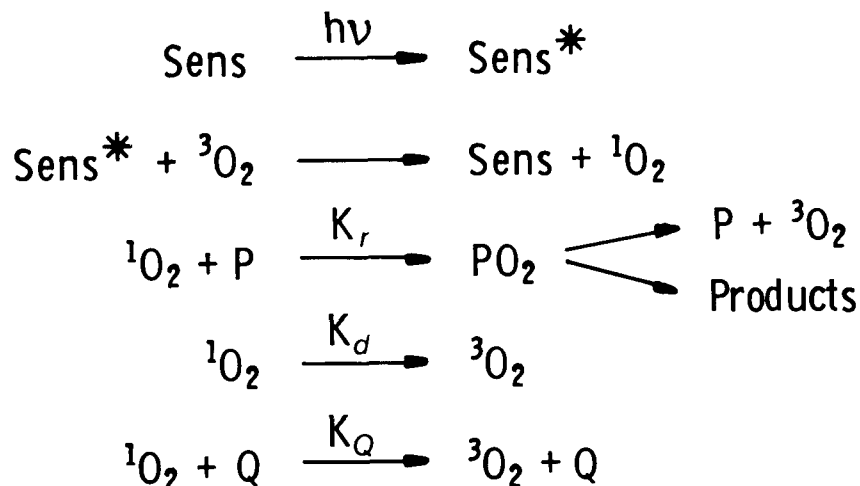
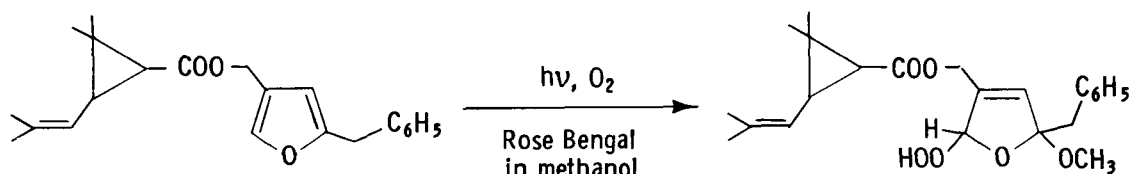


Figure 8. Mechanism for generation of singlet oxygen in the aquatic environment

Merkel and Kearns⁴⁷ have shown that the rate constants for reaction (K_r) are relatively insensitive to solvent changes, but the rate constant for radiationless decay of singlet oxygen (K_d) varies greatly from one medium to another. The value of K_d is much larger in water than in organic solvents. The lifetime of singlet oxygen may be shortened in natural waters by the presence of "quenchers," Q, such as amines, that return it to its ground state (Figure 9).

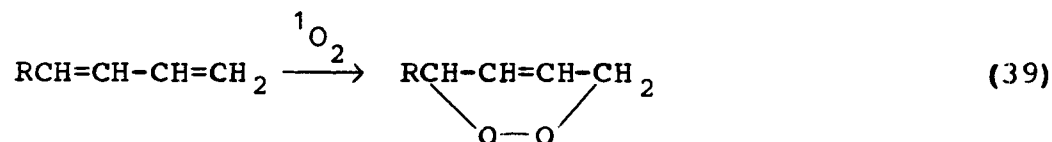
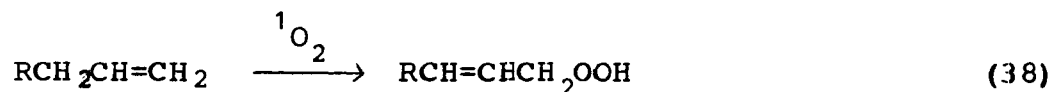


K. Ueda, L. Gaughan, and J. Casida, *J. Agr. Food Chem.*, **22**, 212 (1974).

Figure 9. Photosensitized oxidation of cis-resmethrin

Numerous publications have appeared concerning the role of singlet oxygen in atmospheric⁴⁸ and other environmental systems⁴⁹. These studies have shown that singlet oxygen participates in three important reaction types; oxidation of olefins (eq 38), addition to conjugated dienes or similar

compounds (eq 39), and oxidation of compounds containing heteroatoms, such as alkyl sulfides (eq 40)



Peroxides formed by reactions of singlet oxygen with naturally-occurring substances⁴⁹ can also serve as free radical initiators for autooxidation of pollutants. Pollutants containing the above structural features are most likely to react with singlet oxygen. For example, cis-resmethrin, which contains a furan moiety, reacts with singlet oxygen⁵⁰ to form a product which results from methanol addition to the expected endoperoxide intermediate (Figure 9)⁴⁶. This is a good example of addition of singlet oxygen to a dienoid moiety (eq 39). Other examples will be discussed later in the report. Recent studies by Heitz and his co-workers have demonstrated that singlet oxygen, generated photochemically, readily oxidizes the acetylcholinesterase from imported fire ants⁵¹. Irradiation of fire ants that have been fed singlet oxygen photosensitizers results in symptoms similar to classical nerve poisoning⁵².

Kinetic equations describing photosensitized oxygenation in a natural water are shown in Figure 10. The average rate $(-d[P]/dt)$ at depth l is proportional to the quantum yield for reaction (ϕ_s) , the fraction of light absorbed by the singlet oxygen photosensitizer $(\epsilon_s \lambda C_s / \sum \epsilon_\lambda C)$, and the intensity of sunlight (G_λ) . At low pesticide concentrations, the quantum yield becomes directly proportional to the pesticide concentration and the kinetics obey a first-order rate law. Foote has expressed singlet oxygen reactivities in terms of β values where $\beta (K_d/K_r)$ is the concentration of "acceptor" required to react with half of the singlet oxygen formed in a system⁴⁶. The rate is inversely proportional to the β value.

$$-\frac{d[P]}{dt} = \frac{\Phi_s}{I} \sum \frac{\epsilon_{s\lambda} C_s G_\lambda}{\sum \epsilon_\lambda C}$$

$$\Phi_s = K \frac{K_r [P]}{K_r [P] + K_d}$$

If $K_d \gg K_r [P]$,

$$\Phi_s \cong \frac{K K_r}{K_d} [P] = \frac{K}{\beta} [P]$$

C. S. Foote, Accounts Chem. Res., 1, 104 (1968).

Figure 10. Kinetics equations for photosensitized oxidation involving singlet oxygen

Although Plimmer¹¹ and Crosby¹² have both suggested that singlet oxygen may play a role in the photooxidation of pesticides, no data concerning the kinetics of ¹O₂-pesticide reactions have appeared in the literature. This lack of data prompted the singlet oxygen studies that are discussed later in this report.

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SECTION VI

MATERIALS AND METHODS

MATERIALS

Sources and purification methods for the pesticides used in this study are listed in Table 4. Synthetic procedures are described below. Products of chemical and photochemical reactions were obtained commercially whenever possible, but in most cases they were synthesized as described.

Chlorohydroxyphenoxyacetic acid esters

The acids, 2-chloro-4-hydroxyphenoxyacetic acid and 4-chloro-2-hydroxyphenoxyacetic acid, were synthesized as described by Brown and McCall¹. Esters were prepared by acid-catalyzed reaction of the acids with appropriate alcohols. Mass spectra of methyl 2-chloro-4-hydroxyphenoxyacetate and that of the lactone obtained from thermal decomposition of esters of 4-chloro-2-hydroxyphenoxyacetic acid are shown in Figure 11. The lactone formed quantitatively during gas chromatographic analysis of the esters.

O,O-Dimethyl phosphorodithioic acid

Phosphorus pentasulfide (Eastman) (35.2 g, 0.158 mol) was added to 40 ml of benzene. The slurry was stirred and maintained at 40°; 28.8 ml (0.713 mol) of absolute methanol was added dropwise over a period of three hours. The reaction mixture was filtered and the solvent removed by flash evaporation. The O,O-dimethyl phosphorodithioic acid was purified by distillation (12" Vigreux column), and the fraction distilling at 34-35° (0.15 mm Hg); [lit. 42-44° (0.5 mm Hg)] was collected. The ir spectrum compared with the literature spectrum².

O,O-Dimethyl-S-(1-carbethoxy-2-carboxy) ethyl phosphorodithioate (β -monoacid)

Following a procedure similar to that of Chen *et al.*³, O,O-dimethyl phosphorodithioic acid and ethyl hydrogen maleate⁴ were reacted in the presence of pyridine. The reaction mixture was cooled and 10 ml of water was added. The mixture was slowly titrated with sodium hydroxide (1 M) until the residue dissolved (pH below 6). The solution was washed with 10 ml of chloroform and separated; the resulting aqueous layer was acidified to pH 2.5 (10% HCl) and extracted with

Table 4. SOURCES AND PURIFICATION TECHNIQUES FOR PESTICIDES

Pesticide	Source	Purification Technique
Atrazine	Ciba-Geigy	Recrystallized from CHCl_3
Captan	Matheson, Coleman, and Bell	Recrystallized from CCl_4
Carbaryl	Union Carbide	Recrystallized from ether
Diazinon	Ciba-Geigy	Used as received
2,4-D Esters	Synthesized	Distilled or recrystallized from methanol
Malathion	American Cyanamid	Low temperature recrystallization
Parathion	Monsanto	Distilled, then recrystallized from 10% ether-hexane
Methoxychlor	Synthesized	Recrystallized from 95% ethanol
Toxaphene	Hercules	Used as received

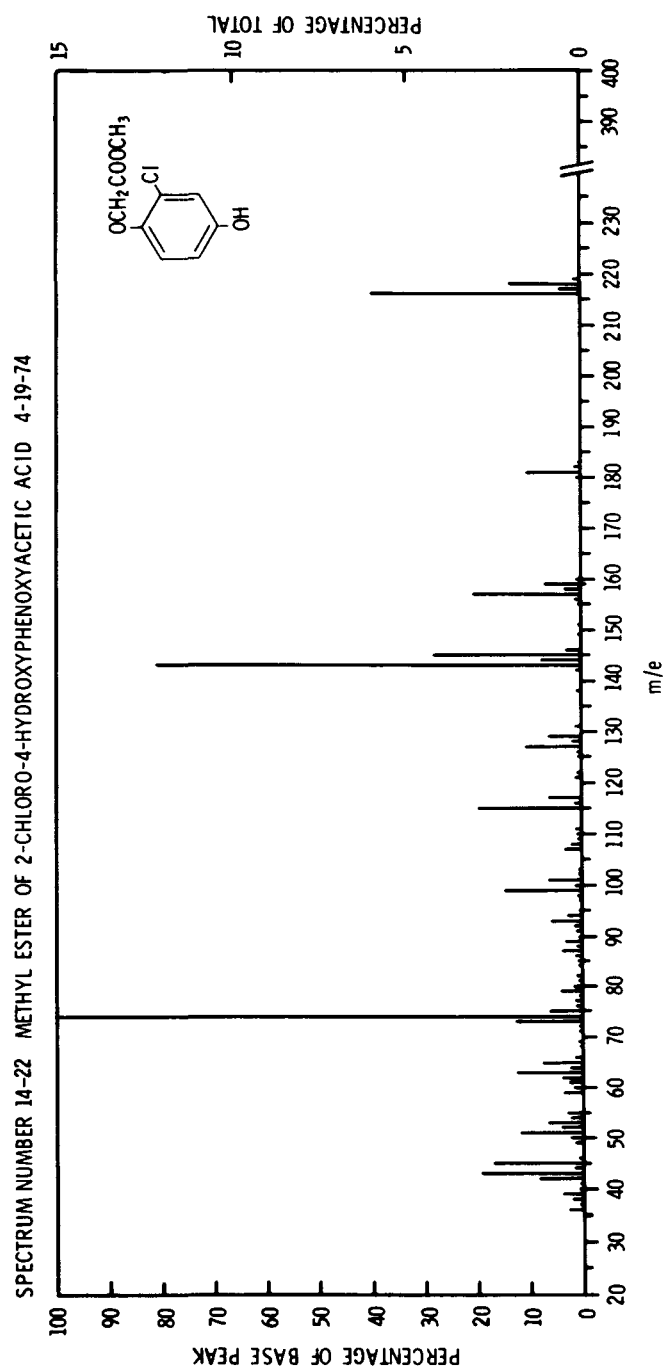


Figure 11(A). Mass spectra of methyl 2-chloro-4-hydroxyphenoxyacetate

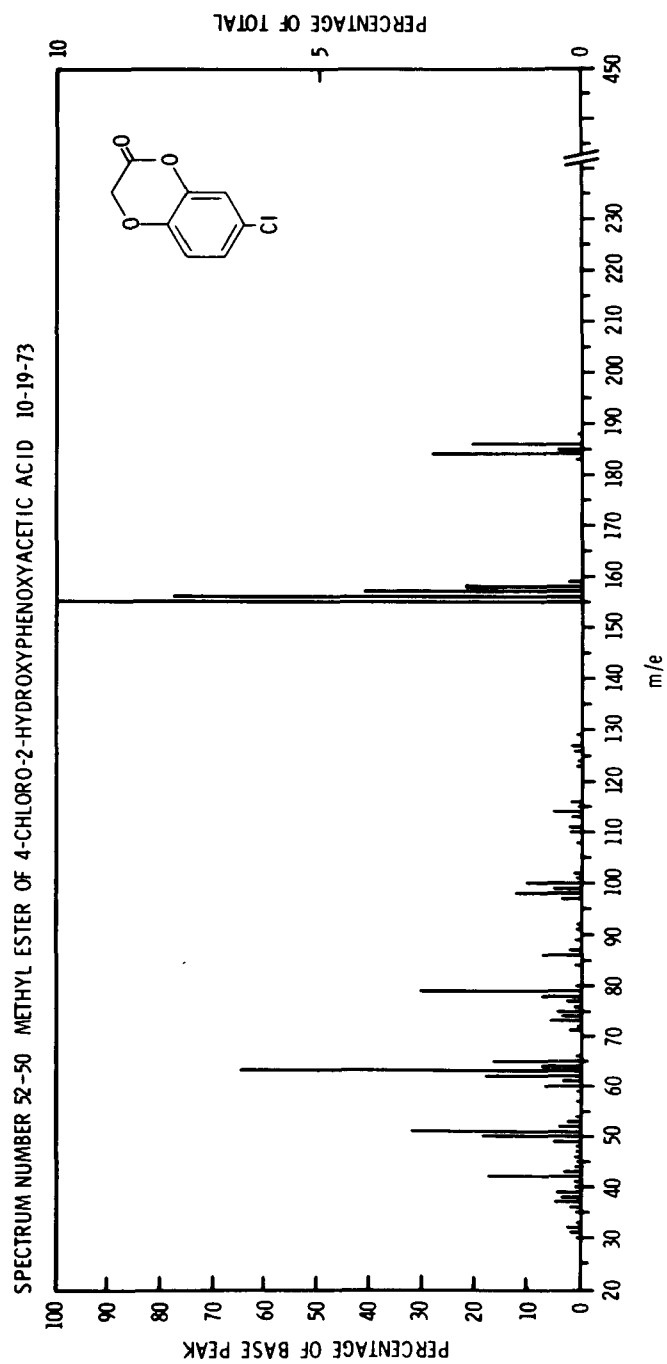


Figure 11(B). Mass spectra of lactone derived from thermal decomposition of esters of 4-chloro-2-hydroxyphenoxyacetic acid

three 50-ml portions of chloroform. Workup yielded 0.78g (85%) of a colorless oil that slowly crystallized on standing. Analysis by lc showed the mixture to consist of the β -isomer (97%) and the α -isomer (3%). Recrystallization from chloroform-hexane gave white crystals [mp 42-45°; lit. 51-52°].³ The ir⁵ and proton nmr³ compared with those reported in the literature.

O,O-Dimethyl-S-(1-carboxy-2-carbethoxy) ethyl phosphorodithioate (α -monoacid)

To 0.158 g (1.0 mmol) of O,O-dimethyl phosphorodithioic acid in 10 ml of 50% benzene-hexane v/v was added 0.144 g (1.0 mmol) of ethyl hydrogen maleate⁴. 1',1',1'-Triphenylbenzeneazomethane (Eastman) (1 mg) was added; the solution was cooled to 0° and irradiated through Pyrex with a Hanovia medium pressure 450 watt lamp for one hour. The malathion monoacid product mixture contained the α -isomer (95%) and the β -isomer (5%) as shown by lc analysis. The reaction mixture was worked up as described above, yielding 0.120 g (40%) of a white solid. Crystallization from chloroform-hexane gave white crystals, mp 55-57° [lit. an oil].³ The ir and nmr spectra compared with the literature spectra^{3,5}.

O,O-Dimethyl-S-(1,2-dicarboxy) ethyl phosphorodithioate (diacid)

Following the above procedure, 23.7 g (0.150 mol) of O,O-dimethyl phosphorodithioic acid was added to 14.7 g (0.150 mol) of maleic anhydride (Aldrich, recrystallized) and one drop of pyridine. The reaction was maintained at 60° for three hours. The residue was dissolved in 150 ml of chloroform, washed with three 100-ml portions of water, and dried (Na₂SO₄). To 11.8 g (0.046 mol) of the anhydride was added 40 ml of water; the resulting solution was heated at 70° for one hour. The aqueous solution was washed with 10 ml of chloroform, acidified to pH 2 (conc. HCl), and extracted with four 50-ml portions of ether. Evaporation of solvent yielded a white solid, which crystallized from chloroform to give 9.8 g (71%) of the diacid: mp 115-118°. Recrystallization from chloroform yielded crystals with a melting point of 127-129°. The ir spectrum matched that reported in the literature⁶.

O,O-Dimethyl-S-(1-carbethoxy-2-carboxy) ethyl phosphorothiolate (malaoxon β -monoacid)

A 10% solution of bromine in water was added dropwise with stirring to malathion β -monoacid (1 g, 3.3 mmol) dissolved in 100 ml of 50% aqueous ethanol (v/v) (27°) until a faint yellow color persisted. The aqueous solution was extracted with three 150 ml portions of chloroform, and the organic layer

dried (Na_2SO_4). Concentration gave 0.91 g (96%) of a colorless oil. The glc retention time, after methylation (diazomethane), was less than the retention time of methylated starting material, and the ir spectrum was consistent with the title compound. Attempts to crystallize or distill the oil under reduced pressure failed.

2,4-D Esters

Commercial 2,4-D (Aldrich) was reacted with appropriate alcohols in the presence of an acid catalyst (usually dilute sulfuric acid). The methyl ester was subsequently purified by recrystallization (mp 38-39°) and the liquid esters were purified by vacuum distillation. Their mass spectra were consistent with the assigned structures.

Methoxychlor

Chloral was condensed with anisole using aluminum trichloride as catalyst in alcohol-free chloroform. After stirring at room temperature for twelve hours, the purple reaction mixture was hydrolyzed with a large excess of water and the chloroform layer was dried over anhydrous sodium sulfate. Upon evaporation a yellow oil was obtained which crystallized upon standing. Pure methoxychlor was obtained by chromatographing the product on Woelm neutral alumina, then recrystallizing it five times from 95% ethanol [mp 88-89°; lit.⁷ mp 87-88°].

2- and 4-Chlorophenoxyacetic Acid Esters

Methyl esters were synthesized from the commercially obtained acids by Clinton and Laskowski's procedure⁸. Butoxyethyl esters were prepared by the acid-catalyzed reaction of the acids with 2-butoxyethanol. The mass spectra of the esters were consistent with their assigned structures.

N-Methyl-1-hydroxy-2-naphthamide

The acid chloride of 1-hydroxy-2-naphthoic acid was prepared by refluxing the acid in thionyl chloride containing a trace of dimethylformamide. An ethereal solution of the acid chloride was slowly added to a stirred 1:1 mixture of ether and 40% aqueous methylamine with occasional cooling by an ice bath. The reaction mixture was neutralized by addition of hydrochloric acid, then the ether layer was washed by water, 5% aqueous sodium bicarbonate, and water. After drying over magnesium sulfate, the ether was removed under vacuum to yield the acid amide. Recrystallization from benzene-hexane yielded the pure amide, [mp 122°; lit.⁹ mp 123-124°].

N-Methyl-4-hydroxy-1-naphthamide

The methyl ester of 4-hydroxy-1-naphthoic acid was prepared by a procedure described elsewhere¹⁰. The ester was dissolved in 40% aqueous methylamine and the mixture was heated at 100°C for three days. Upon cooling, the amide crystallized from the reaction mixture.

1,1-Bis(p-methoxyphenyl)-2,2-dichloroethylene (DMDE)

DMDE was synthesized by reaction of methoxychlor with potassium hydroxide in boiling 95% ethyl alcohol⁵ [mp 111-111.5°; lit.¹¹ mp 109°]. The mass spectrum was the same as that reported by MacNeil *et al.*¹²

1,1-Bis(p-methoxyphenyl)-2,2-dichloroethane (DMDD)

DMDD was synthesized as previously described¹³ [mp 116-117°; lit.¹³ mp 114.5-115°]. The mass spectrum agreed with the spectrum previously reported¹².

1,1-Bis(p-methoxyphenyl)-2-chloroethylene

1,1-Bis(p-methoxyphenyl)-2-chloroethylene was prepared from DMDD by the same procedure used to synthesize DMDE from methoxychlor [mp 76-77°].

Other Materials

Water used in most of the experiments was distilled, passed through ion exchange columns, then redistilled twice. The final distillation was carried out from permanganate in an all-glass apparatus with retention of a middle cut. Natural water samples were collected from inland surface waters in the southeastern United States. The natural waters used in photochemical experiments were sterilized by passage through 0.22-micron Millipore filters.

Benzene was acid-washed, dried, and distilled. Acetonitrile was purified following Mann's procedure,¹⁴ then distilled on a spinning-band column. Other reagent-grade solvents were used as received. Chemical Samples Co. 2,4-hexadien-1-ol and *cis*-1,3-pentadiene were distilled and stored at -20° to prevent oxidation. Singlet oxygen quenchers, β -carotene and 1,4-diazabicyclo-(2,2,2)-octane were obtained from Sigma Chemical Co. and Chemicals Procurement Laboratories, respectively. Valerophenone was purified by vacuum distillation.

ANALYTICAL PROCEDURES

Gas-liquid chromatography (glc) using flame or electron-capture detection was employed to analyze reaction mixtures in most cases. Liquid chromatography (lc) was used to analyze mixtures containing carbaryl¹⁵ and atrazine. Preparative lc on a Micropak SL-10 column with 5% methanol in dichloromethane as mobile phase was employed to separate malathion α - and β -monoacids. Valerophenone actinometers¹⁶ were analyzed by glc on glass columns containing 10% SILAR 5CP on Gas Chrom Q; methyl benzoate was employed as internal standard. Mixtures containing cis and trans 1,3-pentadiene were analyzed by glc on a 15-ft 20% 1,2,3-tris(2-cyanoethoxy)propane column.

APPARATUS

Glc analyses were performed on Tracor MT-220 and 550 gas chromatographs. Glc peaks were integrated by Autolab 6300 Digital Integrators. The liquid chromatograph was a DuPont Model 820 equipped with an ultraviolet (254 nm) photometric detector.

Kinetic studies of thermal reactions were carried out in a thermostated oil bath that regulated temperature within $\pm 0.05^\circ\text{C}$. Photolysis studies were conducted in a photochemical apparatus described in detail elsewhere¹⁷. A Hanovia 450 watt mercury lamp was the light source. Mass spectra were obtained on a Finnigan 1015 SL quadrupole mass spectrometer coupled with a Varian Aerograph Model 1532-B gas-liquid chromatograph and a Systems Industries 150 digital computer. Nuclear magnetic resonance (nmr) and infrared (ir) spectra were obtained, respectively, on a Varian HA-100 NMR Spectrometer and a Perkin Elmer 621 Grating Infrared Spectrophotometer. Carbon-13 magnetic resonance spectra were recorded on a JEOL-PFT-100 Spectrometer with the JEOL EC-100 20K data system. Ultraviolet-visible absorption spectra were obtained on a Perkin-Elmer model 602 Digital Spectrophotometer.

HYDROLYSIS PROCEDURES

Malathion

Kinetics--The following kinetic procedure based on extraction and glc analysis for the determination of the malathion disappearance rate constant is representative of the procedures used throughout these studies. A buffer solution (99 ml) of 0.008 M boric acid and 0.002 M sodium hydroxide was prepared. The flask was placed in a constant temperature bath at $27.00^\circ \pm 0.02^\circ$ and allowed to equilibrate. Then one ml of

a stock solution of 1.41×10^{-2} M malathion in acetonitrile was added to the buffer solution to give a 1.41×10^{-4} M malathion solution containing 1% acetonitrile. The pH of the solution was determined to be 8.56, employing a pH meter calibrated with standard buffer solutions.

A 5-ml aliquot was removed and the reaction quenched by extraction of the malathion with a 5-ml aliquot of chloroform containing 3,4,6,2',5' pentachlorobiphenyl (PCB) (2.79×10^{-4} M) as an internal standard. The time was recorded and taken as 0% reaction. Aliquots were withdrawn at various time intervals through approximately two malathion disappearance half-lives. At the end of ca 10 half-lives, an aliquot was withdrawn and used as an infinity point. Analysis of this infinity point showed that greater than 98% of the malathion had reacted. The concentration of malathion was determined for each aliquot based on PCB-malathion peak area ratios.

Pseudo-first-order rate constants were obtained using the integrated first-order rate equation where

$$k = \frac{1}{t} \ln \frac{C_o - C_{oo}}{C_t - C_{oo}} \quad (41)$$

and

C_o = malathion concentration at zero time

C_t = malathion concentration at time t

C_{oo} = malathion concentration after ten half-lives.

The rate constant was taken as the slope of the line obtained by a linear least squares analysis of the data. The second-order rate constant was obtained by dividing the pseudo-first-order rate constant by the hydroxide ion concentration.

Following the same procedure, kinetic runs were carried out at elevated temperatures in the constant temperature baths. The temperatures were $47.00^\circ \pm 0.02^\circ$ and $67.00^\circ \pm 0.05^\circ$. Kinetic data were obtained at $0.0 \pm 0.5^\circ$ using an ice bath.

Activation parameters were calculated from reaction rate constants obtained at two temperatures different by at least 20° .

Several kinetic studies dealt with the formation and disappearance of malathion acid products. In these studies, diphenylacetic acid was added to the reaction solution as an

internal standard. Aliquots were removed, acidified to pH 2 with 10% hydrochloric acid, and extracted with ether. The ether extracts were methylated with diazomethane. Malathion acid concentrations were then calculated based on the internal standard-malathion peak area ratios.

The rate constants for disappearance of malathion, (k_{md}), formation of malathion monoacids (k_{mh}), and O,O-dimethyl phosphorodithioic acid (k_{me}) were obtained by computer curve fitting techniques. Pseudo-first-order rate constants were assumed for formation of malathion acid and O,O-dimethyl phosphorodithioic acid. The following constraints were employed.

$$k_{md} = k_{mh} + k_{me} \quad (42)$$

where k_{mh} and k_{me} are > 0 .

The concentration of O,O-dimethyl phosphorodithioic acid [E] was obtained by

$$[E] = [M_0] - [A] - [M]$$

where

$[M_0]$ = initial malathion concentration

$[A]$ = monoacid concentration

$[M]$ = malathion concentration

The rate of disappearance of malathion and the rate of formation of products were obtained from the following three differential equations:

$$-\frac{d[M]}{dt} = k_{md}[M] \quad (44)$$

$$\frac{d[A]}{dt} = k_{mh}[M] \quad (45)$$

$$\frac{d[E]}{dt} = k_{me}[M] \quad (46)$$

Product Studies--Product studies were carried out at the end of one half-life. In general the solution (100 ml) was acidified to pH 2 with 10% hydrochloric acid and extracted with three 50-ml portions of ether. The organic fractions were combined, dried (Na_2SO_4), and concentrated. Thin-layer

chromatography was used for qualitative identification of malathion, malathion monoacids, malathion dicarboxylic acid, and O,O-dimethyl phosphorodithioic acid. Quantitative determinations were carried out by methylation (diazomethane) of the ethereal extract followed by glc analysis. Confirmation of products was obtained by glc-ms and nmr. The relative amounts of malathion α - and β -monoacid isomers were determined by lc. Nmr and glc analysis of the reaction mixture was used to verify the presence of diethyl fumarate, ethyl hydrogen fumarate, and thiomalic acid.

2,4-D

Kinetics--Hydrolysis of the methyl and n-butoxyethyl esters of 2,4-D were carried out in buffered aqueous solutions containing 0.1 to 1% acetonitrile. Starting ester concentrations were 10^{-5} M and the concentration of ester was followed through approximately two disappearance half-lives. At recorded time intervals, aliquots of the hydrolysis solution were extracted with an aliquot of benzene containing 10^{-5} M PCB as an internal standard. The concentration of ester at known times was determined by glc analysis from the peak area ratio of ester to the PCB standard.

Pseudo-first-order rate constants were obtained using the integrated form of the first-order rate equation. Second-order rate constants were obtained by dividing the pseudo-first-order rate constant by the hydroxide or hydrogen ion concentration.

Product Studies--Product studies were carried out after ten half-lives. The reaction solution was acidified to pH 2 and extracted with ether. The ethereal extraction was methylated (diazomethane) and analyzed by glc. In all kinetic runs 2,4-D was found as the product in greater than 98% of theoretical yield.

Methoxychlor

Acid degradation of methoxychlor was carried out at 1×10^{-7} M in distilled water or 1×10^{-6} M in 5% acetonitrile water. A 25-ml portion was titrated to the desired pH with hydrochloric acid. The acidified solution was placed in 5-ml ampoules. At given time intervals the ampoules were opened and the aqueous solution was extracted with benzene. The benzene extract was then analyzed by glc(ec) and the methoxychlor reaction determined by comparison with an ampoule which had been stored at -10° .

Basic degradation was carried out in a manner similar to acid degradation. A 25-ml portion of 1×10^{-7} M methoxychlor

in distilled water or 1×10^{-6} M methoxychlor in 5% acetonitrile-water was titrated to the desired pH with sodium hydroxide. The ampoules were opened, extracted with benzene, and analyzed by glc. Methoxychlor concentration was determined by comparison with an ampoule which was stored at -10° .

Elevated temperature studies were carried out by placing the ampoules in an oil bath at $45.00^{\circ} \pm 0.02^{\circ}$, $65.00^{\circ} \pm 0.02^{\circ}$, and $85.00^{\circ} \pm 0.05^{\circ}$.

Captan

Kinetics--The rate of disappearance of captan (1×10^{-5} M) was followed by a glc method. Reactions were carried out under buffered reaction conditions in water containing 0.3 to 1% acetonitrile. pH's were determined with a pH meter which was calibrated with standard buffer solutions. Solutions were thermostated in a constant temperature bath at $27.00^{\circ} \pm 0.02^{\circ}$, $37.00^{\circ} \pm 0.02^{\circ}$, and $8.0^{\circ} \pm 0.5^{\circ}$. Five-ml aliquots were withdrawn at recorded time intervals and the reaction quenched by extraction with 5 ml of benzene.

Pseudo-first-order rate constants were determined employing the integrated form of the first-order rate expression.

Product Studies--Product studies were carried out at 27° at the end of one and ten half-lives. Organic compounds were tentatively identified by glc and confirmed by gc-ms and ir.

Chloride ion was confirmed by first extracting the ten half-lives reaction solution with benzene and treating the aqueous layer with silver nitrate. The change in hydrogen ion concentration was determined by use of a pH meter. Sulfur was qualitatively confirmed as a product by solid probe ms.

Carbaryl

Kinetics--The rate of alkaline hydrolysis of carbaryl under buffered conditions was determined by an lc technique. Carbaryl (100 ml), 2×10^{-4} M in water, was buffered at pH 9.42 (boric acid-sodium hydroxide). Aliquots were withdrawn at recorded times and the reaction quenched by making the solution slightly acidic with 10% HCl. Aliquots of the aqueous reaction solution were then analyzed directly by lc. The concentration of carbaryl was determined by comparison with a standard based on peak height. Dilution of a standard solution showed the lc response to be linear over the concentration ranges used in the studies. Rate constants were obtained as described above.

Product Studies--Based on lc and glc retention times, α -naphthol was identified as a product of hydrolysis. Lc analysis at one half-life and ten half-lives showed α -naphthol to be formed in 48 and 98% yield, respectively.

Atrazine

Kinetics--Atrazine hydrolysis was carried out using the general technique described for malathion. A 2×10^{-4} M solution of atrazine in water was made by stirring the calculated amount of atrazine in water for 24 hours. The atrazine solution was then adjusted to the desired pH with 10% HCl or 1 M NaOH as determined by a pH meter. The solution was hydrolyzed at $25.00^\circ \pm 0.02^\circ$ and three aliquots removed at recorded time intervals, extracted with chloroform and the atrazine concentration determined by glc analysis.

The rate constants were determined by calculating the half-life from a plot of log concentrations vs time. The pseudo-first-order rate constants were obtained from the relationship

$$k_{\text{obsd}} = \frac{0.693}{t_{1/2}} \quad (47)$$

Product Studies--Hydroxyatrazine was identified as a product of both acid and alkaline degradation based on comparison of lc retention times with an authentic sample.

Diazinon

The hydrolysis rate of diazinon in 5% acetonitrile-water was determined by the glc method. Alkaline and acid studies were carried out at 0.0900 M NaOH and 0.002 M HCl, respectively, with 3.8×10^{-4} M diazinon at $25.00^\circ \pm 0.02^\circ$. Aliquots were removed at recorded times and extracted with chloroform. Diazinon concentrations were determined by comparison with standards.

Pseudo-first-order rate constants were determined from half-life values which were obtained from plots of log concentration vs time.

Parathion

Parathion hydrolysis was not investigated. Faust¹⁸ has reported kinetic data for the hydrolysis of this compound over a wide pH range at 20° .

Toxaphene

A 100-ml stock solution of 1.3 ppm toxaphene in 5% acetonitrile-water was prepared. A portion of this solution was titrated to pH 3.7 with 10% HCl. Aliquots were sealed in ampoules and placed in an oil bath at 65°. At recorded times, ampoules were removed, opened, and the aqueous solution was extracted with chloroform. The amount of degradation was determined by comparison of the gas chromatographic fingerprints with a standard.

The alkaline degradation studies were carried out in a similar manner at pH 10.0.

OXIDATION PROCEDURES

Malathion

Aliquots of a 3.06×10^{-4} M solution of malathion in water buffered at pH 5.25 (phosphate buffer system) were placed in ampoules. The solutions were saturated with oxygen, the ampoules sealed, and placed in the constant temperature bath for recorded time intervals.

Sample analysis was similar to that described for hydrolysis products.

2,4-D

Oxidation studies were carried out in air-saturated water solutions and in one study, hydrogen peroxide (1×10^{-3} M) was added as an oxidant. A standard solution of 2,4-D (2×10^{-4} M in water) was used throughout the study. Aliquots were allowed to react in sealed ampoules as described above.

The solutions were analyzed directly by glc.

Methoxychlor

A solution of methoxychlor (1×10^{-7} M) in water was employed as a stock solution. Aliquots were saturated with oxygen, sealed in ampoules, and placed in a thermostated bath at $47^\circ \pm 2^\circ$, $67^\circ \pm 2^\circ$, and $87^\circ \pm 2^\circ$. One ampoule beside the bath served as a standard. Ampoules were removed at given time intervals and stored at -20° . At the end of the run, the ampoules were opened, extracted with benzene and the concentration of methoxychlor determined by glc analysis.

Studies involving hydrogen peroxide as a reactant were carried out as described above.

Product studies were carried out at 1×10^{-4} M methoxy-chlor in 30% 1-propanol-water solution. The products were analyzed by glc.

PHOTOLYSIS PROCEDURES

General

Screening studies were conducted by irradiating in parallel 13.0 mm Pyrex tubes containing 2.80 ml of saturated aqueous solutions of the pesticides. The tubes transmitted only wavelengths > 280 nm. First-order rate constants were obtained from logarithmic plots of pesticide concentration vs time.

Quantum yield studies were conducted by parallel irradiation of pesticide and actinometer solutions using filtered light from the mercury lamp. Filter solutions (1.0-cm thick) were as follows: 313 nm - 0.001 potassium chromate in 3% aqueous potassium carbonate; 436 nm - 40 g cupric sulfate, 68 ml concentrated ammonium hydroxide, and 500 g sodium nitrite in one liter of water; 578 nm - 50 g cupric chloride (hydrated), 150 g anhydrous calcium chloride and 150 g potassium dichromate in 500 ml water acidified by hydrochloric acid. Valerophenone¹⁹, 1-phenyl-4-methyl-1,2-pentanedione²⁰, and ferrioxalate²¹ actinometers were used respectively for 313, 436, 578 nm light. Quantum yields for dilute solutions of pesticides were calculated from slopes of first-order plots of pesticide concentration vs time in seconds. For weakly absorbing systems (absorbance < 0.02), the slope is equal to $k_a\phi$ where k_a is the specific absorption rate and ϕ is the quantum yield. The value of k_a was calculated according to eq. 48

$$k_a = 2.303 \epsilon_\lambda I_\lambda \ell \quad (48)$$

where ϵ_λ is the molar extinction coefficient of the pesticide at wavelength λ , I_λ is a constant expressed as einsteins liter⁻¹ sec⁻¹, and ℓ is the effective cell path length in cm. I_λ is equal to $I_0 S/V$ where I_0 is the incident light intensity (einsteins cm² sec⁻¹) at wavelength λ , S is the surface area exposed to light, and V is the cell volume. The value of I_λ was measured directly by actinometers that absorbed all the light. Generally, we assumed that ϵ_λ in water was the same as that measured in acetonitrile-water. The value of ℓ was determined as described below.

Determination of Cell Path Length for Quantum Yield Studies

A series of solutions containing 0.122 M cis-1,3-pentadiene and 0.0012 to 0.05 M benzophenone in benzene were prepared. Equal volumes (2.80 ml) of the solutions in 13.0 mm tubes were degassed under high vacuum by several freeze-thaw cycles. The solutions were then exposed to equal amounts of 313 nm light by parallel irradiation in the photochemical apparatus. The percentage of trans-1,3-pentadiene formed by the photosensitized isomerization²² was determined by glc analysis of the solution. These percentages were then corrected for back reactions of the trans to cis-diene as described by Lamola and Hammond²². The cell path length was determined from the slope of a plot of $-\log(1 - X)$ versus ϵC for the various solutions (Figure 12), where X is the ratio of trans isomer formed at benzophenone concentration C to trans isomer formed in the 0.050M benzophenone solution (percent absorbed > 99), and ϵ is the extinction coefficient of benzophenone at 313 nm. Least squares analysis of the data indicated that the cell path length was 10.0 ± 0.2 mm.

Kinetic Studies under Sunlight

Air-saturated, aqueous solutions of the pesticides were exposed to sunlight in tightly stoppered quartz tubes that were suspended six inches above a black cloth parallel to the earth's surface. Generally experiments were carried out during the summer months of June through September. Dark controls (tubes wrapped in aluminum foil) were also used in all experiment. In most cases, no change in concentration of pesticide occurred in the dark controls during the experiments.

Photochemical Studies in Natural Waters

Saturated solutions of the pesticides in filter-sterilized natural waters were photolyzed in the laboratory or under sunlight as described above. Generally, solutions of pesticide in distilled water were simultaneously irradiated for comparison. Dark controls were also used in these experiments.

Singlet Oxygen Studies

Singlet oxygen was generated photochemically using methylene blue as photosensitizer. Air- or oxygen-saturated solutions containing pesticide and methylene blue (MB) (10^{-5} to 10^{-4} M) were irradiated by 436 nm or 578 nm light. Under these conditions singlet ($^1\Delta_g$) oxygen is generated with a quantum yield near unity²³. Acetonitrile and water were used as solvents for these experiment. Prolonged irradiation of

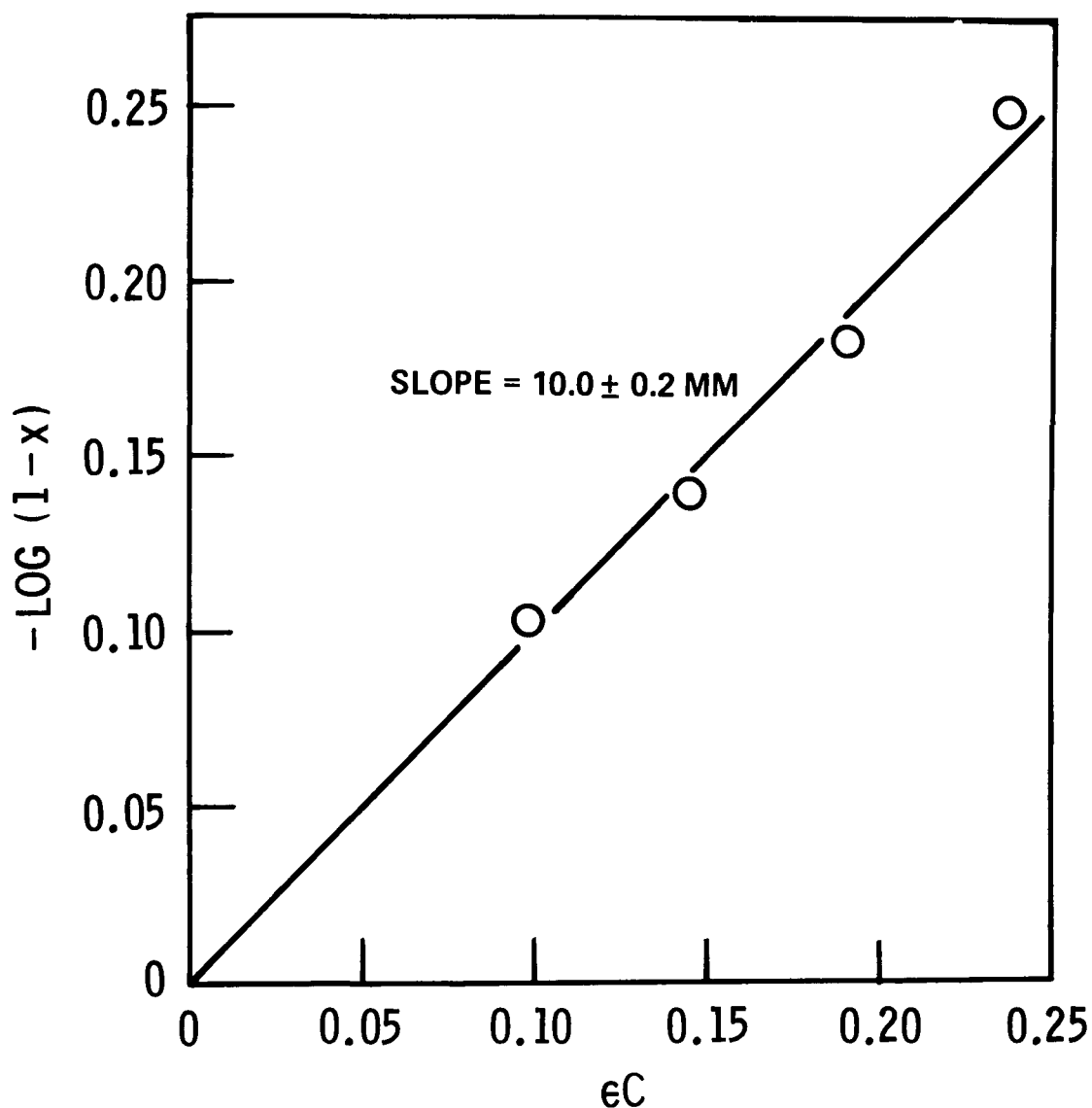


Figure 12. Determination of cell pathlength for quantum yield studies

most of the pesticides resulted in no detectable reaction. Captan and its hydrolysis product, 4-cyclohexene-1,2-dicarboximide, were notable exceptions and more detailed studies of their reaction with singlet oxygen were carried out. The photoreactions of captan and the imide were almost completely inhibited by 1.00×10^{-3} M, 1,4-diazabicyclooctane (DABCO), a singlet oxygen quencher. The concentration dependence of the reaction was determined by irradiating in parallel a series of solutions containing 1.0×10^{-4} MB and varying amounts of captan or imide.

Photolysis Product Studies

The same general procedure was followed for all the pesticides. For direct photolysis product studies, the pesticide solutions (4 l) were irradiated by Pyrex filtered light from a mercury lamp until glc analysis indicated about 30% reaction had occurred. The irradiated solutions were extracted by three portions of 10% ether-chloroform (portion = 100 ml per liter of solution). The combined organic extracts were dried by anhydrous sodium sulfate, then concentrated to one ml. The product mixtures were then characterized by glc-ms or by infrared spectroscopy after isolation of the products by preparative glc or lc. Singlet oxygen products from captan or imide were characterized by glc-ms after reduction of the hydroperoxides to alcohols.

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SECTION VII

PHOTOCHEMICAL SCREENING STUDIES

To obtain a preliminary estimate of the relative direct photolysis rates of the pesticides, aqueous solutions were photolyzed in Pyrex reaction cells using a medium-pressure mercury lamp. The short wavelength cutoff for the cells (1 mm wall thickness) was about 280 nm. The effective cutoff for sunlight is close to 297 nm. For most of the pesticides studied, the most effective portion of the light was in the 280-305 nm range; irradiation through a 4-mm thick Pyrex filter (cutoff 300 nm) generally caused only extremely slow photoreaction (notable exceptions were parathion and carbaryl).

Rate constants for the pesticide photolyses were determined from the slopes of first-order plots. In each experiment, the ultraviolet light intensity was determined using a chemical actinometer that strongly absorbed only light of wavelengths < 300 nm; *i.e.*, the butoxyethyl ester of 2,4-D in hexane (10^{-3} M). Relative photolysis rates, normalized to a uniform light intensity, are summarized in Table 5. The light intensity from the mercury lamp, after Pyrex filtration, was found to be about 80 times more intense than midday sunlight¹⁰ in the 280-300 nm range (lat. 30°N, summer). Accordingly, the experimental rate constants were divided by this factor to give the normalized half-lives in Table 5. This procedure gives only a crude estimate of the sunlight photolysis half-lives because the spectral distribution of the Pyrex-filtered light from the mercury lamp differs from that of sunlight. The half-lives of pesticides such as parathion and carbaryl, that absorb strongly at wavelengths > 320 nm, are shorter than indicated in the table. The lamp intensity was found to be only eight times greater than sunlight in the 280-370 nm range. On the other hand, the direct photolysis half-life of methoxychlor is much longer than that indicated by the screening procedure. The intensity of Pyrex (1 mm) filtered UV light from the mercury lamp is much higher at wavelengths < 295 nm than that of sunlight. Since methoxychlor absorbs strongly from 280 to 290 nm, but absorbs very weakly at wavelengths > 295 nm, the screening procedure gave a false indication of its photoreactivity under sunlight.

We conclude that the screening studies can be a useful tool for determining those pesticides that are not likely to react efficiently under sunlight. However, if Pyrex-filtered light efficiently degrades a pesticide, more detailed studies

should be carried out to ascertain its direct photolysis rate under sunlight.

The data in Table 5 indicated that methoxychlor, carbaryl, and the butoxyethyl ester of 2,4-D were the most photoreactive compounds. Accordingly, more detailed direct photolysis studies of these three pesticides were carried out.

Table 5. RELATIVE DIRECT PHOTOLYSIS RATES OF SELECTED PESTICIDES IN SCREENING STUDY

Pesticide	Relative Rate	Normalized Photolysis Half-life (Hrs) ^a
Atrazine	8	3×10^3
Captan	< 10	$> 2 \times 10^3$
Carbaryl	100	2×10^2
Diazinon	16	1×10^3
2,4-D BEE ^b	300	1×10^2
Malathion	1	2×10^4
Methoxychlor	800	3×10^1
Parathion	10	2×10^3
Toxaphene	< 1 ^c	$> 2 \times 10^4$

^aCalculated for a light intensity of 3×10^{13} photons $\text{cm}^{-2} \text{sec}^{-1}$ from 280 to 300 nm.

^bButoxyethyl ester of 2,4-D.

^cNo change in flc profile during period of exposure.

SECTION VIII

RESULTS & DISCUSSION: MALATHION

HYDROLYSIS

Data pertaining to the breakdown of malathion in the aquatic environment are not generally available. Paris *et al.*¹ isolated a heterogeneous bacterial population capable of utilizing malathion as a carbon source. At low concentrations of malathion and bacteria, the rate of bacterial degradation was described mathematically by a second-order rate expression. The major metabolite was malathion β -monoacid.

There are several potential pathways by which malathion may be chemically degraded under reaction conditions common to the aquatic environment (Figure 13). Carbon-sulfur cleavage proceeding through an elimination reaction would give O,O-dimethyl phosphorodithioic acid and diethyl fumarate as products. Phosphorus-sulfur bond cleavage would give diethyl thiomalate and O,O-dimethyl phosphorothionic acid. However, O,O-dimethyl phosphorothionic acid would be in equilibrium with its tautomer O,O-dimethyl phosphorothiolic acid. Carbon-oxygen bond cleavage by carboxyl ester hydrolysis would result in two possible products, malathion α - and β -monoacids. Continued carboxyl ester hydrolysis would result in malathion dicarboxylic acid formation. Another possible reaction would be oxidation of the phosphorus-sulfur double bond to a phosphorus-oxygen double bond to give malaaxon.

Muhlmann and Schrader² reported that malathion underwent acid breakdown to give diethyl thiomalate and O,O-dimethyl phosphorothionic acid. Cowart *et al.*³ studied the rates of hydrolysis of seven organophosphorus pesticides (pH about 6) and reported a half-life for malathion of about one week. Ruzicka *et al.*⁴ found malathion had a half-life of 7-8 hours (20% ethanol-water, pH = 6 at 70°C); on the other hand, Goldberg *et al.*⁵ reported that malathion did not undergo reaction under either alkaline or acidic conditions.

Synthesis and characterization of potential degradation products and detailed kinetic studies are reported in this section.

A synthetic scheme was needed to selectively synthesize each malathion monoacid. Chen *et al.*⁶ reported that O,O-dimethyl phosphorodithiodic acid reacted with ethyl hydrogen maleate to produce an oil, which, based on proton nmr

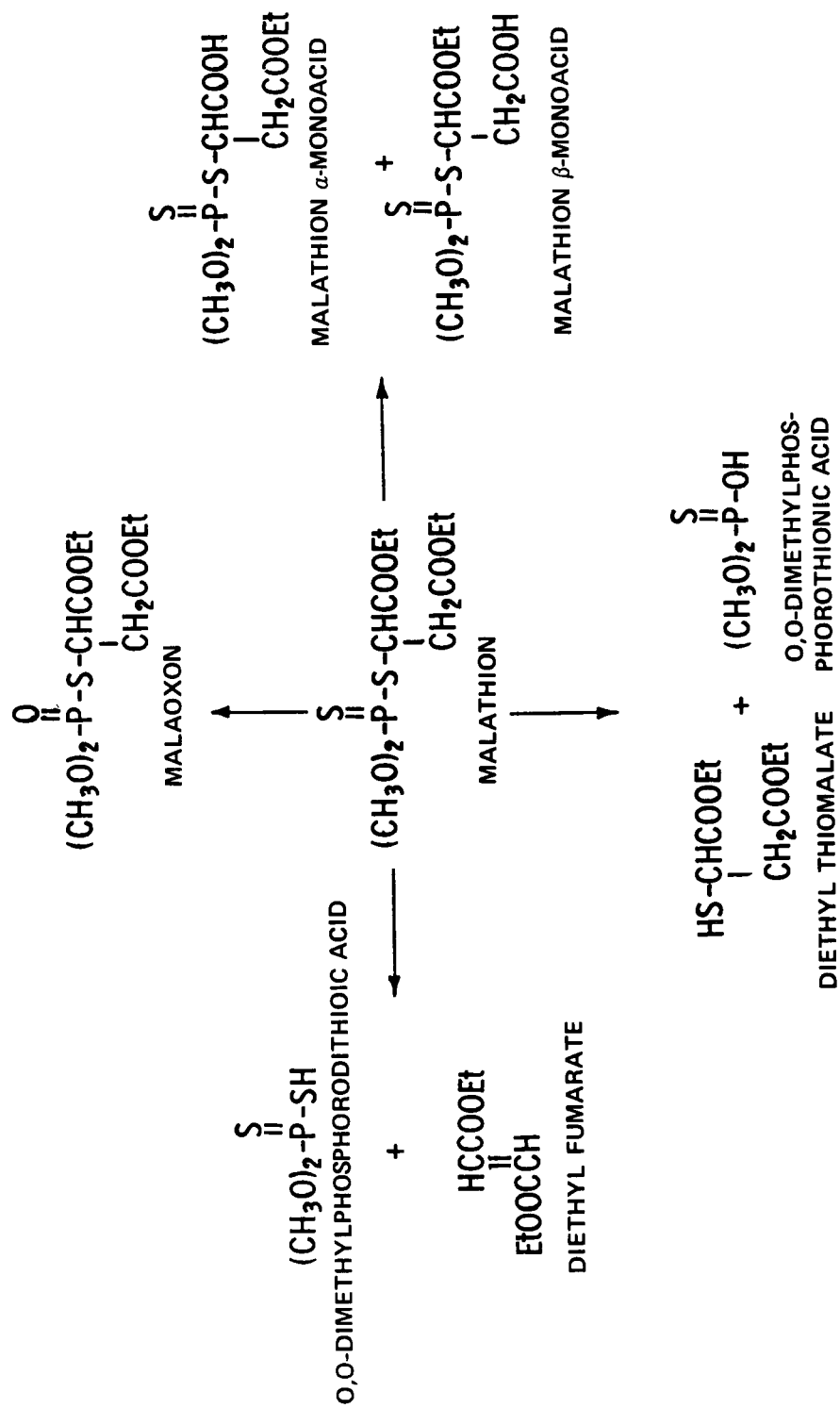


Figure 13. Potential chemical pathways for malathion degradation

analysis, was believed to be a single monoacid. Based on the chemical shifts of the methylene groups, they designated this product as the β -monoacid. Following a modified procedure (Figure 14), the reaction gave an oil which based on lc analysis consisted of the β -monoacid (97%) and the α -monoacid (3%).

The predominance of β -monoacid formation is consistent with an ionic mechanism in which O,O-dimethyl phosphorodithioic acid undergoes acid-catalyzed nucleophilic addition to the carbon-carbon double bond. This addition pathway is favored in preference to electrophilic addition because of deactivation of the carbon-carbon double bond by the carboxy and carbethoxy groups.

The α -monoacid was obtained by carrying out the addition reaction in the presence of a free radical source. Bacon and LeSuer⁷ reported that O,O-dimethyl phosphorodithioic acid in the presence of peroxides added to alkenes in an anti-Markovnikov addition. In the absence of peroxides, normal Markovnikov addition was observed. Huang⁸ found that under homolytic addition reaction conditions, the trichloromethyl radical added to the carbethoxy group of ethyl hydrogen maleate. 1',1',1'-triphenylbenzeneazomethane (PAT) was employed as a free radical initiator. The reaction was carried out in a non-polar organic solvent at 0° and the free radicals were generated by irradiation of PAT with Pyrex-filtered light (Figure 14). Liquid chromatographic analysis showed the product mixture to consist of the α -monoacid (95%)

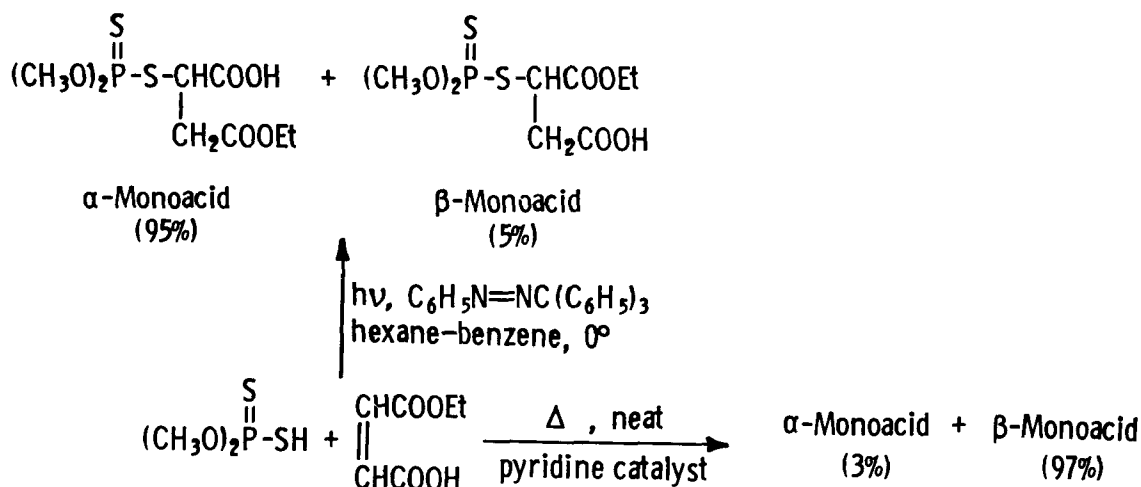


Figure 14. Scheme for synthesis of malathion monoacids

and the β -monoacid (5%) (Figure 15). The isomer distribution is sensitive to reaction conditions. The maximum relative selectivity for the β -isomer was 95%.

Malathion diacid [O,O-dimethyl S-(1,2-dicarboxy)ethyl phosphorodithioate] was expected to be of value in making the ^{13}C nmr assignments in the monoacids⁹; addition of water to the anhydride give the diacid (Figure 16). Addition of one equivalent of ethanol instead of water to the intermediate

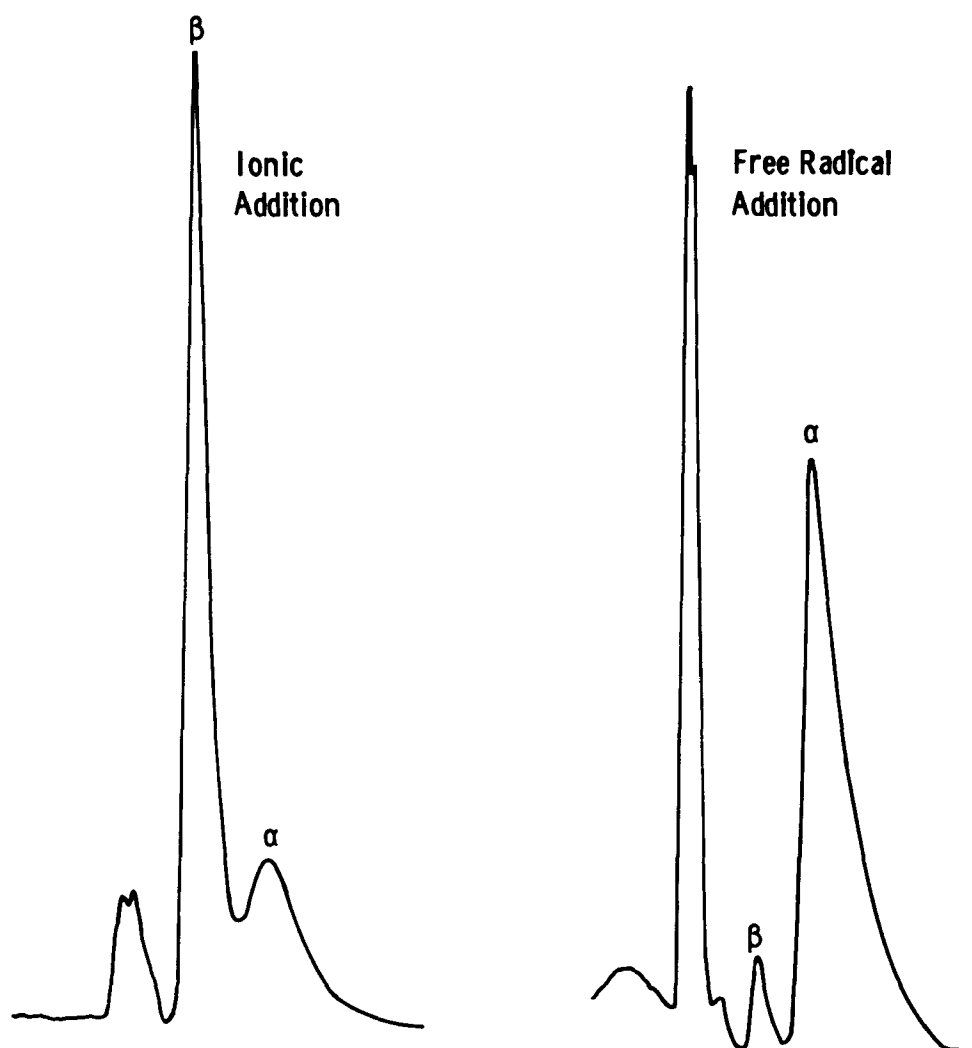


Figure 15. Liquid chromatograms showing the relative amounts of malathion monoacids formed in synthesis

anhydride yielded a mixture of α - and β -monoacids. No attempt was made to separate the mixture.

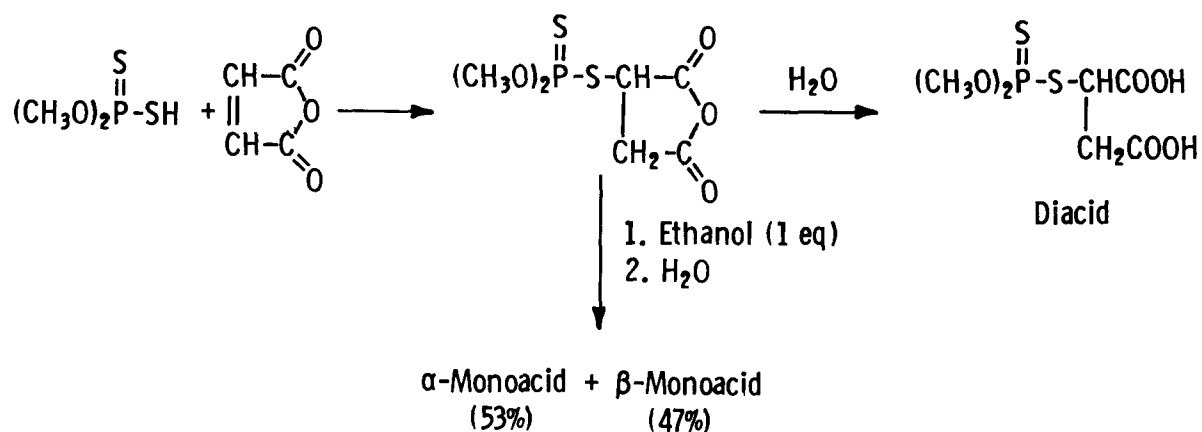


Figure 16. Scheme for synthesis of malathion diacid and monoacids

Malaoxon and its derivatives were obtained by oxidation of the corresponding malathion compound. Both malaoxon and the β -malaoxon monoacid were readily obtained by oxidation with bromine in aqueous ethanol¹⁰ (Figure 17).

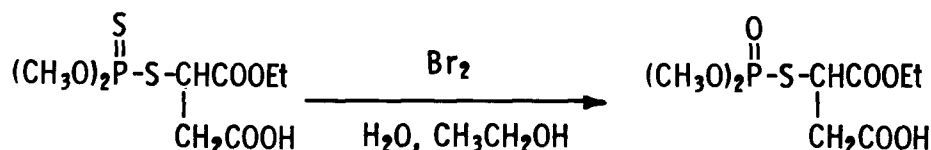


Figure 17. Synthesis of malaoxon monoacid

The carbon-13 chemical shifts and carbon-phosphorus coupling constants obtained for malathion and several related compounds are given in Table 6. Representative spectra are reproduced in Figures 18 and 19. The proton noise-decoupled spectrum of malathion exhibits nine carbon resonances as expected. Assignment of these peaks to the carbons of malathion was made from comparison with the spectra of the related compounds in Table 6, off-resonance proton coupling, and from expected trends in the chemical shifts and phosphorus-carbon coupling constants.

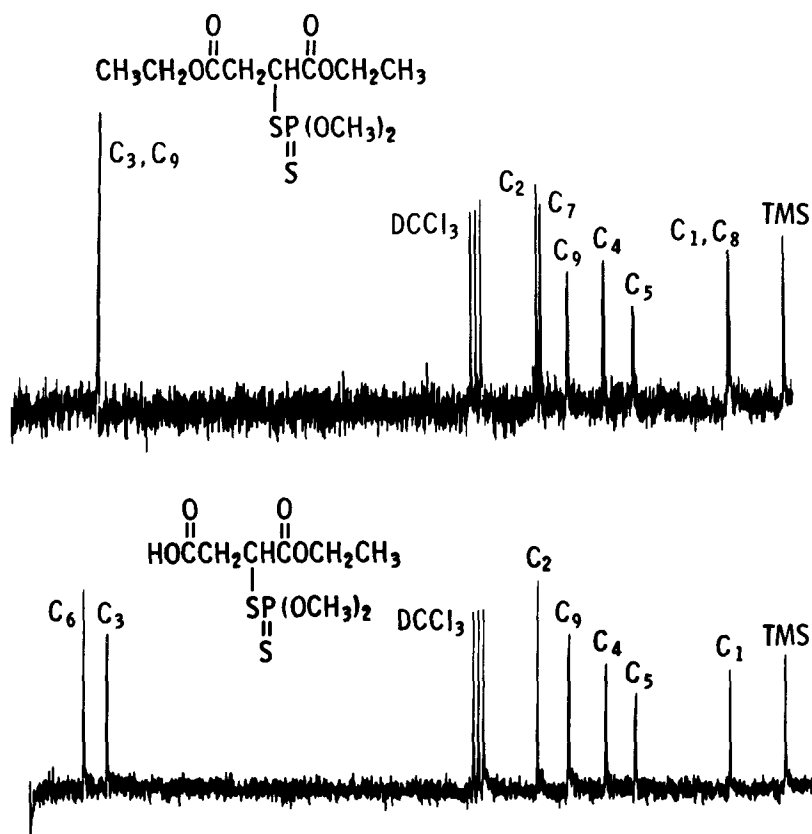


Figure 18. Carbon-13 spectra of malathion and malathion β -monoacid

Considerations similar to those above were used to assign the carbons in the carbon-13 spectrum of malaoxon and establish that the monoacid obtained from the chemical hydrolysis of malaoxon is the β -isomer (Figure 19).

The stability of malathion in water at acidic pH's was investigated. It was found that malathion was stable in water at pH 2.5 and 25°C for up to ten days. Therefore the kinetic studies were carried out at elevated temperatures (67° and 87°). The extrapolated second-order rate constant (k_{aex}) is $(4.8 \pm 0.2) \times 10^{-5} \text{ M}^{-1} \text{ sec}^{-1}$ at 27° (Table 7).

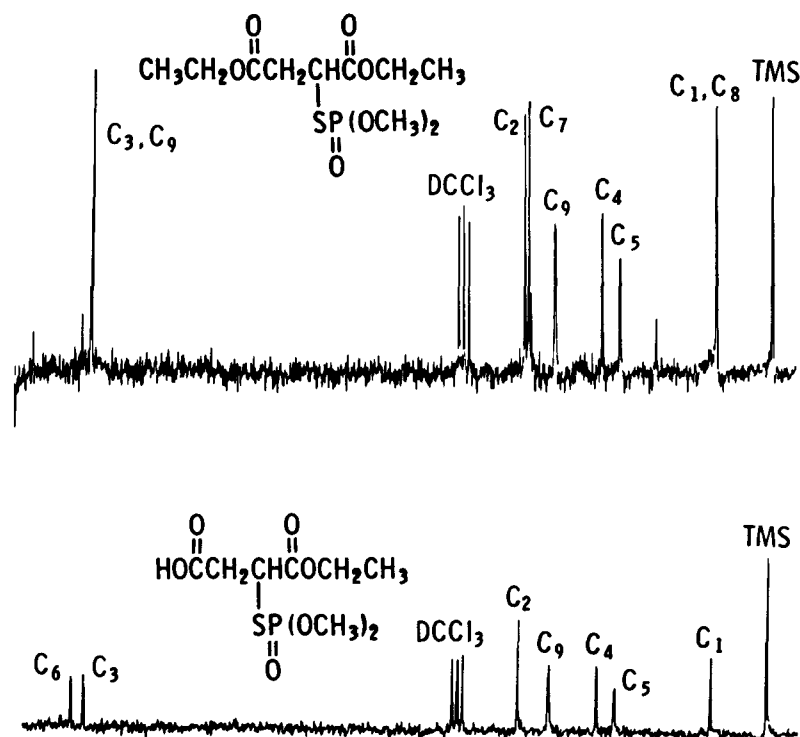


Figure 19. Carbon-13 spectra of malaoxon and malaoxon β -monoacid

Table 7. MALATHION ACID-CATALYZED DEGRADATION KINETIC DATA

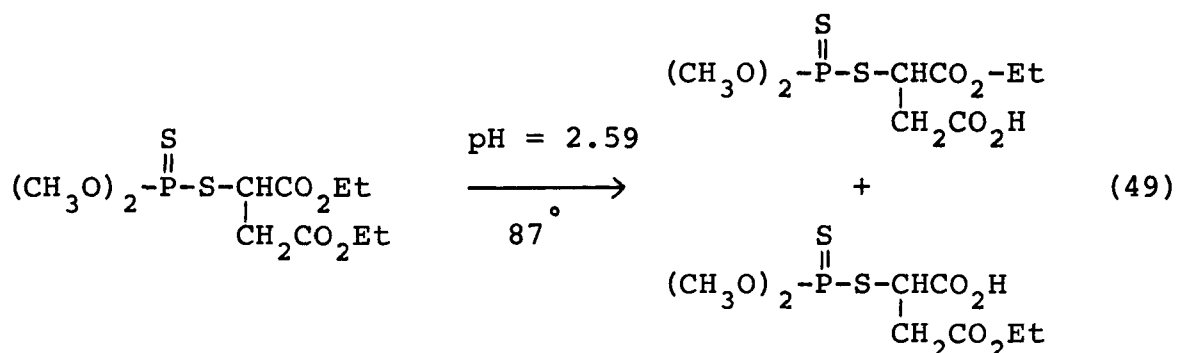
Temp ($^{\circ}\text{C}$)	k $\text{M}^{-1} \text{sec}^{-1}$	ΔH^{\ddagger} kcal/mole	ΔS^{\ddagger} eu
87	$(2.88 \pm 0.01) \times 10^{-2}$		
67	$(4.36 \pm 0.04) \times 10^{-2}$	22.3 ± 0.1	-4.1 ± 0.4
27 ^a	$(4.8 \pm 0.20) \times 10^{-5}$		

^aExtrapolated rate constant.

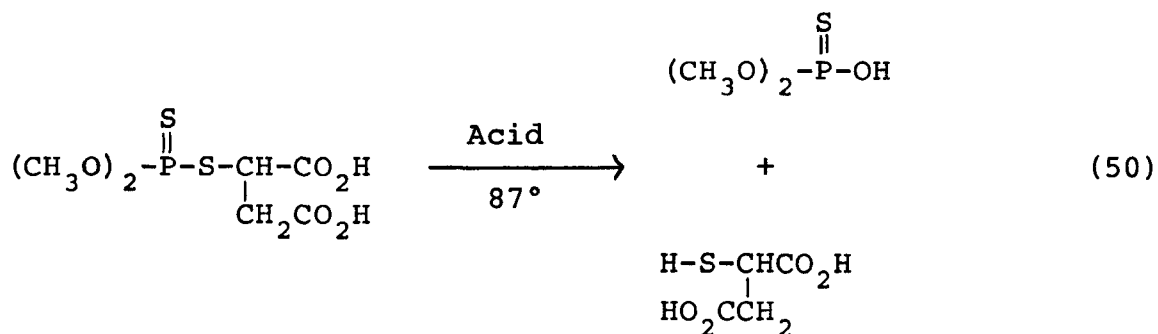
Based on the extrapolated rate constant, the reaction of malathion with hydrogen ion would have a half-life greater than one year at pH 4. At temperatures and pH's common to the

aquatic environment, this degradative pathway would be too slow to be significant.

Product studies, carried out at the end of one malathion degradation half-life at 87°, indicated that the malathion monoacids formed in 48% yield (eq. 49). No malathion diacid was found although it was an anticipated product at longer reaction times.



The diacid was subjected to similar reaction conditions. Although the analysis was not carried out quantitatively, glc-ms analysis showed the presence of methyl O,O-dimethylphosphorothionate and dimethyl thiomalate. Thus, malathion diacid undergoes phosphorus-sulfur cleavage to give O,O-dimethyl phosphorothionic acid and thiomalic acid (eq. 50).



This reaction sequence is consistent with the results reported by Muhlmann and Schrader² who found malathion breakdown products in aqueous ethanol solvent at elevated temperatures to be O,O-dimethyl phosphorothionic acid and diethyl thiomalate. Under their reaction conditions, however, they would not have found malathion monoacids.

The kinetics of alkaline malathion degradation and the resulting products were also investigated. Malathion is more susceptible to basic degradation and significant chemical breakdown would be anticipated under certain environmental conditions. Temperature and in some cases chemical species common to aquatic ecosystems might be expected to influence malathion persistence.

The malathion second-order disappearance rate constant for alkaline degradation (k_{md}) is $5.5 \pm 0.3 \text{ M}^{-1} \text{ sec}^{-1}$ at 27° (Table 8). Based on this rate constant, malathion would have a 36-hour half-life in water at pH 8 and 27°. As anticipated, an increase in temperature results in a decrease in malathion half-life. At pH 8 and 40° the half-life is about one hour, while at 0° (pH 8) the half-life is about twelve days. At lower temperatures found in the environment, although somewhat slower, malathion alkaline degradation could still be significant.

Table 8. TEMPERATURE EFFECT ON THE MALATHION ALKALINE DEGRADATION RATE CONSTANT

Temp. (°C)	$k_{md} \text{ M}^{-1} \text{ sec}^{-1} \text{ }^a$
0	0.067 ± 0.003
27	5.5 ± 0.3
47	47 ± 1
67	730 ± 20

^aMalathion disappearance rate constants.

Product studies were carried out (glc) after one malathion half-life. Based on initial malathion concentration, the products were malathion (50%), malathion monoacid (15%), diethyl fumarate and ethyl hydrogen fumarate (35%), and O,O-dimethyl phosphorodithioic acid. These products show that at 27° malathion is undergoing two competing reactions (Figure 20).

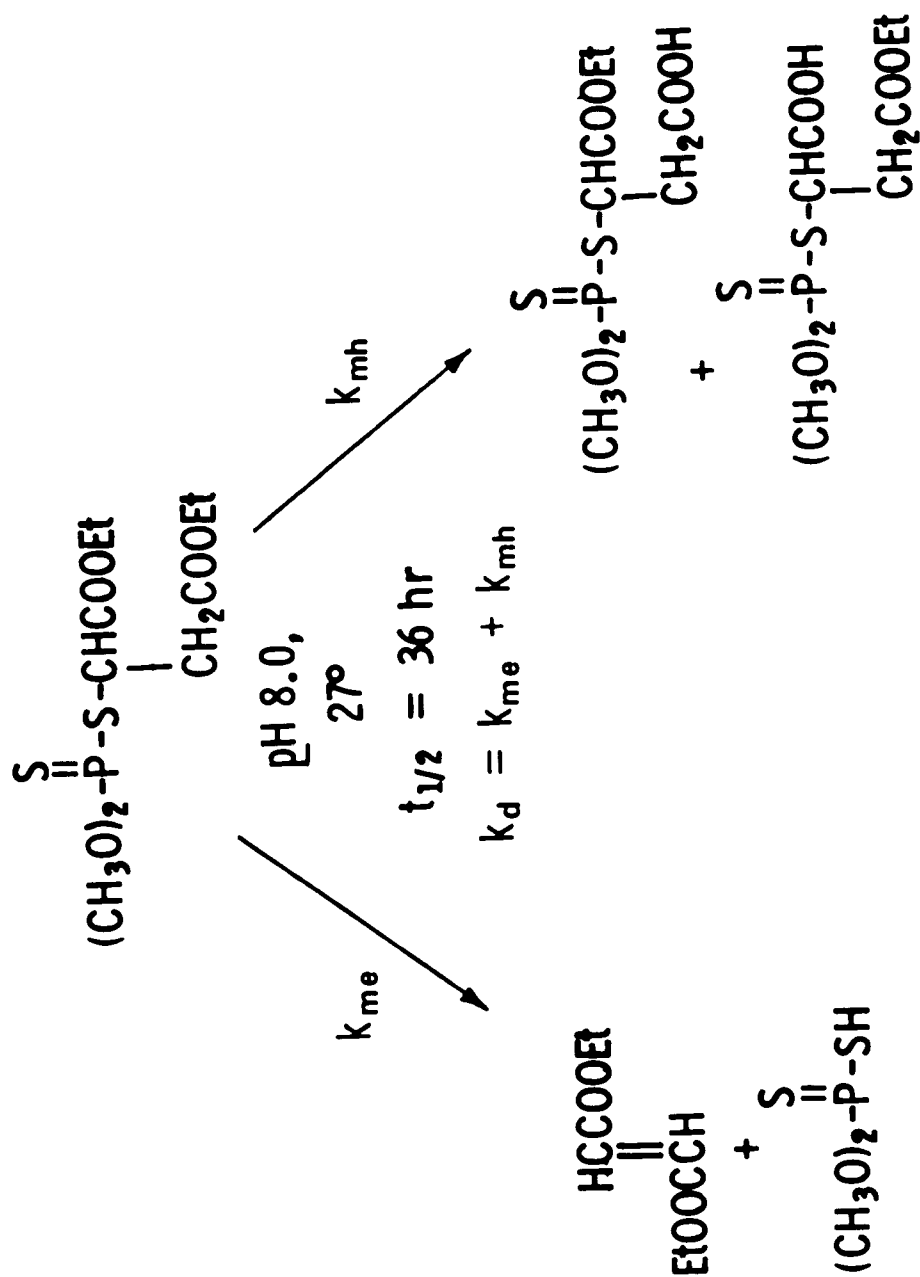


Figure 20. Alkaline degradation of malathion

The build-up of the products at 27°C as a function of time is shown in Figure 21.

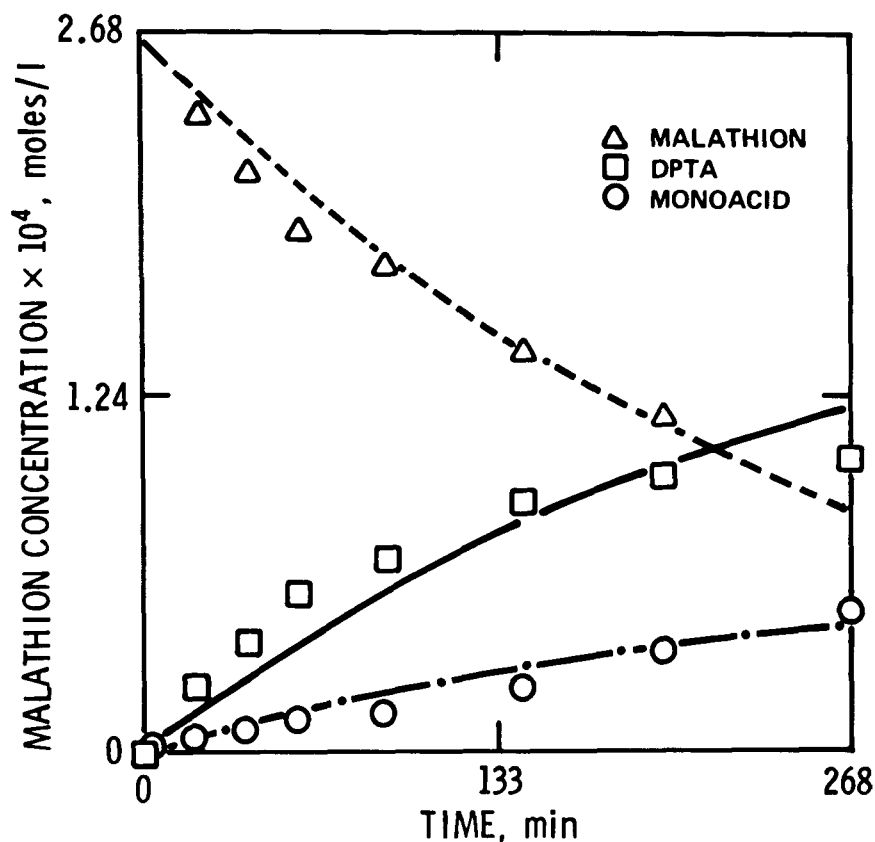


Figure 21. Malathion disappearance and product formation at 27°C

A temperature effect on product formation became evident when products were investigated at other temperatures. At 47° after one half-life, analysis showed approximately 5% malathion monoacid, at 67° there was a trace of monoacid detected, and at 0° (Figure 22) the monoacid product is important. It is apparent that carboxyl ester hydrolysis is favored at lower temperatures and elimination is favored at elevated temperatures (compare Figures 21 and 22).

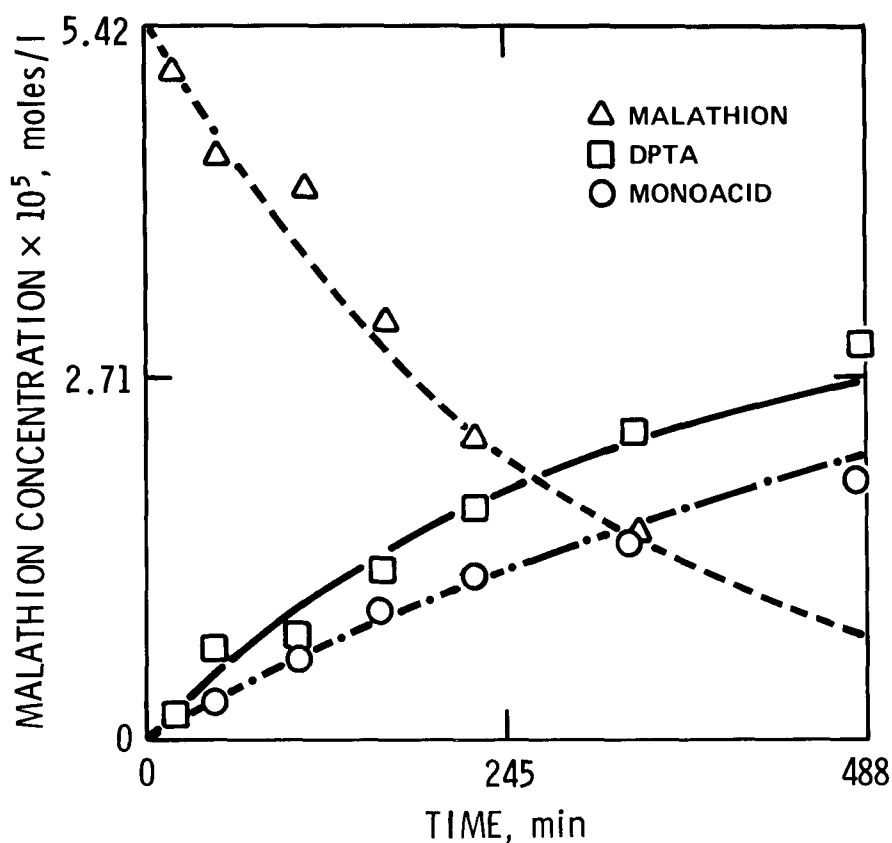


Figure 22. Malathion disappearance and product formation at 0°C

Second-order rate constants for elimination and carboxyl ester hydrolysis at 27° and 0° were obtained by following malathion disappearance and monoacid formation. Table 9 contains the rate data for the individual competing reactions along with the activation parameters for the reactions. The rate constant for elimination (k_{me}) is $3.9 \pm 0.2 \text{ M}^{-1} \text{ sec}^{-1}$ and for carboxyl ester hydrolysis (k_{mh}) $1.4 \pm 0.1 \text{ M}^{-1} \text{ sec}^{-1}$ at 27°. Based on these rate constants malathion is undergoing 74% elimination and 26% ester hydrolysis at this temperature.

The effects of pH and temperature on degradation rate are shown in Figure 23 where malathion half-life is plotted as a function of pH at various temperatures. This figure shows that malathion has a maximum half-life at pH 4.

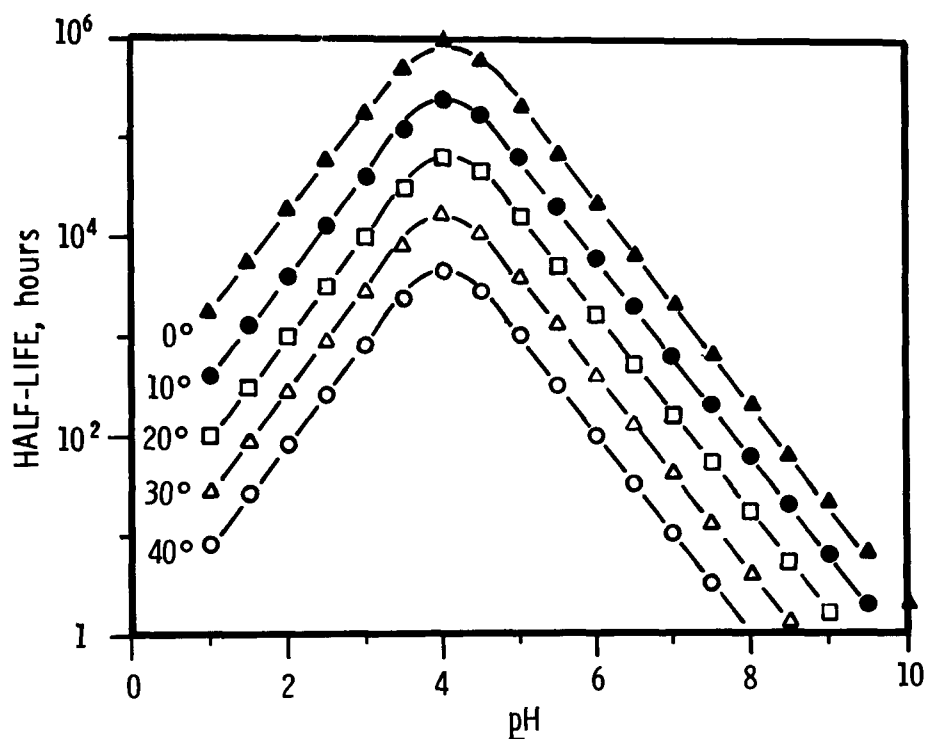


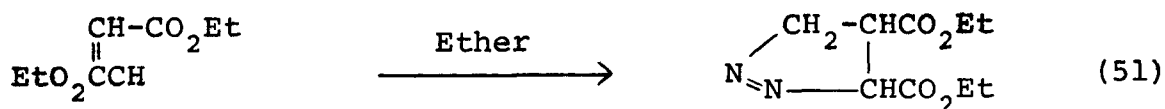
Figure 23. Temperature effect on malathion degradation at several pH values

Table 9. RATE CONSTANTS FOR MALATHION ELIMINATION AND CARBOXYL ESTER HYDROLYSIS REACTIONS

Reaction	Temp. °C	k M ⁻¹ sec ⁻¹	ΔH^\ddagger kcal/mole	ΔS^\ddagger eu
Elim (k_{me})	0	4.0×10^{-2}		
	27	3.9×0.2	27.8	-2.8
	47	4.1×10^1		
	67	6.6×10^2		
Ester (k_{mh})	0	2.5×10^{-2}		
	27	1.4×0.1	20.7	-2.9
	47	6.7		
	67	6.8×10^1		

There are two possible malathion monoacids which can result from malathion carboxyl ester hydrolysis. Qualitative determination of both isomers was made using thin-layer chromatography (tlc).¹¹ An estimate of the relative amounts of each isomer present at the end of one malathion reaction half-life was obtained by liquid chromatographic (lc) analysis. The relative percentages were α -monoacid, 85%, and β -monoacid, 15%. Paris *et al.*¹ reported that microbial degradation of malathion gave the β -monoacid as the major product (99%).

Analysis of the monoacid required methylation prior to gas chromatography. However, it should be noted that it was necessary to analyze (glc) for diethyl fumarate prior to methylation with diazomethane. This is because diazomethane reacts with the carbon-carbon double bond to form a pyrolazine (eq. 51) which was not detected under the glc condition employed.



To determine if this laboratory data could be extrapolated to natural waters, the malathion half-life was determined in a natural water sample obtained from a South Georgia river, the Withlacoochee River (pH 8.21). The half-life predicted from laboratory rate data was 20 hours. The experimentally determined half-life in Withlacoochee River water was 22 hours. This is in good agreement with laboratory rate data obtained in distilled water experiments.

The effect of inorganic species common to the aquatic environment which in some way might catalyze malathion degradation was also investigated. Payne and Feisal nutrient medium,¹² which have a high concentration of inorganic salts, did not effect malathion degradation at pH 6.8 in two weeks.¹ Sodium chloride (0.05 M) had no apparent catalytic effect on degradation of malathion at pH 6.5 as shown by no detectable degradation at the end of three weeks.

General base catalysis¹³ might be expected to be important in the elimination pathway. However, there was no detectable difference in the rate of disappearance of malathion over nearly a tenfold change in buffer concentration (boric acid-sodium hydroxide) at constant ionic strength (sodium chloride). Thus, any general base catalysis contribution would likely be insignificant in natural waters.

Bender,¹⁴ in fish toxicity studies, has investigated nine potential malathion degradation products for toxicity to the carp. His data showed that in some cases the breakdown products were as toxic as the parent pesticide. However, Bender did not investigate the toxicity of the malathion monoacids. Because they are anticipated products, we examined their persistence under alkaline reaction conditions.

The disappearance second-order rate constant (k_{ad}) obtained on starting with a mixture of 53% α -monoacid and 47% β -monoacid was $(3.1 \pm 0.2) \times 10^{-1} \text{ M}^{-1}$ (Table 10). Assuming no large difference in reactivity for the two isomers (Figure 24), at pH 8 the monoacids would have a half-life of about 24 days. Thus malathion monoacids are about 18 times more stable than malathion under the same alkaline conditions.

Half-life product studies by glc, after acidification and extraction with ether showed the presence of ethyl hydrogen fumarate. Methylation of the reaction mixture (diazomethane) and glc analysis showed the presence of malathion monoacid (50%), malathion dicarboxylic acid (15%), and O,O-dimethylphosphorodithioic acid.

Table 10. ALKALINE DEGRADATION RATE CONSTANTS FOR MALATHION MONOACIDS AND MALATHION DIACID IN WATER AT 27°.

Rate Constant $\text{M}^{-1} \text{ sec}^{-1}$		
k_{ad}^1	=	$(3.1 \pm 0.02) \times 10^{-1}$
k_{ah}^2		$(1.3 \pm 0.1) \times 10^{-1}$
k_{ae}^3		$(2.0 \pm 0.1) \times 10^{-1}$
k_{dd}^4		$(1.8 \pm 0.2) \times 10^{-2}$

¹Malathion monoacid disappearance rate constant.

²Malathion monoacid carboxyl ester hydrolysis rate constant.

³Malathion monoacid elimination rate constant.

⁴Malathion diacid elimination rate constant.

Figure 25 is a plot of malathion disappearance and monoacid and dicarboxylic acid formation as a function of time at 27°. The monoacid elimination rate constant (k_{ae}) is (2.0

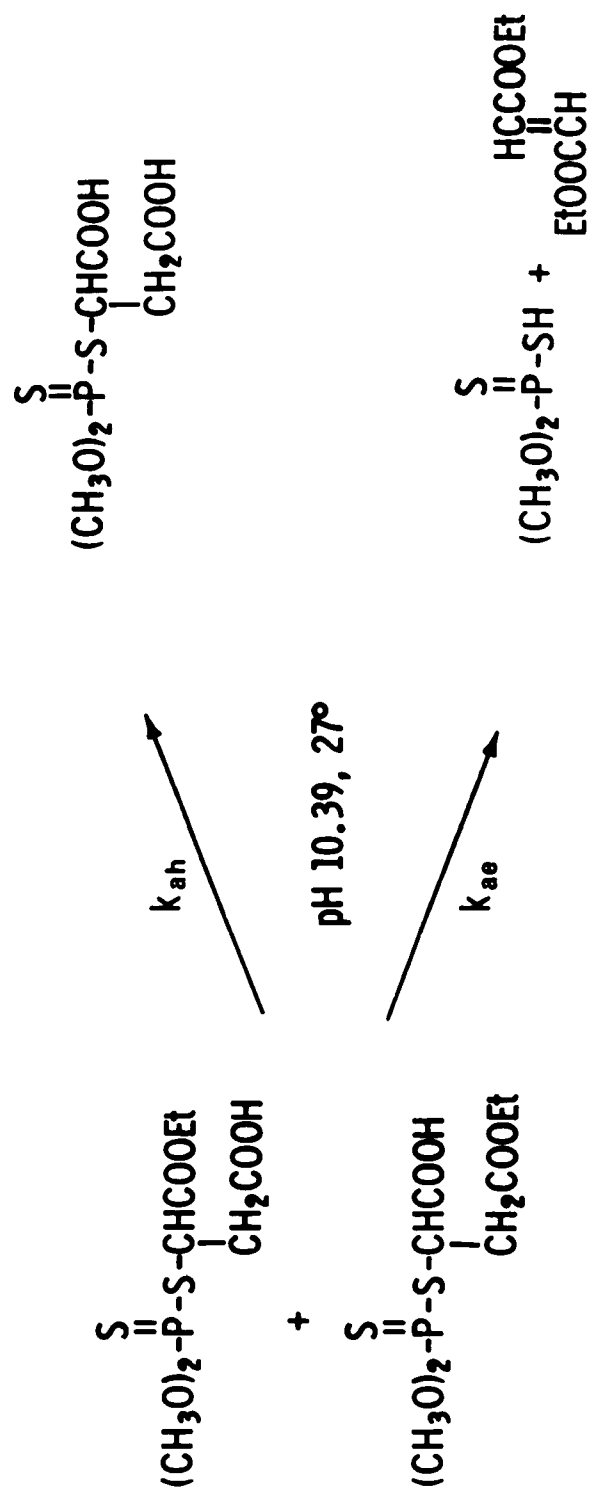


Figure 24. Alkaline degradation of malathion monoacid

$\pm 0.1) \times 10^{-1} \text{ M}^{-1} \text{ sec}^{-1}$ and the ester hydrolysis rate constant is $(1.3 \pm 0.1) \times 10^{-1} \text{ M}^{-1} \text{ sec}^{-1}$ at 27° . Based on rate constants the monoacids are undergoing about 40% ester hydrolysis and about 60% elimination.

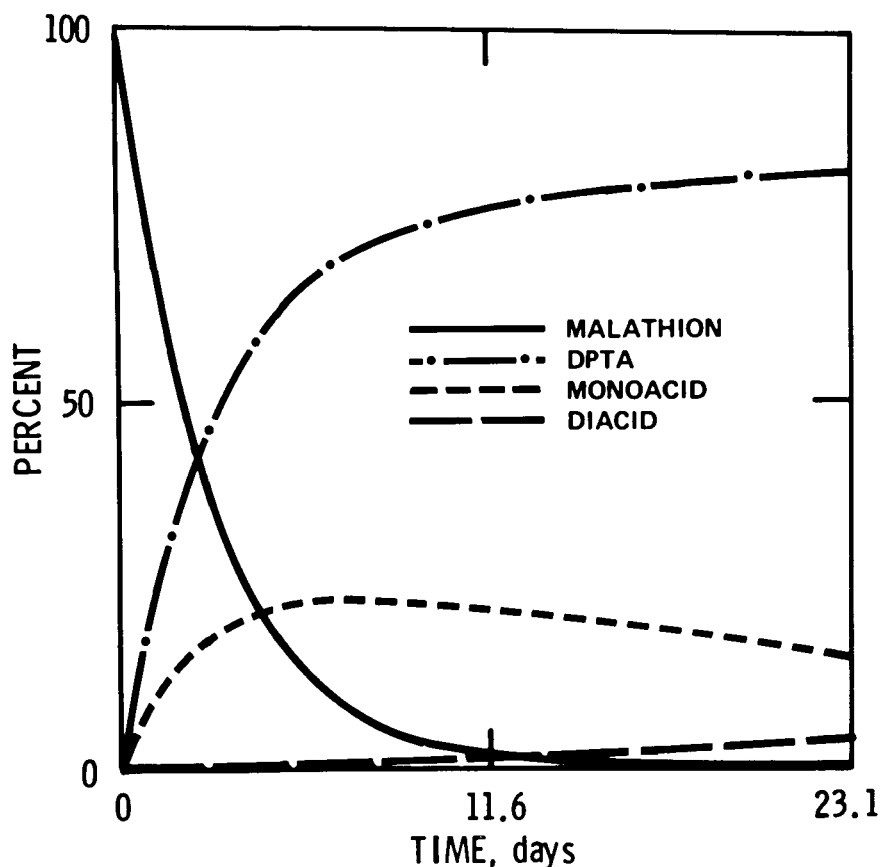


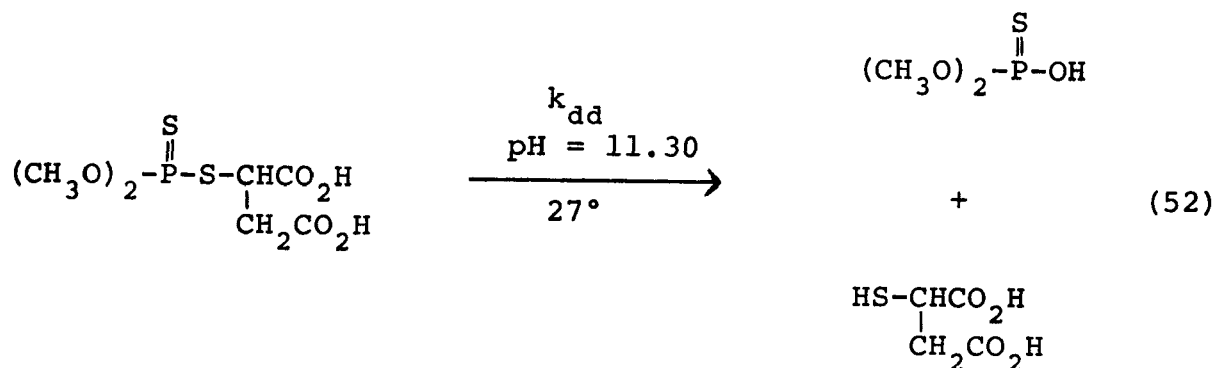
Figure 25. Time dependence of malathion disappearance and product formation at 27°C

Temperature effects on the two competing reaction pathways for monoacid degradation were not investigated. However, it is anticipated that malathion dicarboxylic acid formation will be favored at low temperatures and the elimination reaction to give O,O-dimethyl phosphorodithioic acid and ethyl hydrogen fumarate will dominate at elevated temperatures.

Because malathion diacid is anticipated to be a significant breakdown product, we determined its stability under alkaline reaction conditions. The diacid disappearance second-order rate constant (k_{dd}) is $(1.8 \pm 0.2) \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$ at 27° (Table 10). These data indicate that at pH 9 the degradative half-life would be about a year. Thus, under

alkaline conditions malathion diacid is approximately 200 times less reactive than malathion.

Product studies at the end of one half-life were carried out. Extraction and methylation (diazomethane) followed by glc-ms analysis showed that O,O-dimethyl phosphorothionic acid and thiomalic acid were products of hydrolysis (eq. 52).



The overall alkaline degradative reaction scheme for malathion and its acid derivatives is given in Figure 26. The end products of alkaline degradation are shown to be fumaric acid, O,O-dimethyl phosphorodithioic acid, thiomalic acid, and O,O-dimethyl phosphorothionic acid. However, the intermediate malathion monoacids are degraded at a rate slower than malathion and may have an impact on the aquatic environment. Analysis for malathion in environmental samples is generally carried out by glc methods under conditions where the malathion acids are not detected.

We expect the malathion monoacids to form under certain environmental conditions. However, the impact to these monoacids on aquatic ecosystems has not been investigated. Both monoacids are now readily obtained through one-step synthetic schemes and are available for environmental studies. The unambiguous assignment of their structures is straightforward using carbon-13 nmr and illustrates the potential of this technique for structural studies involving environmental problems.

Acid-catalyzed degradation of malathion is not likely to be important at most pH's found in the aquatic environment. But, at acidic pH's photolysis and microbial degradation may be important pathways. Under alkaline pH's chemical transformation will be competitive. At lower temperatures the dominant degradation pathway is through formation of the mono and diacids and thence to the dimethyldithio and dimethylthionic acids.

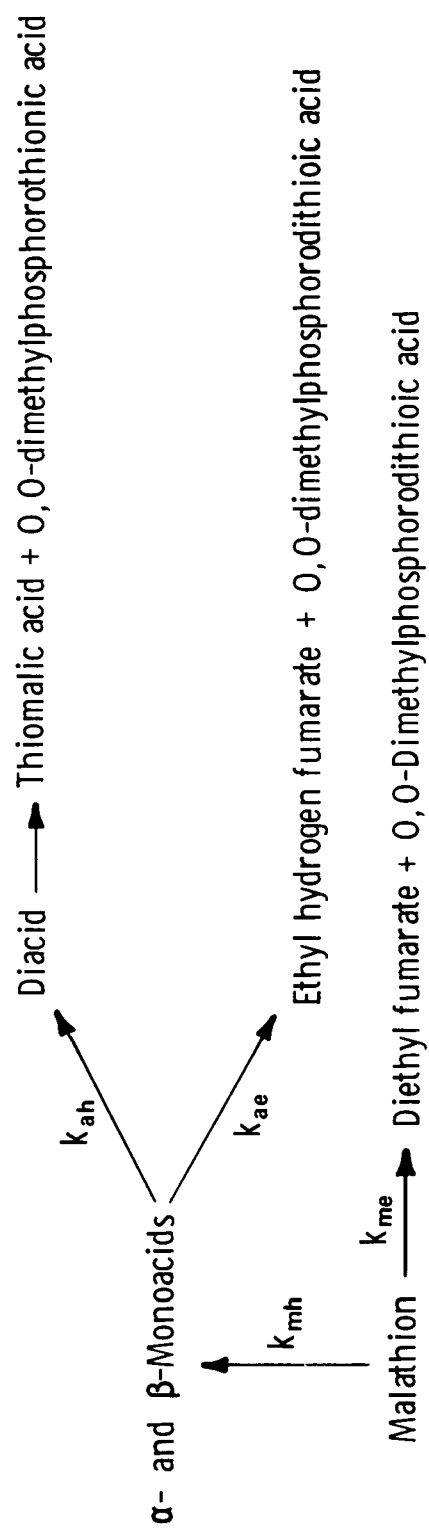


Figure 26. Pathways of alkaline degradation for malathion and malathion acid derivatives at 27°.

OXIDATION

Malathion is readily oxidized to malaoxon by a variety of oxidizing reagents in the laboratory. Therefore, one might anticipate oxidation by molecular oxygen in the environment. However, experiments showed that malathion was stable in oxygen-saturated water at acidic pH's for up to two weeks. Therefore, oxidation by molecular oxygen does not appear environmentally significant.

PHOTOCHEMISTRY

Malathion was distinguished by the fact that its direct photolysis was the slowest of all the pesticides examined. Since direct photolysis cannot compete with the hydrolysis of malathion in the pH 5 to 9 range, no attempt was made to characterize the direct photolysis products.

The decomposition of malathion was photosensitized by acetone and by natural materials dissolved in water from the Suwannee River (pH 4.7). Wavelength studies established that ultraviolet light of wavelengths less than 340 nm caused the decomposition in the river water. The photolysis half-life of malathion in the river water was 15 hours under September sunlight (lat. 34° N). Photolysis was not sensitized in water from two other rivers, the Withlacoochee and the Santa Fe in north Florida, suggesting that photosensitized decomposition of malathion may not be a general phenomenon in natural waters. Products from the sensitized transformations were not determined, although it was established that malaoxon was not a product. Malathion was found to be unreactive towards singlet oxygen in both acetonitrile and distilled water (β value > 37.5 in water).

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SECTION IX

RESULTS & DISCUSSION: 2,4-D ESTERS

The widespread application of phenoxy herbicides has prompted numerous studies of their biological,¹ chemical,¹ and photochemical² degradation. However, few publications concerned with the chemical behavior of the esters of 2,4-D have appeared, although 2,4-D usually is introduced into the environment as an ester. The esters are often sprayed onto surface waters to control aquatic weeds; they also enter lakes and rivers in the runoff from field application.³

HYDROLYSIS

In accord with previous extensive studies of ester hydrolysis,⁴ three reactions considered in kinetic studies of the 2,4-D esters were acidic, neutral, and alkaline hydrolysis. As expected, product studies showed that 2,4-D was formed quantitatively in these reactions.

Detailed studies of the reactions of the 2-butoxyethyl and methyl esters indicated that the hydrolysis rate ($-d[E]/dt$) could be expressed by equations 4 and 5.

A plot of $\log k_{obs}$ vs pH for the butoxyethyl ester was nearly V-shaped (Figure 27), indicating that neutral hydrolysis is unimportant relative to acidic and basic hydrolysis.⁴ Table 11 presents rate constants for acidic and alkaline hydrolysis in water, measured by hydrolyzing the esters at low and high pH. Activation parameters were determined by measuring hydrolysis rates at different temperatures (Table 11).

The kinetic data in Table 11 can be used to calculate hydrolysis rates as a function of pH and temperature. Reaction kinetics become pseudo-first-order when the water is buffered, as often occurs in natural water. Since k_{OH^-} is much larger than k_{H^+} , the half-life for the pH 5 to 9 range can be adequately expressed by

$$t_{1/2} = \frac{0.693}{k_{OH^-} [OH^-]} \quad (53)$$

Using equation (53) and structure-reactivity relationships for the alkaline hydrolysis of various acetic acid esters,⁵ we

Table 11. KINETIC DATA FOR THE ACID AND BASE HYDROLYSIS
OF METHYL AND n-BUTOXYETHYL ESTERS OF 2,4-D

2,4-D Esters	Temp. °C	$k_{H^+} (M^{-1} sec^{-1})^c$	$k_{OH^-} (M^{-1} sec^{-1})^c$	ΔH^\ddagger Kcal/mole	ΔS^\ddagger eu
BBE ^a	28		$(3.02 \pm 0.23) \times 10^1$	20.1 ± 1.4	14.8 ± 4.2
	47		$(2.35 \pm 0.13) \times 10^2$		
	67	$(6.59 \pm 0.13) \times 10^{-4}$		17.6 ± 0.9	121.29 ± 2.9
	87	$(2.96 \pm 0.18) \times 10^{-3}$			
	28	$(2.0 \pm 0.5) \times 10^{-5d}$			
ME ^b	28		$(1.73 \pm 0.23) \times 10^1$		

^aButoxyethyl. ^bMethyl. ^cDetermined from pseudo-first-order rate constants.

^dExtrapolated value.

have estimated hydrolysis half-lives for commonly used 2,4-D esters (Table 12). These data demonstrate that the chemical hydrolysis rate for a given ester varies greatly within the pH range normally found in natural waters (pH 5 to 9) and that hydrolysis rates are much higher in basic than in acidic waters. Ester structure also strongly influences hydrolysis rates. The esters possessing ether linkages near the ester carboxyl group generally hydrolyzed more rapidly than the hydrocarbon chain esters. For example, the hydrolysis rate of the 2-butoxyethyl ester was about an order of magnitude greater than that of the 1-octyl ester.

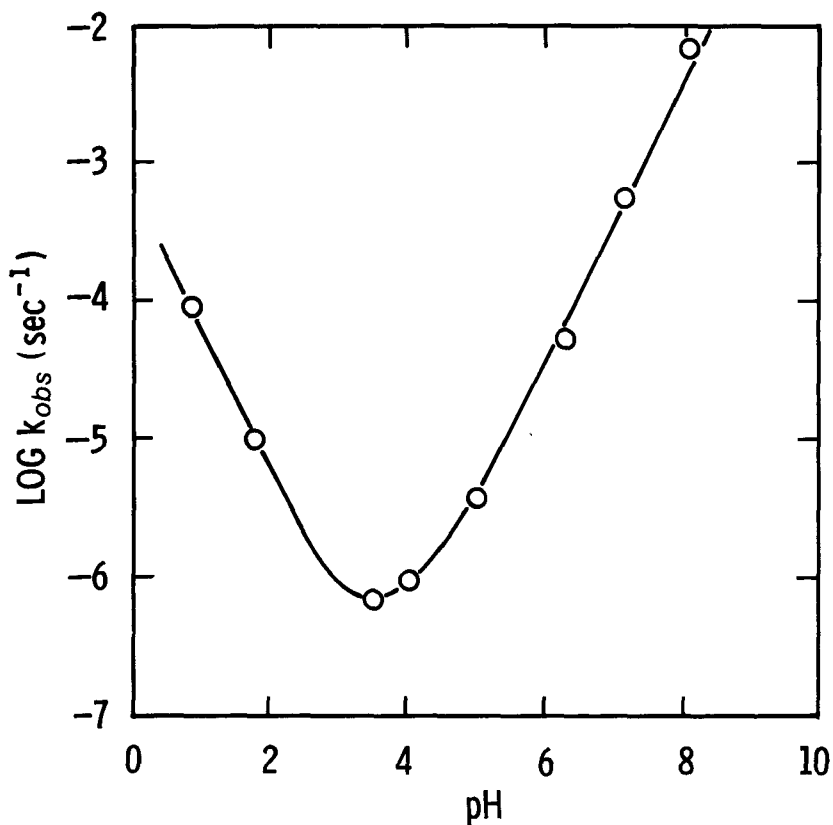


Figure 27. pH-rate profile for 2,4-D butoxyethyl ester at 67° in water

The rapid hydrolysis of 2,4-D esters in basic distilled water suggests that chemical hydrolysis is often the major pathway for degradation of the esters in basic natural waters.

Table 12. KINETIC DATA FOR HYDROLYSIS OF 2,4-D ESTERS
IN WATER AT 28°C.

Ester (days)	k_{OH^-} M ⁻¹ sec ⁻¹	pH 9 (hrs)	$t_{1/2}$ pH 6
Methyl ^a	17.3	1.1	44
2-Propyl ^b	1.1	17	710
1-Butyl ^b	3.7	5.2	220
1-Octyl ^b	3.7	5.2	220
2-Octyl ^b	0.52	37	1500
2-Butoxyethyl ^a	30.2	0.6	26
2-Butoxy- methylethyl ^b	4.3	4.4	180

^aCalculated from data in Table 11. ^bCalculated assuming structure-reactivity relationship for 2,4-D esters is the same as that for acetic acid esters.⁵

To check this point, the disappearance of the butoxyethyl ester was studied in water collected from the Withlacoochee River in South Georgia. As shown in Figure 28, the observed disappearance rate matched the hydrolysis rate calculated from data in Table 11, using the pH of the river water (pH 8.1). Since 2,4-D esters hydrolyze much more slowly in acidic waters, other processes such as those discussed below are probably more important in such waters.

PHOTOCHEMISTRY

Conflicting reports concerning the photoproducts of 2,4-D esters in water have appeared in the literature. Aly and Faust⁶ reported that several 2,4-D esters yielded 2,4-dichlorophenol as the photoproduct. Identification of this photoproduct, however, was based upon a colorimetric technique that would not have distinguished 2,4-dichlorophenol from other phenolic products. Binkley and Oates⁷ have recently reported that only monochlorophenoxyacetic acid (2- and 4-CPA) esters result from photolysis of 2,4-D esters in water.

However, other studies have shown that photolysis of chlorinated aromatics in water results in replacement of chlorine by a hydroxyl group.⁸

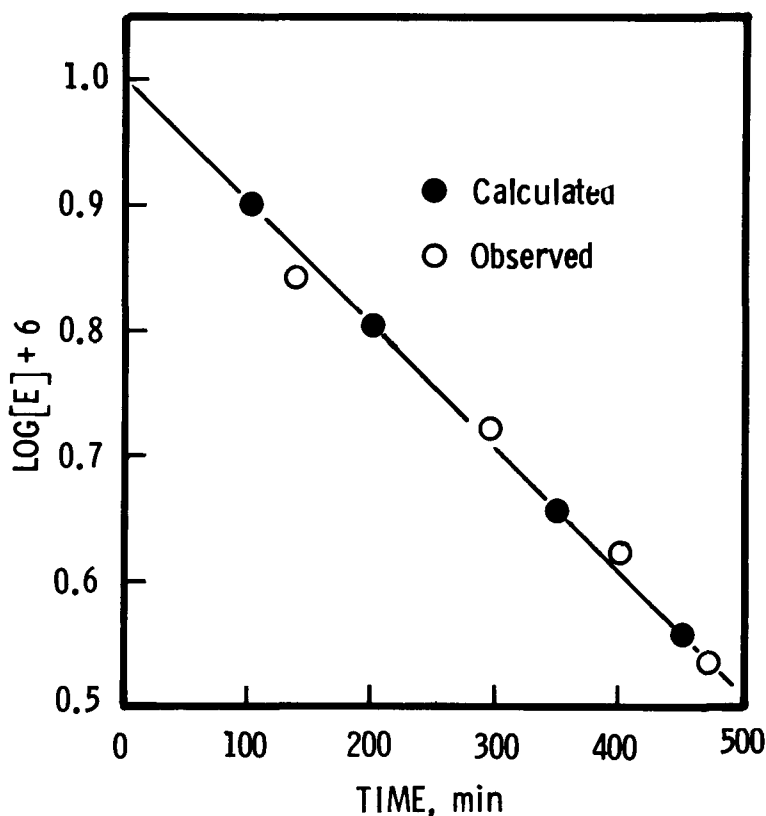


Figure 28. Hydrolysis of 2,4-D butoxyethyl ester in water from the Withlacoochee River

Our product studies were carried out in both water and organic solvents. The latter studies were prompted by the suggestion that organic films are a likely site for a photoalteration of pesticides.⁹

In the hydrocarbon media, photoreaction involved quantitative replacement of one of the chlorines by hydrogen, likely via free radical intermediates.¹⁰ In both hexane and hexadecane, replacement of the ortho chlorine accounted for > 90% of the photoreaction.

Studies in water were conducted at several concentrations. At concentrations well exceeding their solubility limits (> 300 ppm), the esters formed emulsions and the major photoproducts, 2- and 4-CPA esters, were the same as those formed in the hydrocarbon solvents. However, irradiation of

very dilute (< 1 ppm), air-saturated solutions yielded products very similar to those resulting from photolysis of the 2,4-D acid.¹¹ Major photoproducts were 2,4-dichlorophenol and compounds resulting from replacement of one chlorine by hydroxyl. The lactone formed by elimination of alcohol from the ester of 4-chloro-2-hydroxyphenoxyacetic acid was eluted from the gas chromatograph. The alcohol elimination was found, however, to be the result of thermal degradation in the injection port (180°C). Results of these product studies are summarized in Figure 29.

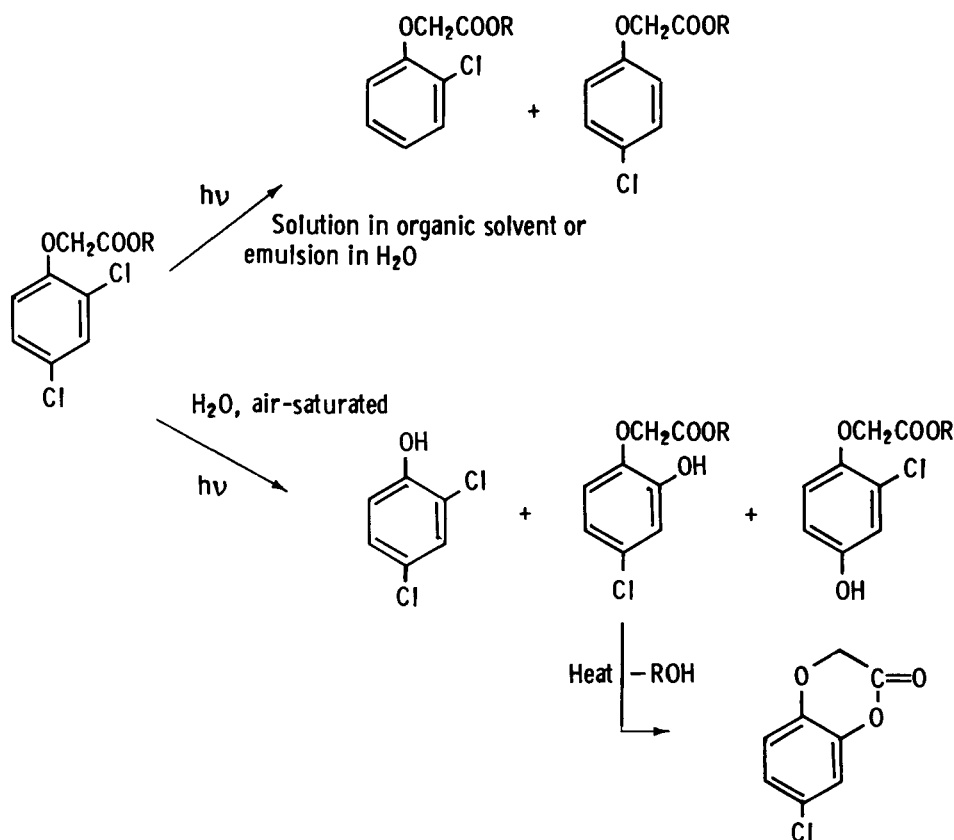


Figure 29. Photoreactions of 2,4-D esters

Kinetics of phenoxy herbicide photoalteration have received very little study. Photolysis of 2,4-D and its esters was reported to be rapid when short wavelength, high intensity light is employed;⁶ however, Crosby and Wong¹² have reported that photoalteration of 2,4-D is relatively slow when less intense, longer wavelength light is used.

Ultraviolet spectra of 2,4-D esters in water were very similar to that of 2,4-D itself. Spectra of the methyl and

butoxyethyl esters were identical. Although two absorption maxima occur in the 280-295 nm wavelength range, the point of maximum spectral overlap with midday summer sunlight occurs at 300 nm.

Quantum yields for photoalteration of 2,4-D esters (Table 13) were far lower than unity and were considerably lower in water than in hydrocarbon solvents. Variations of pH (between 5 and 8) caused no change in quantum yield although the phenolic photoproducts were further photodegraded at higher rates in basic water. The quantum yields in hexane and hexadecane, solvents with very different viscosities, were identical, although photoreactions involving formation of free radicals are often viscosity-dependent.¹³ The lack of efficient photosensitization by acetone, a triplet sensitizer, indicated that the direct photolysis proceeds from the excited singlet state of 2,4-D esters. The extremely short lifetimes of the excited states that lead to 2,4-D ester photolysis preclude any significant quenching by species dissolved in natural waters. Ester structure also affected the photolysis rate. The methyl ester had a lower quantum yield and therefore a lower photolysis rate than did the butoxyethyl ester.

Table 13. DISAPPEARANCE QUANTUM YIELDS FOR PHOTOLYSIS OF 2,4-D ESTERS AT 313 nm (28°C).

Ester	Solvent	Quantum Yield, ϕ
BEE ^a	Water, pH 5.3	0.056
	Water, pH 6.6	0.052
	Water, pH 7.8	0.056
	n-Hexane	0.17
	n-Hexadecane	0.17
ME ^b	Water, pH 6.6	0.031
ME	n-Hexadecane	0.13
BEE	n-Hexane, Acetone-sensitized	0.0080

^aButoxyethyl. ^bMethyl.

Photolysis rates of the butoxyethyl ester were calculated as a function of time for a clear September day in the Southern United States (Figure 30). Because k_a varies throughout the day, we calculated the photolysis rates of the butoxyethyl ester integrated over the 12-hour period of daylight. As shown in Table 14, measured photolysis rates for September agreed closely with the calculated values.

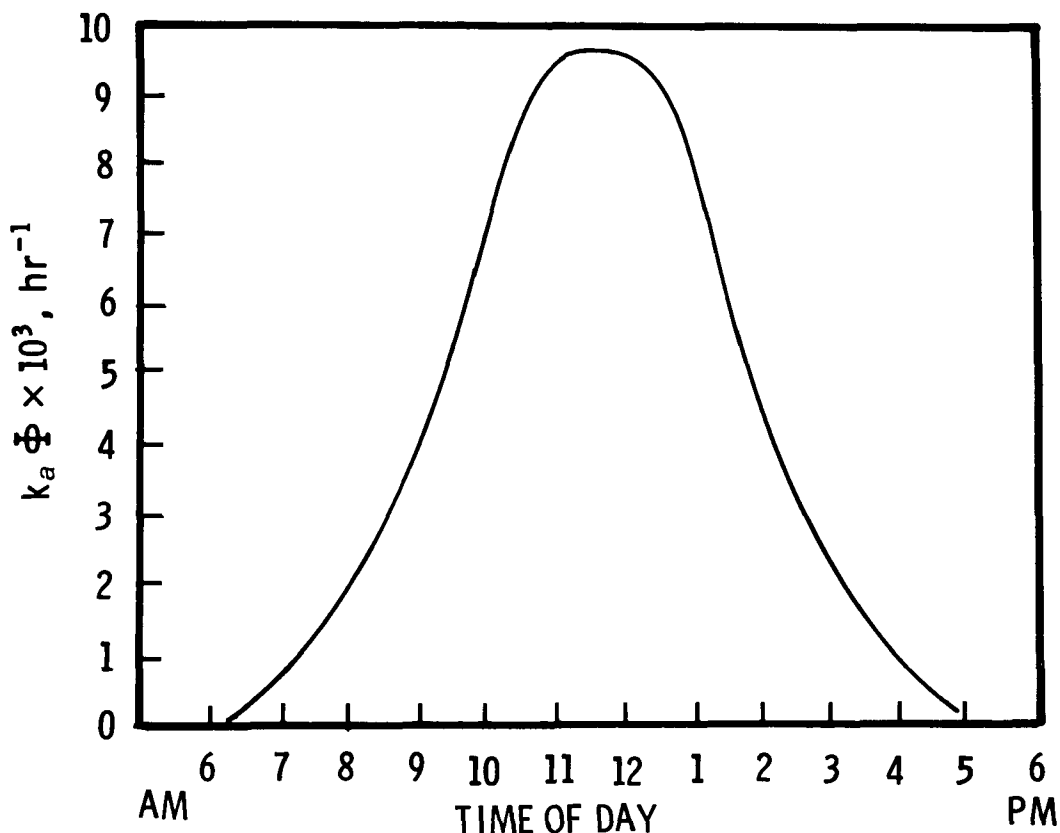


Figure 30. Computed dependence of 2,4-D butoxyethyl ester photolysis rate upon time of day in the Southern United States

We also investigated the photoalteration of an ester in a natural water sample. The butoxyethyl ester (1.0 ppm) was irradiated ($> 290 \text{ nm}$) in filter-sterilized water from the Suwannee River (pH 4.7). The major photoproducts found in distilled water (Figure 29) were also found in the river water although the yield of 2,4-dichlorophenol was much higher and the yields of the hydroxylated phenoxy esters were lower. As with distilled water, no monochlorinated phenoxy esters were formed in the river water. The overall photolysis was actually more rapid in the river water than in distilled

water. This acceleration is attributed to photosensitization by humic materials dissolved in the river water. Since photolysis of 2,4-D esters by direct absorption of sunlight is slow, sensitized photolysis may be more important in many natural waters.

The sensitized photolysis of 2,4-D esters in river water cannot involve singlet oxygen. The β value for the butoxyethyl ester was > 37.5 in water, indicating that singlet oxygen reacts very slowly with 2,4-D esters.

Table 14. COMPARISON OF PHOTOLYSIS DATA FOR
2,4-D BUTOXYETHYL ESTER

Data	Water	Medium Hydrocarbon
$(k_a)_{\text{intg}}, \text{ day}^{-1}$	1.04	1.07
ϕ	0.056	0.17
$(k_a)_{\text{intg}}\phi, \text{ day}^{-1}$	0.058	0.18
Calculated half-life, days	12	3.8
Empirical half-life, days	14	4.0

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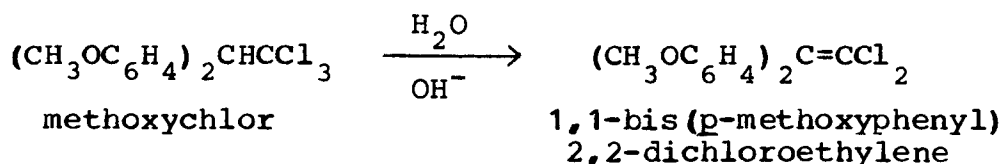
SECTION X

RESULTS & DISCUSSION: METHOXYCHLOR

HYDROLYSIS

Crosby¹ has reported that at alkaline pH's, methoxychlor eliminates hydrogen chloride to give the corresponding diphenylethylene derivative. Merna *et al.*² reported the half-life of methoxychlor in distilled water buffered at pH 7 and 8 to be 270 days. In distilled water which had previously contained fish, the half-life was reduced to 8 days. In natural water samples, the half-life was 7-18 days depending on the water sample employed.

Cristol³ reported the results of a kinetic study of the dehydrochlorination (Eq. 54) of substituted diphenylchloroethanes related to DDT in 95% ethanol-water. (Table 15) Based on these data, DDT is about 200 times more reactive than methoxychlor in the hydrogen chloride elimination reaction at 30°. The half-life predicted using these data is 12 days for DDT and 7 years for methoxychlor at pH 9. Although these studies were carried out in aqueous ethanol, they should provide a good indication of relative reactivity in water.



Data from our studies with methoxychlor in water and 5% acetonitrile-water are given in Table 16. Based on the rate constants methoxychlor degradation is pH independent over the pH range 3 to 10 due to reaction with water. Above pH 10 the reaction rate increases with pH indicating dehydrochlorination as the dominant pathway.

In agreement with this, at pH 13, 1,1-bis(p-methoxyphenyl)-2,2-dichloroethylene (DMDE) is the major product. Below pH 10, only 2-4% theoretical DMDE was found. The major product was not identified.

The pseudo-first-order rate constant for DDT, under similar reaction conditions (pH 7) is $7.6 \times 10^{-6} \text{ sec}^{-1}$ at 85°. This corresponds to a half-life of 25 hours. Thus DDT is about 3 times less reactive than methoxychlor at this temperature.

Table 15. KINETIC DATA FOR DEHYDROCHLORINATION OF METHOXYCHLOR AND DDT.^a

Compound	Temp. ^o	k M ⁻¹ sec ⁻¹	E _a , kcal
DDT	20.11	2.48 x 10 ⁻²	18.2
	30.37	6.96 x 10 ⁻²	
Methoxychlor	20.11	9.18 x 10 ⁻⁵	19.1
	30.37	3.06 x 10 ⁻⁴	

^aTaken from Reference 3.

While methoxychlor hydrolysis may be slow in distilled water, at environmental temperatures its chemical degradation may be fast in some natural waters. Methoxychlor degradation was studied in natural river water samples at 65°. In water samples from the Tombigbee River (pH 8.0) and Alabama River (pH 7.7), there was an apparent rate acceleration. However the amount of degradation as a function of time was very erratic and factors other than hydrolysis appeared operative.

Table 16. RATE CONSTANTS FOR METHOXYCHLOR DEGRADATION IN WATER.^a

pH	k _{OH} ⁻ (M ⁻¹ sec ⁻¹) ^b 25°	k _{H₂O} (sec ⁻¹) ^c	
		65°	85°
3		--	2.1 x 10 ⁻⁵
5		3.3 x 10 ⁻⁶	2.6 x 10 ⁻⁵
7		4.0 x 10 ⁻⁶	2.4 x 10 ⁻⁵
9		2.6 x 10 ⁻⁶	2.6 x 10 ⁻⁵
11		--	4.5 x 10 ⁻⁵
13	3.6 x 10 ⁻⁴		

^aRate constants were obtained either in water or 5% acetonitrile-water. ^bSecond-order rate constant. ^cPseudo-first-order rate constant.

OXIDATION

Preliminary experiments with methoxychlor in natural water samples at 65° indicated methoxychlor was being degraded at a rate too fast to be accounted for by hydrolysis.

We therefore investigated the degradation of methoxychlor in the presence of various concentrations of hydrogen peroxide to determine if free radical degradation might account for the increased reactivity (Table 17).

The reaction appears to be a free radical reaction based on the catalysis by hydrogen peroxide and the effect of species in the waters employed. The significance of free radical oxidative degradation under environmental reaction conditions is hard to assess at this time. However, the importance of this pathway should not be overlooked.

PHOTOCHEMISTRY

Direct Photolysis

Products. Several studies have established that methoxychlor, like DDT, is photodecomposed to a wide variety of products. Other investigators have reported that the major photoproducts in aqueous alcohol were p,p'-dimethoxybenzophenone (MDCO), p-methoxybenzoic acid (MBA) and p-methoxyphenol (MP)^{4,5}. Photolysis of methoxychlor in butteroil⁶ reportedly yielded the above products along with several dimeric products similar to those derived from photolysis of concentrated solutions of DDT⁷. MacNeil and co-workers⁸ found that 1,1-bis(p-methoxyphenyl)-2,2-dichloroethane (DMDD) and, to a lesser extent, 1,1-bis(p-methoxyphenyl)-2,2-dichloroethylene (DMDE) were the major glc amenable photoproducts in nitrogen-saturated heptane.

Given the multiplicity of products found in these studies we were not surprised to find that the photolysis of methoxychlor is highly dependent upon its reaction medium. In agreement with the above studies, we found that the major photoreaction in oxygen-free hexane involves stepwise replacement of chlorine by hydrogen to initially give DMDD; small amounts of DMDE were also formed (Figure 31). The presence of air altered the nature of the products; MDCO became the major product and DMDD, DMDE, and MP were minor products (Figure 31).

Table 17. HALF-LIVES FOR METHOXYCHLOR DEGRADATION WITH VARYING AMOUNTS OF HYDROGEN PEROXIDE ADDED AT 65°.

H ₂ O ₂ Concentration (M)	Half-life (hrs)
0.0	58 ^a
0.0	58 ^b
1.0 x 10 ⁻¹	< 1 ^b
8.0 x 10 ⁻²	< 1.7 ^b
8.0 x 10 ⁻³	2.0 ^b
8.0 x 10 ⁻⁴	17 ^b
8.0 x 10 ⁻⁵	25 ^b

^aCarried out in water at 1 x 10⁻⁷ M methoxychlor.

^bCarried out at 1 x 10⁻⁶ M methoxychlor in water containing 5% acetonitrile.

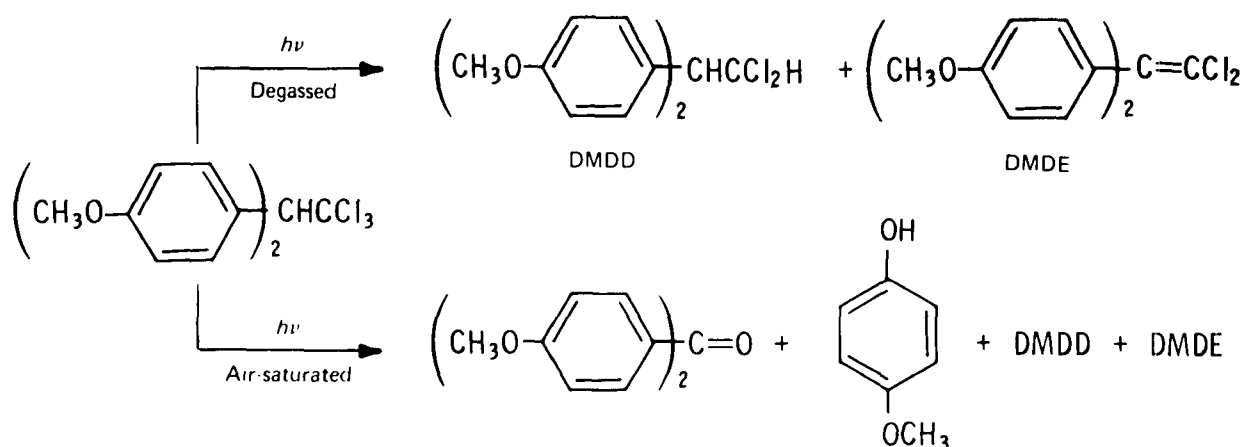


Figure 31. Products from direct photolysis of methoxychlor in hydrocarbon solvents

Direct photolysis of methoxychlor (25 ppb) in air-saturated distilled water by > 280 nm light yielded DMDE as the major product (Figure 32). After partial reaction (~ 10% conversion of methoxychlor), DMDE accounted for 60% of the

products. The yield decreased with increasing conversion because of subsequent photolysis of DMDE. After further reaction (30 to 50% conversion) we also found *p*-methoxybenzaldehyde but no MDCO in organic extracts of photolyzed solutions (Figure 30). Control experiments established that MDCO should have been detected if it had formed. Experiments were also conducted at higher methoxychlor concentrations (0.3 g/liter) in an air-saturated solution of 1.1 M water in acetonitrile; under these conditions DMDE (60% yield) and a yellow non-volatile product were formed. In degassed water-acetonitrile, DMDE was the major glc amenable product but its yield was lower (~ 20%). Addition of the free radical scavenger, 2-mercaptoethanol (0.036 M), to the degassed water-acetonitrile mixture resulted in a sharp decrease in the yield of DMDE and formation of a new product, DMDD, the major product that formed in degassed hexane.

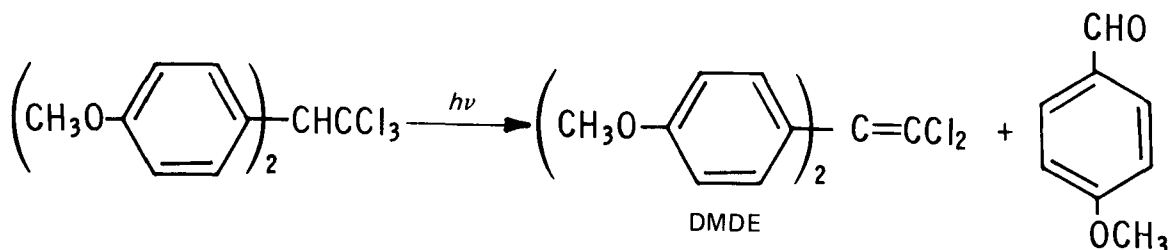


Figure 32. Photoproducts of methoxychlor in pure water

These results suggest that the primary photochemical process for methoxychlor is the same as that for DDT -- homolysis of one of its carbon-chlorine bonds to form free radical intermediates [Eq. 55]^{9,10}. Subsequent chemical reactions of the free radicals with themselves, oxygen, or the solvent determine the nature of the products. Some possible reactions that account for the major products in water are shown in Equations 56-59 where Ar represents a *p*-methoxyphenyl group and RSH is a thiol.

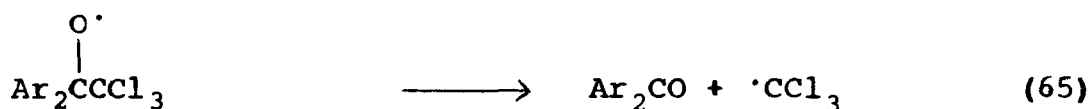
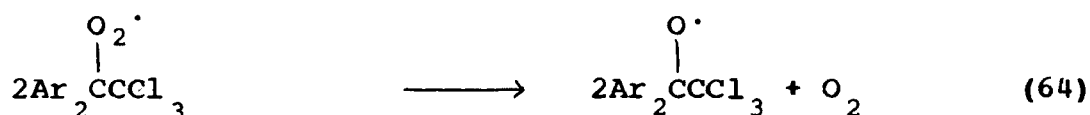
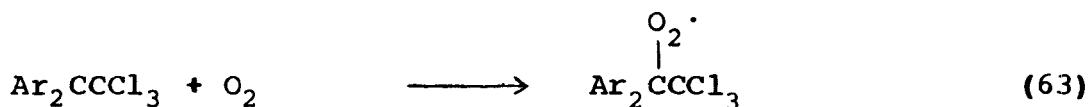


The thiol scavenged the free radical intermediate as shown in Equation 59, forming DMDD and inhibiting DMDE formation. Plimmer and his co-workers¹⁰ suggested that the free radical intermediate obtained from DDT photolysis reacts with oxygen according to Equations 60 and 61.



In the case of methoxychlor in aqueous media, such a reaction sequence would ultimately lead to formation of bis(*p*-methoxyphenyl)acetic acid. This product was not found presumably because reactions such as those in equations 56-58 occur much more rapidly in the case of methoxychlor. Other studies have demonstrated that abstraction of benzylic hydrogen atoms by chlorine atoms and oxygen free radicals is markedly accelerated by *para*-methoxy relative to *para*-chloro ring substituents¹¹.

No detailed studies were made of the photooxidation of methoxychlor in hydrocarbons. The observed formation of dimethoxybenzophenone can be accounted for by a mechanism similar to one suggested by Plimmer *et al.*¹⁰ for photooxidation of DDT to dichlorobenzophenone (eq. 62-65). The alkylperoxy radicals, RO₂·, result from reaction of solvent-derived free radicals with oxygen.



Rates. The dearth of information concerning the rate of direct photolysis of methoxychlor under sunlight prompted us to examine the kinetics in some detail. Preliminary experiments under natural sunlight indicated that the photolysis of methoxychlor (30 ppb) in either hexane or distilled water was quite slow. Exposure to 48 hours of

midday (1000 to 1400 E.D.T.) sunlight (June, lat. 34°N) resulted in less than 10% decomposition in both solvents. Assuming first-order kinetics for the photolysis, these data indicated that at least 300 hours of midday sunlight would be required to decompose half of the pesticide.

Quantum yields for direct photolysis of methoxychlor were measured in hexane, 1.1 M water in acetonitrile, and distilled water (Table 18). The quantum yield in hexane was similar to the value of 0.16 previously reported for DDT in hexane⁹. The quantum yield in a degassed 1.1 M water in acetonitrile mixture was not decreased by the addition of 0.036 M 2-mercaptoethanol, a free radical scavenger, or 0.004 M *cis*-1,3-pentadiene, a triplet-state quencher. The latter experiment indicates that dissolved substances in natural waters are too dilute¹² to quench the photolysis by energy transfer processes¹³. The low quantum yields for DDT and methoxychlor may in part be due to recombination of the free radicals initially formed in the photolysis (eq 55, reverse reaction).

Table 18. QUANTUM YIELDS FOR DIRECT PHOTOLYSIS OF METHOXYCHLOR

Solvent	Disappearance ^a Quantum Yield
n-Hexane ^b	0.12
1.1M Water in acetonitrile ^b	0.32
Water ^c	0.3

^aMaximum transmittance of chemical filter was 277 nm.

^bMethoxychlor concentration was 0.00300 M.

^cMethoxychlor concentration was 30 ppb.

The magnitude of the specific sunlight absorption rates of pesticides depends upon the degree of spectral overlap between their electronic absorption spectra and the spectrum of sunlight at the earth's surface. The cutoff for solar radiation is about 295 nm¹⁴. The spectra of carefully purified samples of DDT and methoxychlor in hexane are compared in Figure 33. In water-acetonitrile mixtures the extinction coefficients of methoxychlor at wavelengths > 295 nm are slightly higher than in hexane; the reverse is true for DDT. However, even in the polar solvents, the extinction coefficients of methoxychlor were very low. Specific sunlight

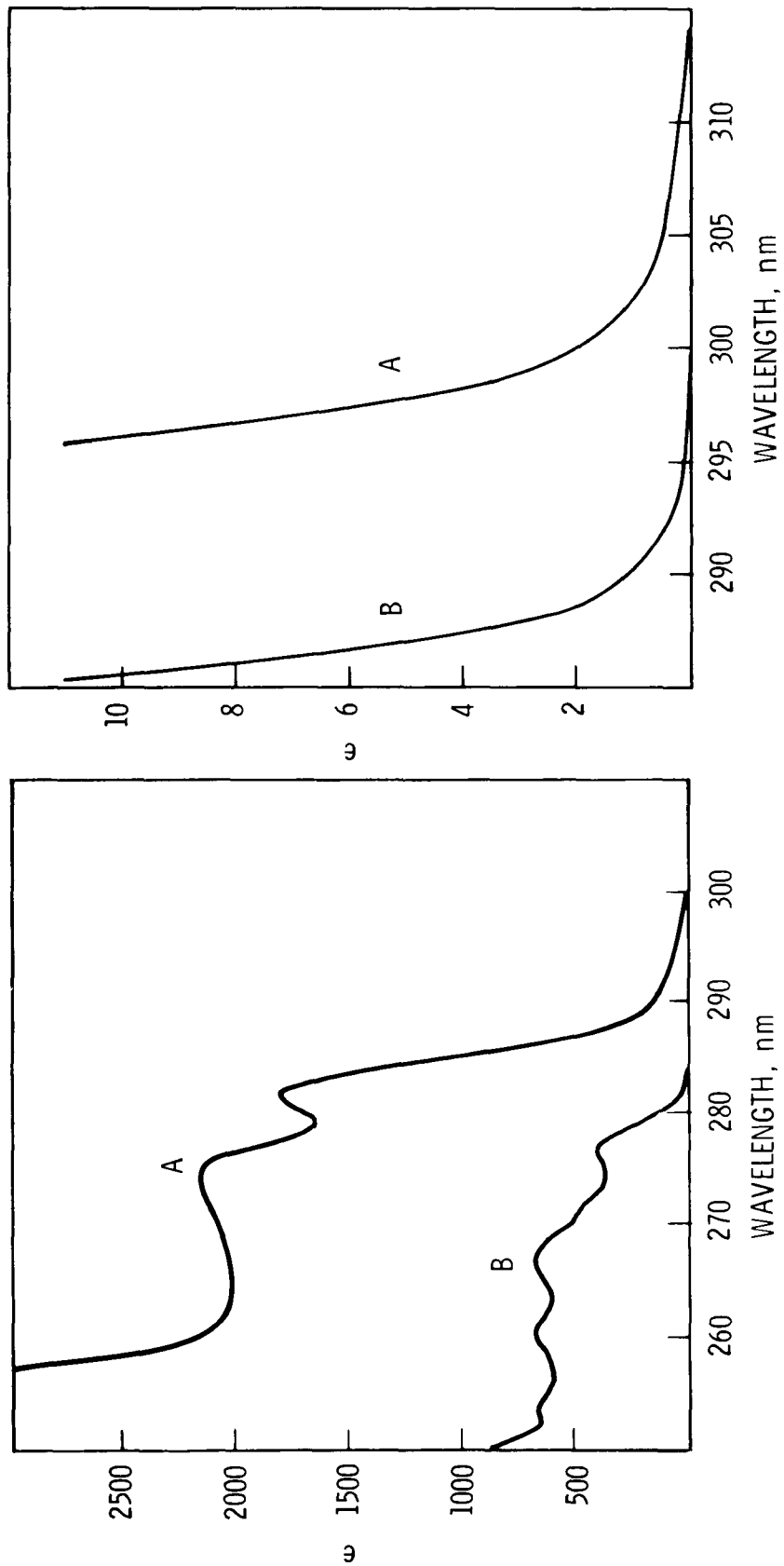


Figure 33. Electronic absorption spectra of methoxychlor (A) and DDT (B) in hexane

absorption rates for both compounds were calculated from the above spectral data and Bener's table of intensities of natural ultraviolet radiation¹⁴.

Kinetic parameters for the direct photolysis of DDT and methoxychlor during mid-summer in the central United States (lat. 40°N) are compared in Table 19. The half-lives, $t_{1/2}$, in Table 19 represent the period of midday sunlight required to decompose the pesticides to half of their original concentration near the surface of a water body [$t_{1/2} = 0.693 (k_a \phi)^{-1}$]. The following conclusions were derived from examination of these parameters:

- Direct photolysis of methoxychlor is at least 300 times more rapid than that of DDT in water.
- Direct photolysis of methoxychlor is nearly six times more rapid in aqueous than in hydrocarbon media. However, the hydrocarbon data are probably relevant only to oil slicks, not surface films formed by naturally occurring surface-active substances. Hautala¹⁵ has found that the electronic absorption spectra and quantum yields for reaction of pesticides are different in micelles formed by surfactants in water than in pure water or hydrocarbons. Similar differences probably occur when pesticides are intimately associated with surface-active films.
- Both DDT and methoxychlor are photolyzed very slowly by sunlight in pure water or hydrocarbons. The data in Table 2 pertain to mid-summer, midday sunlight; the half-lives are longer during other seasons and in the morning or afternoon. Midday half-lives for methoxychlor and DDT, averaged over all seasons, are 1,100 hours and > 460,000 hours, respectively, in water at lat. 40°N. Assuming conservatively that the average daily half-lives are 50% longer than the midday half-lives, the direct photolysis half-lives (in 12-hours days) of methoxychlor and DDT in water are 4.5 months and greater than 150 years respectively (lat. 40°N).

The calculated photolysis half-life of methoxychlor for midsummer is an increasing function of northern latitude (Figure 34). For example, the half-life in the central U.S. is approximately 30% longer than in the tropics.

Table 19. KINETIC PARAMETERS FOR THE DIRECT PHOTOLYSIS OF DDT AND METHOXYCHLOR IN THE CENTRAL UNITED STATES.^a

Pesticide	Medium	$10^9 k$ (sec ⁻¹)	ϕ	$10^{10} k_a \phi$ (sec ⁻¹)	$t_{1/2}$ (hrs)
Methoxychlor	Hydrocarbon	390	0.12	470	4,100
	Water	870	0.3	2800	690
DDT	Hydrocarbon	4.3	0.16 ^b	26.8	280,000
	Water	0.85	-- ^c	--	>227,000 ^d

^aCalculated for midday sunlight during midsummer at latitude 40°N.

^bTaken from Mosier *et al.*⁹

^cData not available.

^dMinimum half-life calculated assuming quantum yield of unity.

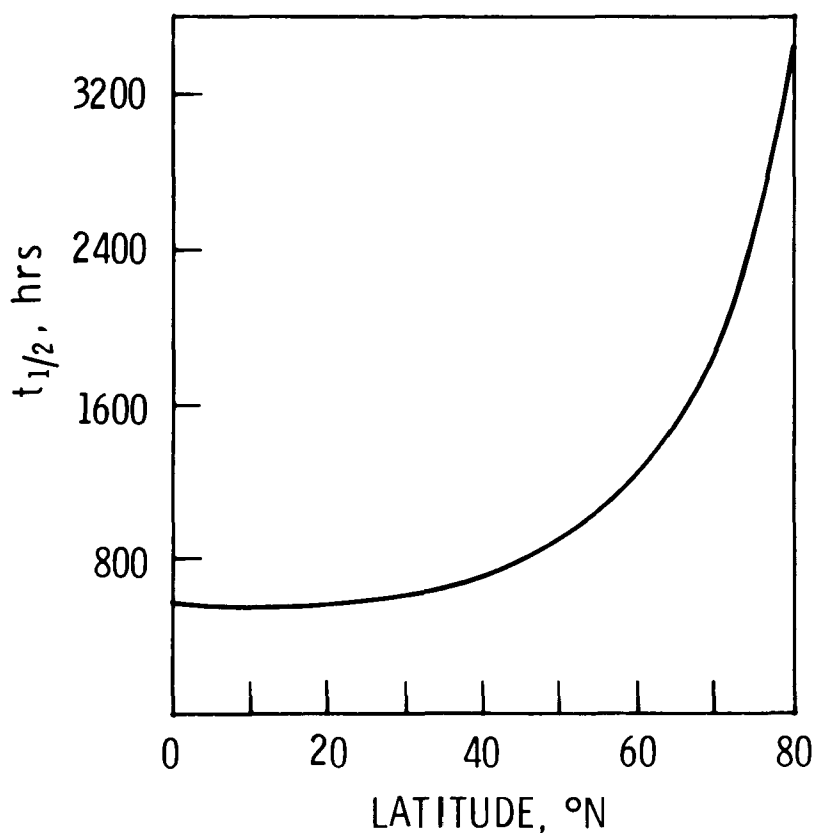


Figure 34. Computed midday half-lives for direct photolysis of methoxychlor in water during summer

Direct photolysis of the 1,1-diphenylethylene derivative, DMDE, was found to be much more rapid than that of methoxychlor. Quantum yields (313 nm) for photolysis of DMDE were found to be 0.20 in hexane and 0.30 in distilled water; Mosier *et al.*⁹ reported that the quantum yield for DDE in hexane is similar, 0.26 at 254 nm. The calculated midday half-lives for DMDE (summer, central United States) were 45 and 60 minutes in water and hydrocarbons, respectively. Photolysis rates measured under natural sunlight agreed closely with the calculated values. DDE also photolyzes much more rapidly than DDT in hydrocarbon media. The calculated midday half-life of DDE is about four hours under the above conditions whereas that of DDT is 280,000 hours. These results provide an interesting contrast to the findings of Moilanen and Crosby¹⁶ that DDT photolyzes more rapidly than DDE in the vapor phase.

The solar intensities employed in the above calculations are based upon average atmospheric ozone amounts (O_3) for a given latitude and season. In fact, natural variations of $\pm 5\%$ in (O_3) occur over a period of years and (O_3) varies longitudinally within a given latitude¹⁷. Recently, several scientists have expressed concern that certain human activities may be leading to depletion of stratospheric ozone¹⁸. Our calculations indicate that variation in ozone amount affects the direct photolysis rate of DDT more than that of methoxychlor (Figure 35). Generally, each 5% reduction in ozone amount should result in about a 10% increase in rate for DDT and a 6% increase for methoxychlor.

Sensitized Photolysis

Although the photolysis of methoxychlor in pure water is slow, we found that photolysis under sunlight was rapid in certain filter-sterilized natural waters (Table 20). The natural waters were collected from rivers in South Carolina, Alabama, Georgia, and Florida; pH values ranged from 4.7 (Suwannee River) to 8.2 (Withlacoochee River). Dark controls showed no decomposition in any of the water samples over the period of sunlight exposure.

Detailed product studies were not carried out. However, the glc traces of organic extracts of the photolyzed solution all had peaks with the same retention time as DMDE. In the Suwannee River water, DMDE formation almost completely accounted for methoxychlor disappearance at 30% conversion of the methoxychlor. The DMDE photolyzed more slowly than methoxychlor in the Suwannee River water; its low photolysis rate was attributed to light screening by the ultraviolet-absorbing materials in the river water.

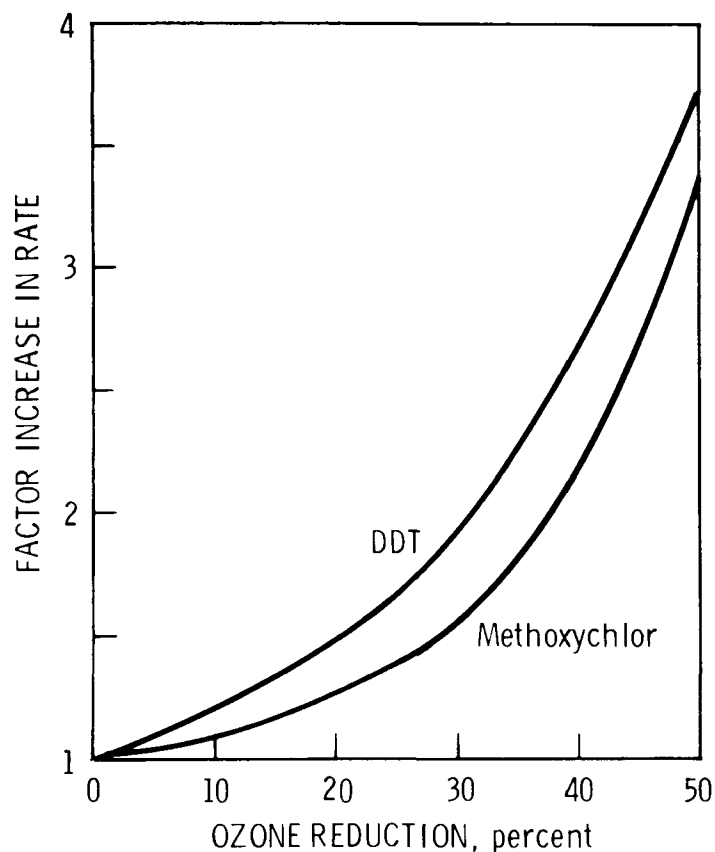


Figure 35. Calculated effects of ozone reduction upon photolysis rates of DDT and methoxychlor

Methoxychlor photodecomposed rapidly in distilled water containing a commercially available derivative of decayed plant materials, Aldrich "humic acid" (Table 20). This material was used because its electronic absorption spectrum was very similar to that of materials dissolved in our natural water samples and because it is likely to contain many of the same chemical moieties. The observed sunlight photolysis rate using 20 ppm of this model substance was roughly comparable to that found in several natural waters.

At present, we know very little about the mechanism(s) for sensitized photolysis in natural waters. However, energy transfer photosensitization cannot account for our results. The triplet state energy of methoxychlor, determined from its phosphorescence spectrum, was found to be 80 kcal mole⁻¹. Since triplet energy transfer occurs efficiently only when the triplet energy of the sensitizer equals or exceeds that of the energy acceptor¹³ only high energy sensitizers can transfer energy to methoxychlor. Such sensitizers may be present in

natural waters, but they absorb only the short wavelength ultraviolet component of sunlight, so their rates of sunlight absorption are not rapid. The quantum efficiencies of energy transfer under natural conditions are also decreased by the presence of competing energy acceptors such as dissolved oxygen. Moreover, studies using filtered light from a mercury lamp indicated that visible light (> 400 nm) caused decomposition of methoxychlor in the Suwannee River water; the energy of visible light is < 71 kcal mole⁻¹ ¹⁸, far lower than the minimum energy required to electronically excite methoxychlor (80 kcal mole⁻¹).

Table 20. HALF-LIVES FOR PHOTOCDECOMPOSITION OF METHOXYCHLOR (40 ppb) UNDER SUNLIGHT IN VARIOUS RIVER WATERS^a

Water	pH	Photolysis Half-life, hr ^b
Distilled	6.3	> 300
Suwannee River	4.7	2.2
Tombigbee River	7.6	5.4
Alabama River	7.7	2.9
Withlacoochee River	8.2	-- ^c
South Georgia Stream ^d	7.2	-- ^c
20 ppm "humic acid" in distilled water ^e	5.2	7.3

^aSolution in sealed quartz cells exposed to midday May sunlight, latitude 34°N.

^bCalculated assuming first-order kinetics, expressed as hours of midday sunlight.

^cNo detectable photolysis after two hours exposure.

^dCollected near Thomasville, GA.

^eHumic acid obtained from Aldrich Chemical Company.

Also, the possibility was investigated that singlet oxygen, an excited form of oxygen¹⁹ (Trozzollo, 1971), may play a role in the light-induced decomposition of methoxychlor in natural waters. Our results indicated that both methoxychlor and DMDE are unreactive towards singlet oxygen.

Other possible mechanisms were not investigated, although the exciplex mechanism suggested by Miller and Narang²⁰ for the amine-induced photolysis of DDT is one attractive possibility. Alternatively, decomposition of methoxychlor may result from attack by free radicals generated by photolysis of materials in the natural water. The latter is a common mechanism for indirect photolysis in the atmosphere²¹.

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SECTION XI

RESULTS & DISCUSSION: CAPTAN

HYDROLYSIS

Several reports dealing with the stability of captan in water have appeared in the literature. Melnikov¹ reported the products of captan hydrolysis are 4-cyclohexene-1,2-dicarboximide (THP), carbon dioxide, hydrochloric acid, and elemental sulfur. Daines *et al*². reported similar products, but instead of sulfur, they reported hydrogen sulfide as a product. Daines *et al*². also reported that hydrolysis of captan in a 2% slurry occurred rather slowly at temperatures below 110°F, but above 110°F hydrolysis was rapid. Von Rumker and Horay³ reported that captan half-life decreased with increasing pH. The half-life at pH 4 (20°) was 4 hours and at pH 10 (20°) less than two minutes. They found decreased half-lives at 40°.

Interest in the chemical reactivity of captan is exemplified by the considerable attention placed on the reaction of captan with thiols. Several of these studies will be reinterpreted in view of our hydrolysis studies. We investigated the rate of hydrolysis of captan in detail and compared it with two other trichlorothiometl containing fungicides, folpet and captafol (Figure 36).

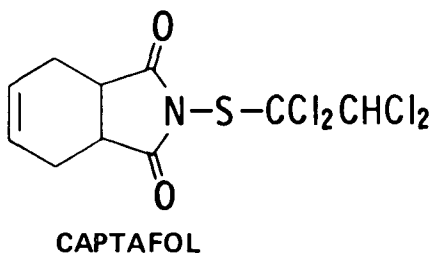
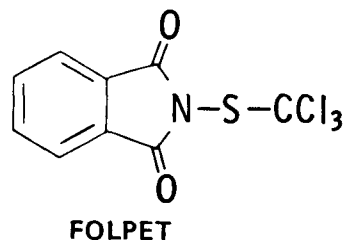
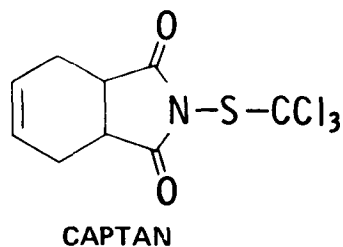


Figure 36. Chemical structures of captan, folpet, and captafol

Kinetic studies employed a glc method to determine the concentration of captan at various time intervals. With column temperatures above 200°, a second peak with a shorter retention time appeared in the chromatogram; since both peak sizes varied with each sample injection, captan was assumed to be decomposing. By using a short column (2') and a column temperature of 160°, the anomalous peak was eliminated. The linearity of response under these conditions over the concentration range of 1.2×10^{-5} M to 1.6×10^{-6} M is shown in Figure 37 as a plot of peak area vs. concentration.

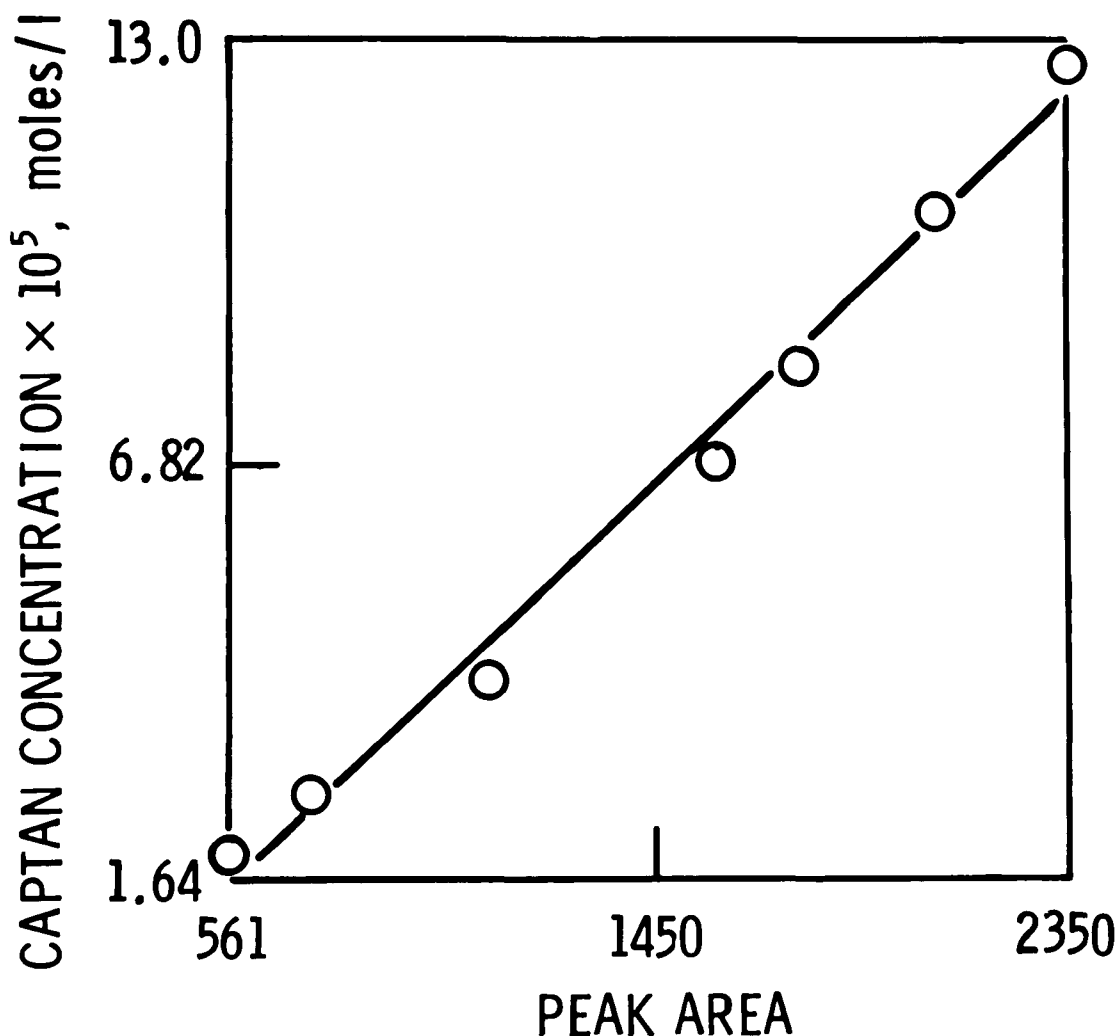


Figure 37. Standard curve for captan response to electron capture detector

It was necessary to add captan to the aqueous solutions with a carrier solvent (acetonitrile) because the rate of solution for water was slow compared to the rate of

hydrolysis. In a separate kinetic experiment the concentration of acetonitrile was reduced with no detectable effect on the rate constant. Thus the 1% organic solvent was not anticipated to have a pronounced effect on the rate constant when compared to water.

Kinetic Studies

Captan (1×10^{-4} M) was first hydrolyzed in an open vessel in non-buffered water (5% acetonitrile) and captan concentration along with pH was followed as a function of time. The results are shown graphically in Figure 38. As captan hydrolyzes the pH of the solution decreases indicating acidic product formation. Also the decrease in pH apparently retards the rate of captan degradation.

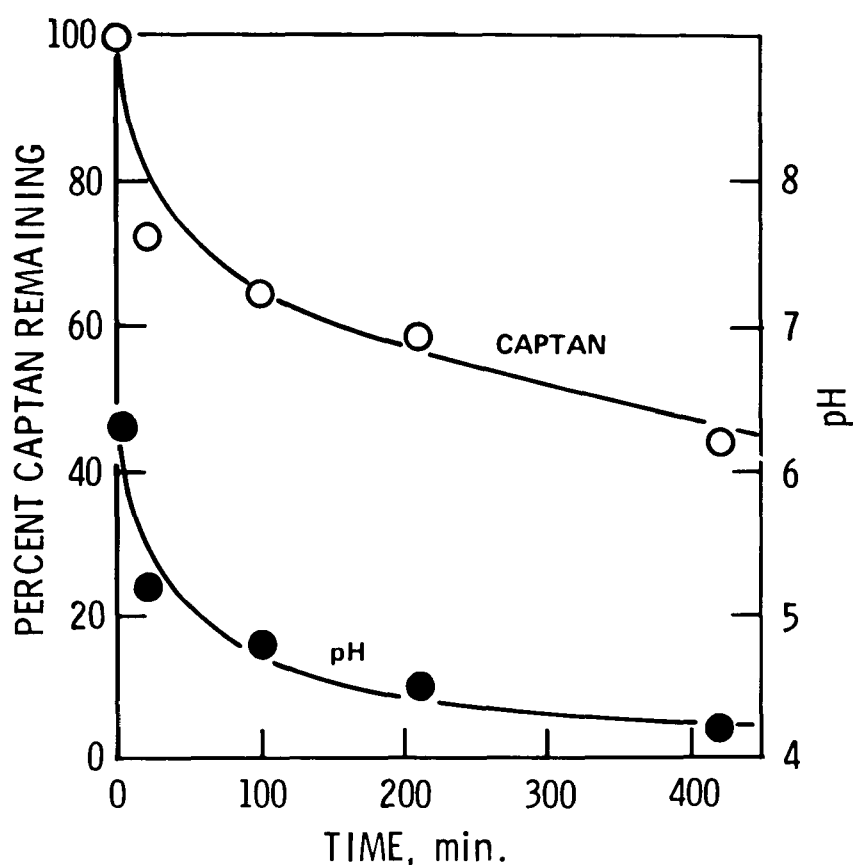


Figure 38. Captan concentration and pH vs. time in non-buffered water at 28°C

Because acidic products altered the pH of the reaction solution, captan kinetic studies were done under pH buffered reaction conditions. These studies were carried out over the

range of pH 2 to pH 8 to evaluate the contributions of acid, base, and water.

Plots of log concentration vs. time are shown in Figure 39 for captan, folpet, and captafol in the buffered pH range of 7.0-7.2. These plots are linear through at least one pesticide degradation half-life and indicate pseudo-first-order reaction conditions. Similarity of the chemical structure of these three pesticides suggests the rates of hydrolysis would be similar. The pseudo-first-order rate constants at 28° are: captan, $k_{\text{obsd}} = 6.5 \times 10^{-5} \text{ sec}^{-1}$ (pH 7.07); folpet, $k_{\text{obsd}} = 1.4 \times 10^{-4} \text{ sec}^{-1}$ (pH 7.14); captafol, $k_{\text{obsd}} = 7.7 \times 10^{-5} \text{ sec}^{-1}$ (pH 7.17).

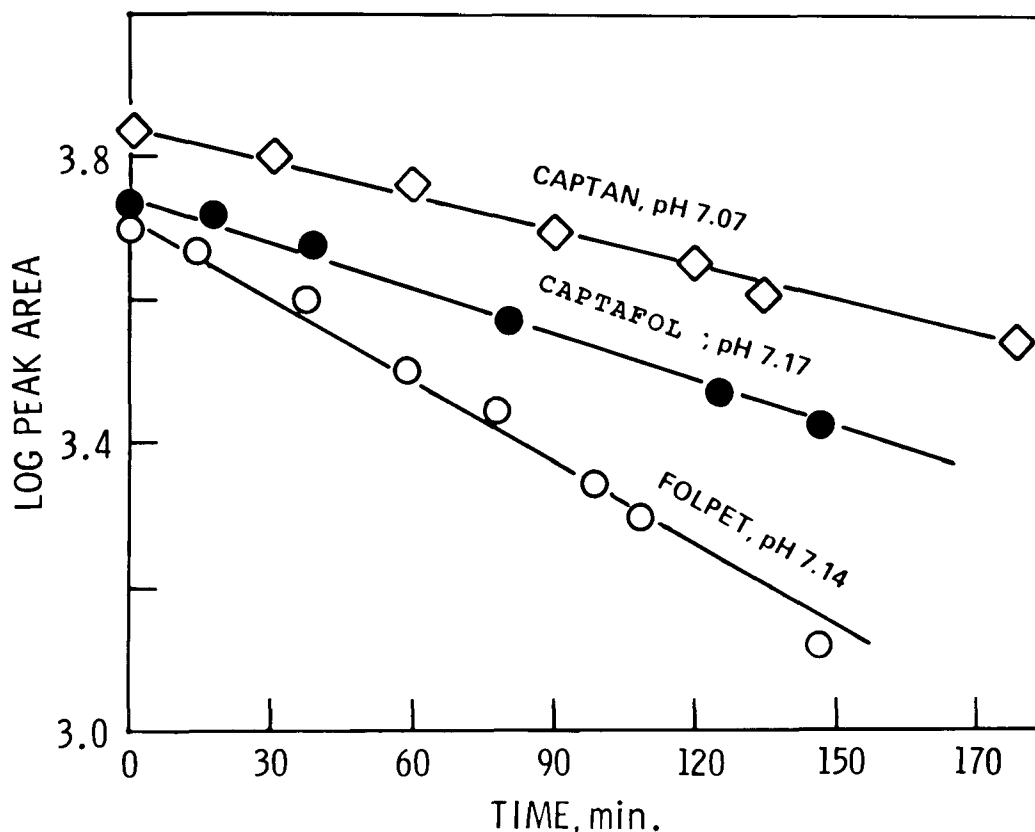


Figure 39. Pseudo-first-order plots for the hydrolysis of captan, folpet, and captafol

The hydrolysis studies for captan were extended to other pH's to determine the contribution of acid and alkaline degradation and to evaluate the contribution of water. Table 21 lists the pseudo-first-order rate constants at the various pH values studied and the buffers employed. The data are plotted in Figure 40 as log k vs. pH to give a pH-rate

Table 21. PSEUDO-FIRST-ORDER RATE CONSTANTS FOR CAPTAN HYDROLYSIS
AT SEVERAL pH's AND TEMPERATURES

Temp	pH	k(sec ⁻¹)	Buffer or Acid
8°	8.39	(1.49 ± 0.03) x 10 ⁻⁴	H ₂ BO ₃ /NaOH
28°	1.97	(1.79 ± 0.06) x 10 ⁻⁵	HCl
	2.48	(1.67 ± 0.08) x 10 ⁻⁵	
	3.39	(1.87 ± 0.08) x 10 ⁻⁵	
	4.83	(1.97 ± 0.08) x 10 ⁻⁵	NaOAc/HOAc
	5.16	(1.87 ± 0.09) x 10 ⁻⁵	
	6.10	(4.6 ± 0.3) x 10 ⁻⁵	Na ₂ HPO ₄ /NaHPO ₄
	7.07	(6.5 ± 0.5) x 10 ⁻⁵	
	7.45	(1.5 ± 0.1) x 10 ⁻⁴	
	7.66	(2.81 ± 0.2) x 10 ⁻⁴	
	7.82	(3.9 ± 0.1) x 10 ⁻⁴	H ₂ BO ₃ /NaOH
	7.93	(4.8 ± 0.2) x 10 ⁻⁴	
	8.08	(6.5 ± 0.1) x 10 ⁻⁴	
	8.25	(1.1 ± 0.1) x 10 ⁻³	
48°	3.3	(3.57 ± 0.09) x 10 ⁻⁴ ^a	HCl

Acid		Base	
ΔH [‡]	28.8 ± 0.7 kcal/mole	ΔH [‡]	22.8 ± 1.6 kcal/mole
ΔS [‡]	13.0 ± 2.5 eu	ΔS [‡]	2.2 ± 5.4 eu

^aAverage of two values.

profile. Between pH's 2 and 5 there is no change in the pseudo-first-order rate constant with pH as the slope of the line is essentially zero. Above pH 7 the pseudo-first-order rate constant increases with increasing pH and the slope of the line is +1. In the pH range 6-7 the plot is not linear due to competing reactions of captan with water and hydroxide.

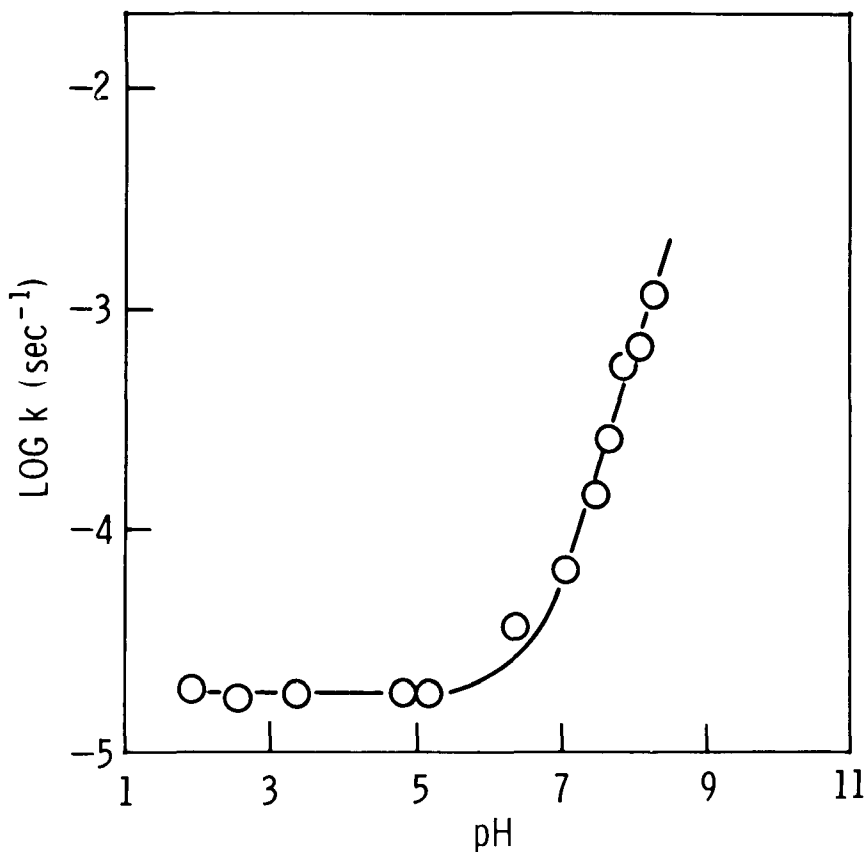


Figure 40. Plot of log k vs. pH for captan hydrolysis at 28°C in buffered aqueous solution

Based on this interpretation of hydrolysis the rate of disappearance of captan under buffered reaction conditions is given by

$$-\frac{d[\text{captan}]}{dt} = k_{\text{H}_2\text{O}}[\text{captan}] + k_{\text{OH}^-}[\text{captan}][\text{OH}^-] \quad (66)$$

where [captan] is the captan concentration, [OH] is the hydroxide ion concentration, $k_{\text{H}_2\text{O}}$ is the pseudo-first-order rate constant for reaction with water and k_{OH^-} is the second-

It was not possible to determine the solubility of captan in water even at low pH's because the rate of hydrolysis is fast enough over the pH range investigated to compete with the rate of solution. When 10 mg of finely divided captan was stirred in 100 ml of water for 16 hours at room temperature, no captan could be detected in the water down to 10^{-6} M concentration. Thus, it appears that for captan the hydrolysis half-life in aquatic systems will be influenced by its rate of solution.

Hydrolysis was also studied in the presence of thioethanol at 1.2×10^{-5} M captan, 1×10^{-3} M thiol, and pH 3.64. The reaction followed first-order kinetics through at least one half-life, but then deviated from first-order kinetics as was shown by an increase in the rate constants during the second half-life. The effect of the thioalcohol was not further investigated and has not been interpreted.

Natural Water Study

To determine if any chemical species in the aquatic environment would alter the kinetics of reaction, we carried out the hydrolysis in a natural water sample obtained from the Tombigbee River, South Carolina (pH 7.0). A plot of the data (Figure 42) shows that degradation follows pseudo-first-order kinetics. While this is only one natural water sample, the half-life is in good agreement with the laboratory data (170 min. measured vs. 155 min. calculated).

Product Studies

To facilitate analysis for products the concentration of captan was increased to 2×10^{-4} M by employing 10% acetonitrile-water as the solvent. At the end of 10 half-lives at pH 9.0 an aliquot of the reaction solution was qualitatively analyzed for chloride. The addition of silver nitrate resulted in formation of a white precipitate interpreted to be silver chloride, thus indicating chloride as a reaction product. The addition of mercuric chloride to a separate aliquot did not produce a precipitate. Thus sulfide or thiols are not products. Also hydrogen sulfide and carbon disulfide could not be detected in the reaction solution by glc-ms analysis of the toluene extracts of a separate aliquot.

Extraction at pH 9.0 with chloroform gave 4-cyclohexene-1,2-dicarboximide (THP). This was identified by glc retention time, melting point, ir spectra, and mass spectral data.

order rate constant for reaction with hydroxide ion. The average pseudo-first-order constant (k_{H_2O}) for the reaction of captan with water in the pH range 2-6 is $(1.8 \pm 0.1) \times 10^{-5} \text{ sec}^{-1}$. The average second-order-rate constant (k_{OH^-}) for alkaline hydrolysis in the pH range 7-9 is $(5.7 \pm 0.4) \times 10^2 \text{ M}^{-1} \text{ sec}^{-1}$.

Computed from the above rate constants and equation 6, a pH-half-life profile is shown in Figure 41. It is apparent from this diagram that the maximum hydrolysis half-life for captan is about 1/2 day. While folpet and captafol were not included in these detailed pH studies, it is anticipated that they would give similar pH-rate profiles.

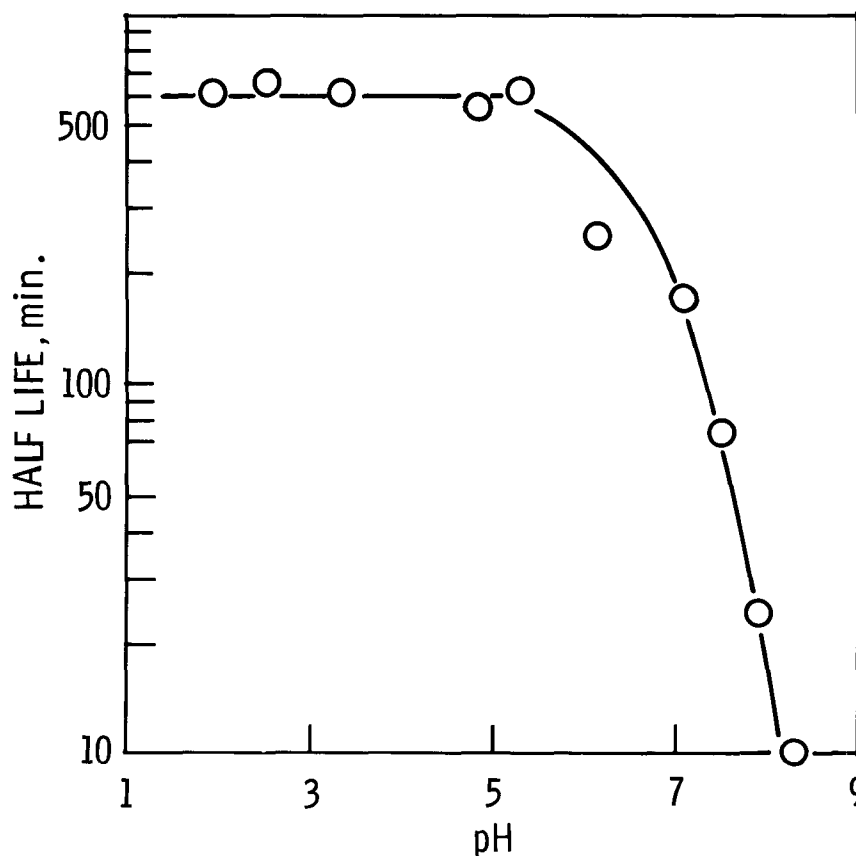


Figure 41. pH-half-life profile for captan hydrolysis in water at 28°C

The temperature effect was determined for both the neutral and alkaline contributions. The activation parameters are included in Table 21. As anticipated the rates of both reactions increase with increasing temperature.

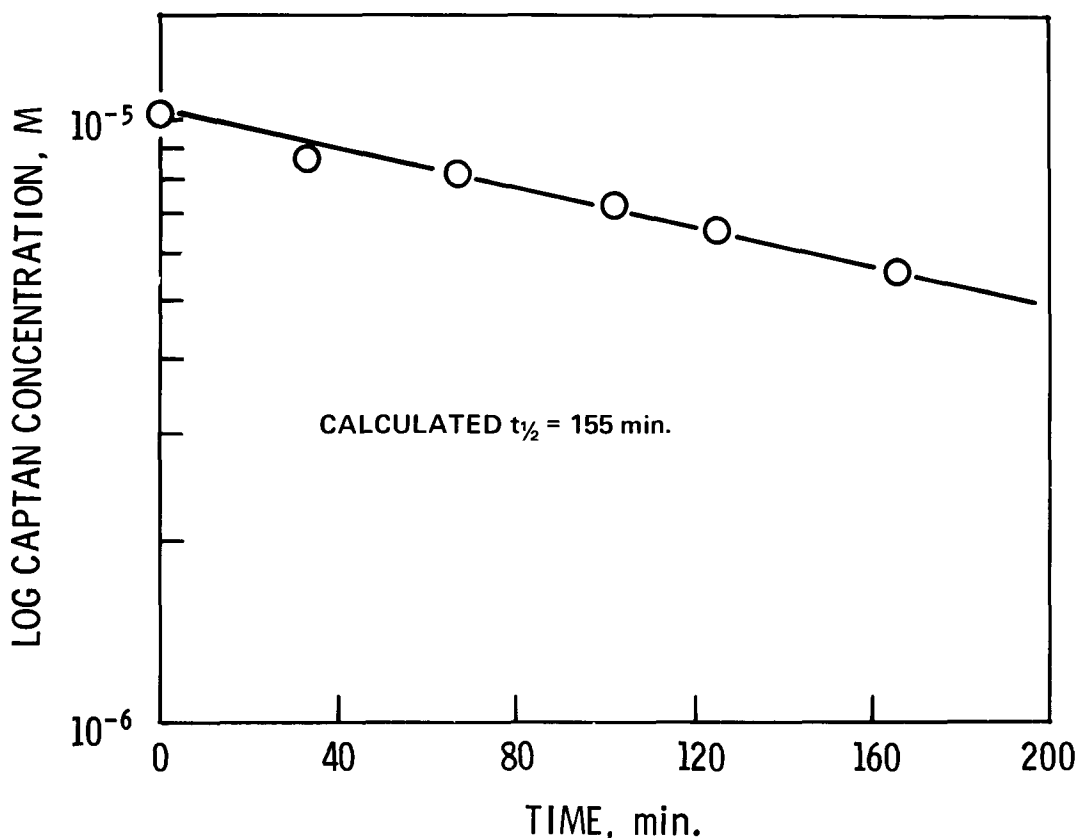


Figure 42. Degradation of captan in water from the Tombigbee River

Subsequent acidification (pH 2.5) and extraction of the reaction mixture with chloroform gave a residue which resisted crystallization. The ir spectrum of this residue differed from that of the THP, but the solid probe mass spectra were compatible with a mixture of elemental sulfur and imide. The gas-liquid chromatogram of the residue had two peaks, whose mass spectra were identical to that of THP and 4-cyclohexene-1,2-dicarboxylic anhydride. The latter may have formed as a result of thermal decomposition of proposed intermediates. Major products that were identified are summarized in Figure 43.

Pathway of Degradation.

Captan has three different functional groups, the trichloromethyl, sulfenimide, and carboxyl groups, which are labile to hydrolysis; the reactivity of these groups should be considered when invoking a degradative pathway. Based on hydrolysis data for phthalimide⁴, the carboxyl functional

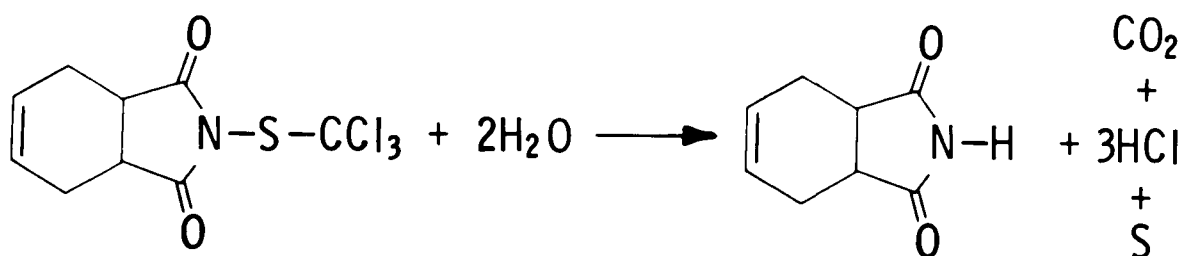


Figure 43. Major products for the hydrolysis of captan

groups of captan would not react under our experimental conditions. On the other hand other compounds with sulfenimide and trichloromethyl groups undergo hydrolysis readily.

We have considered two reaction pathways for captan hydrolysis similar to the heterolytic mechanism proposed by Owens and Blaak⁵ for the reaction of captan with thiols (Figures 44 and 45). The first pathway (Figure 44) involves hydrolysis of the trichloromethyl moiety by nucleophilic substitution of chloride by water or hydroxide⁶. Consideration of this pathway is based on literature hydrolytic data for similar trichloromethyl compounds which are readily hydrolyzed. For example, methyl trichloromethyl ether⁷, trichloromethyl mercaptan⁸, and trichloromethyl benzene⁹ react by this mechanism. In the case of captan rapid nucleophilic substitution and subsequent decarboxylation would give the THP and sulfur as products. The general reaction pathway is outlined in Figure 44 where we have considered only the overall pathway.

The second pathway to be considered (Figure 45) involves nucleophilic substitution at sulfur¹⁰. Sulfenimides are cleaved by acid and alkali to give the free imide and sulfenic acid^{11,12,13}. For captan the primary products would be THP and the unstable trichloromethyl sulfenic acid intermediate¹¹, which would rapidly decompose to hydrogen sulfide and carbon dioxide via the reactive intermediates, thiophosgene and carbonyl sulfide. Trichloromethyl sulfenic acid was the postulated intermediate in the hydrolysis of trichloromethyl sulfenyl chloride to hydrogen sulfide and carbon dioxide¹¹.

Based on our kinetic data one cannot distinguish between the two mechanisms outlined above. Both pathways are compatible with the rate determining step as the reaction of water or hydroxide with either the trichloromethyl or sulfenimide sulfur.

The products that we found are consistent with the mechanism in Figure 44 and are the same as those reported by Melnikov¹. However, we were not able to verify this pathway by isolating or spectrally identifying any of the proposed intermediates. Any intermediates formed by the reaction with water or thiols are very reactive and would have short life times in the aquatic environment. The end products of degradation with the exception of the THP are naturally occurring compounds and would likely have little impact on the environment.

Conclusions

Captan undergoes degradation in water with a maximum hydrolysis half-life of 1/2 day. The reaction is pH independent over the pH range 2-6 and pH dependent from pH 6 to 9. The products of the reaction were identified as sulfur, chloride, and THP. Hydrolysis of captan, as well as of folpet and captafol, is very fast and is likely to be the predominate pathway of degradation in the aquatic environment.

PHOTOCHEMISTRY

Our studies indicated that direct photolysis of captan cannot compete with its rapid hydrolysis, even when we employed ultraviolet light that is 80 times more intense than sunlight. This being the case, no attempt was made to characterize direct photolysis products. The hydrolysis product of captan, THP, is also unreactive due to lack of sunlight absorption.

Although their direct photolysis is unimportant, light may play a role in the decomposition of captan and THP. Sunlight may accelerate the autooxidation of these compounds (Figure 46); cyclohexene itself is autooxidized to an allylic hydroperoxide¹⁴. Captafol, another cyclohexene derivative (Figure 36), may be oxidized in a similar fashion.

Although cyclohexene itself reacts very slowly with singlet oxygen¹⁵, our studies revealed that captan and THP are quite reactive. β values for both compounds were determined by measuring quantum yields (578 nm) at various concentrations (Figure 10)¹⁵; methylene blue was employed as photosensitizer. A representative plot of the data for captan is shown in Figure 47; β values are determined from the slopes of such plots (Figure 10). The photosensitized oxygenations of captan and THP were efficiently quenched by 1,4-diazabicyclooctane (DABCO),¹⁶ and by β -carotene,¹⁷ confirming that the reactions were mediated by singlet oxygen (Figure 48). Comparison of our data with those of Foote¹⁵ (Table 22) indicates that

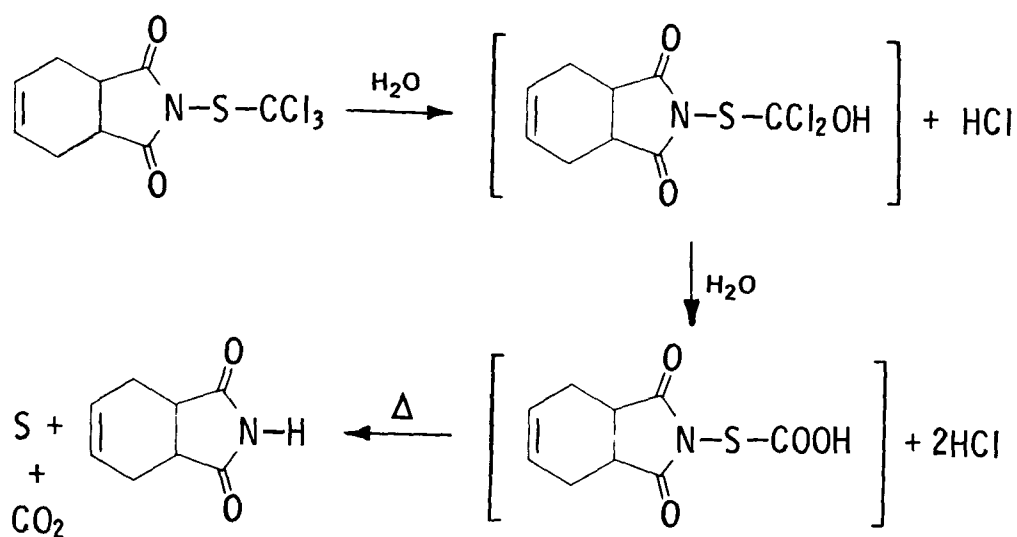


Figure 44. Mechanism for hydrolysis of captan that involves nucleophilic displacement of chloride

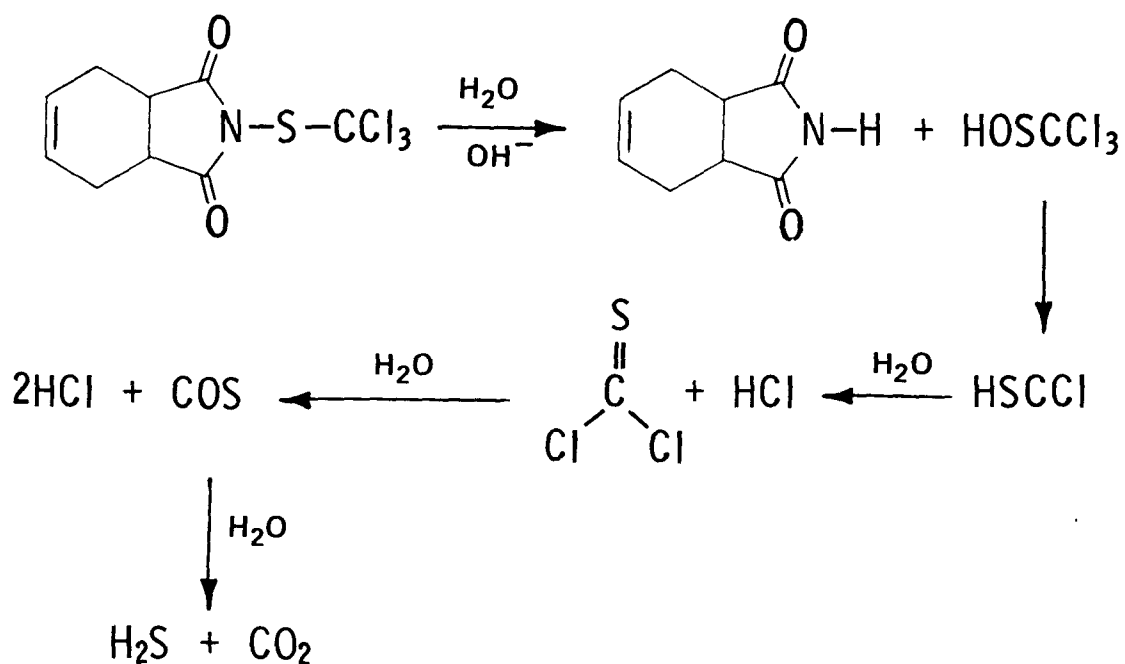


Figure 45. Mechanism for hydrolysis of captan involving nucleophilic substitution at the sulfur atom

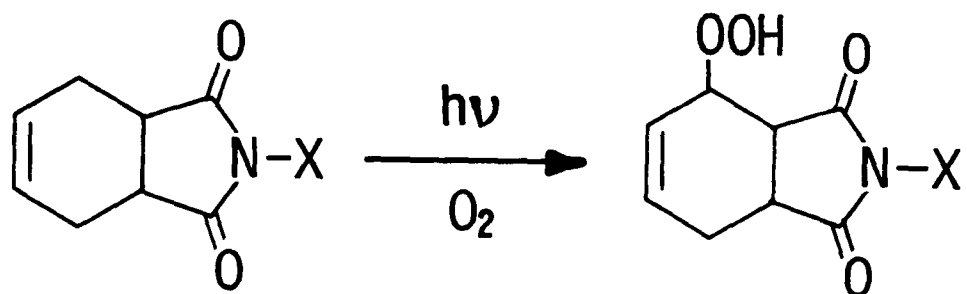


Figure 46. Postulated products for light-initiated autooxidation of captan and 4-cyclohexene-1,2-dicarboximide

captan and THP are 42 times more reactive than cyclohexene. The relatively high reactivities of captan and THP are attributed to conformational effects.

Table 22. SINGLET OXYGEN REACTIVITIES OF CAPTAN, 4-CYCLOHEXENE-1,2-DICARBOXIMIDE, AND CYCLOHEXENE

Acceptor	β, M		
	Acetonitrile	Methanol	Water
Captan	0.30	(1.3) ^b	4.5
4-Cyclohexene-1,2-dicarboximide	0.30	(1.3) ^b	4.5
Cyclohexene ^a	--	55	-

^aTaken from Reference 15. ^bCalculated assuming β values is 4.3 times greater than in acetonitrile than in methanol (Ref. 19).

Photooxygenation products of captan and its hydrolysis products included allylic hydroperoxides derived from the well documented "ene" reaction of olefins¹⁵ (Figure 49). The hydroperoxides were reduced to corresponding alcohols by triethylphosphite. Note that these products differ from the

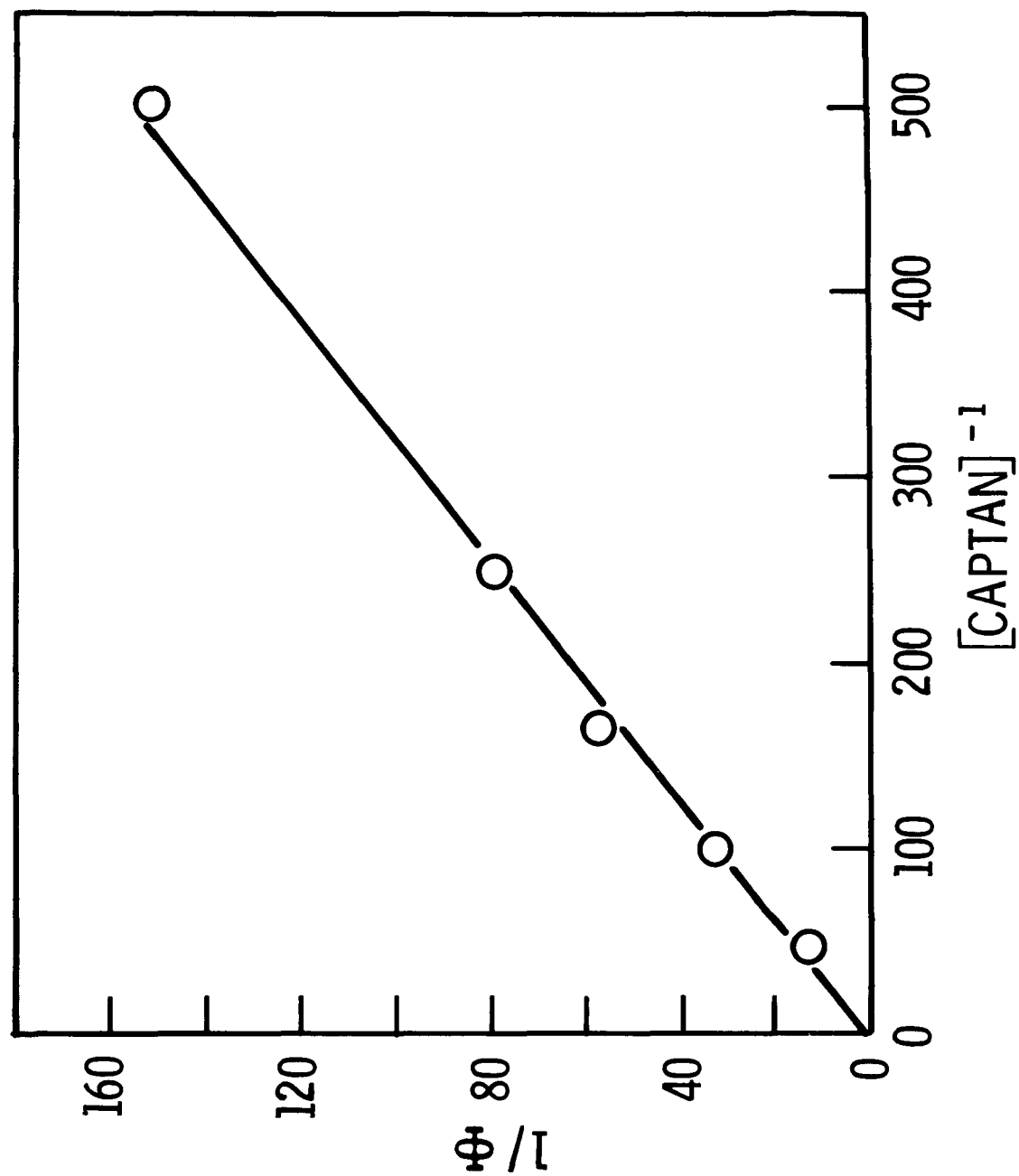


Figure 47. Concentration dependence of the quantum yield for reaction of captan with singlet oxygen in acetonitrile

autooxidation products (Figure 46). Folpet, shown in the lower part of Figure 46, was not readily oxidized by singlet oxygen ($\beta > 11$ in acetonitrile), indicating that the trichloromethylthio moiety in captan is unreactive towards singlet oxygen. Photooxygenation of captan in acetonitrile also led to formation of THP and other minor unidentified products. We postulate that these products result from reaction of unreacted captan with the hydroperoxide products.

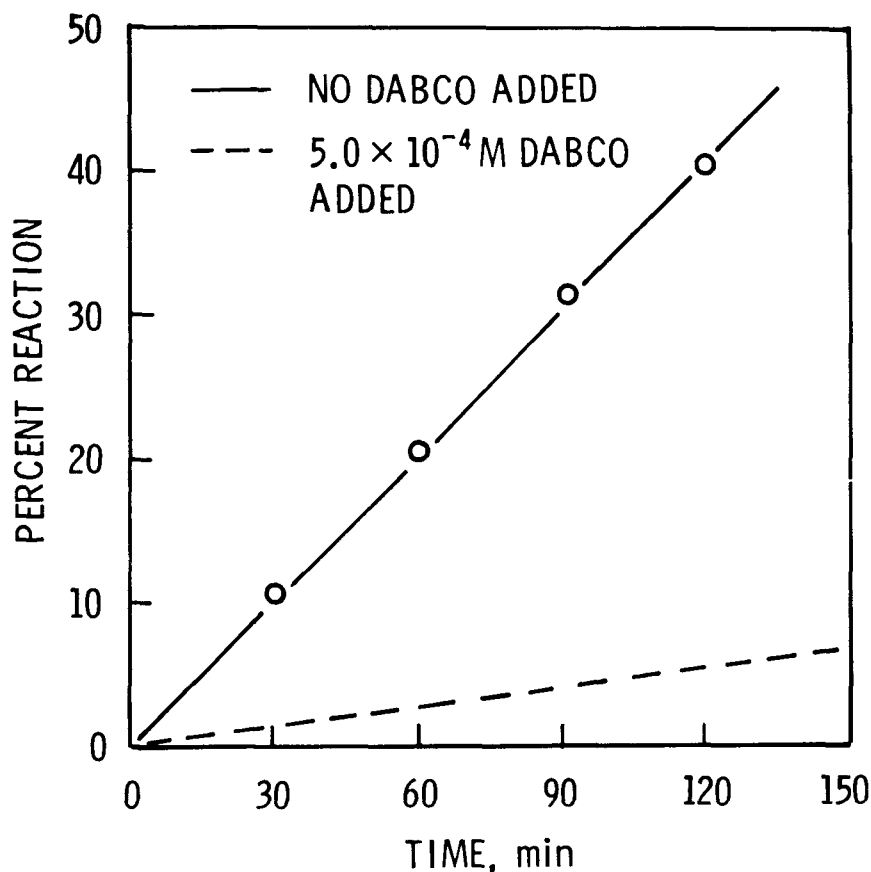


Figure 48. Effect of 1,4-diazabicyclooctane upon the photosensitized oxygenation of captan

Because singlet oxygen reactions can be sensitized by substances in the environment such as chlorophyll¹⁸ that adsorb the intense visible and/or near infrared portion of sunlight, it is possible that these reactions are important under natural conditions.

We found that the half-life of captan (10^{-5} M) in water (pH 5) containing 10^{-4} M methylene blue was only 45 min, under midday, summer sunlight. The hydrolysis half-life measured in a dark control was about 9 hours (Figure 41), indicating that

photooxidation accounted for most of the degradation under sunlight. In a highly colored natural water sample (pH 4.7) from the Suwanee River, the degradation rate of captan under midday sunlight was about 30% more rapid than in the dark. The lower photooxidation rate in the river water was probably mainly due to the presence of phenolic humic materials; phenols efficiently inhibit photooxidations involving singlet oxygen¹⁷. The latter results indicate that hydrolysis of captan is probably more rapid than photooxidation in natural waters. Photooxidation of captan on leaf, fruit, or soil surfaces may be important, however.

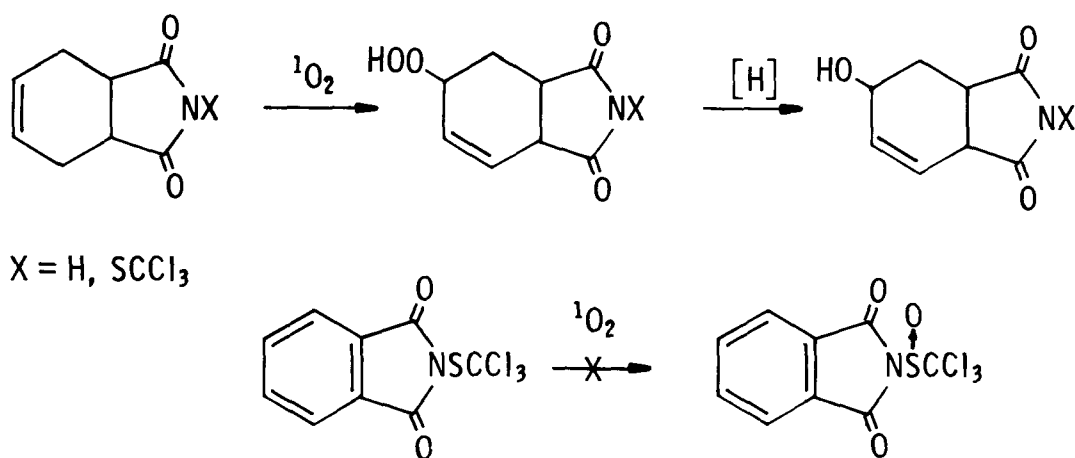


Figure 49. Products from the reaction of captan and 4-cyclohexene-1,2-dicarboximide with singlet oxygen

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SECTION XII

RESULTS AND DISCUSSION: CARBARYL

HYDROLYSIS

Aly and El-Dib¹ reported the hydrolysis of carbaryl along with several other carbamate pesticides, whose structures are shown in Figure 50. They carried out hydrolysis studies under non-buffered reaction conditions over the pH range 4.0 to 10.0 and at various temperatures. The second-order rate constants for these four compounds at 20° are given in Table 23. They reported that carbaryl was stable over the pH range of 3.0-6.0.

Wauchope and Haque² also determined the second-order rate constant for carbaryl in unbuffered water. They report a second-order rate constant of $3.4 \times 10^2 \text{ M}^{-1} \text{ min}^{-1}$ at 25° which is in good agreement with the value reported by Aly and El-Dib, corrected for the temperature difference. Karinen *et al.*³ reported a second-order rate constant of $1.4 \times 10^2 \text{ M}^{-1} \text{ min}^{-1}$ in sea water at 20°. We carried out the hydrolysis of carbaryl under buffered pseudo-first-order reaction conditions at 27° and pH 9.52 (phosphate buffer). The second-order rate constant was found to be $(3.61 \pm 0.02) \times 10^2 \text{ M}^{-1} \text{ min}^{-1}$, in good agreement with the value reported by Aly and El-Dib.¹ Using these data we calculated hydrolysis half-lives for carbaryl at pH values normally found on lakes and rivers (Table 24). Hydrolysis is anticipated to be an important degradation pathway in basic natural waters, but in acidic natural waters hydrolysis is extremely slow.

Table 23. KINETIC PARAMETERS FOR HYDROLYSIS OF CARBARYL AND SEVERAL OTHER CARBAMATE PESTICIDES AT 20°. ¹

Pesticide	$k_{\text{OH}^-} (\text{M}^{-1} \text{ min}^{-1})$	$E_a (\text{kcal/mole})$
Carbaryl	2.04×10^2	16.9
Baygon	3.04×10	15.8
Pyrolan	7.0×10^{-1}	13.7
Dimetilan	3.4×10^{-3}	14.0

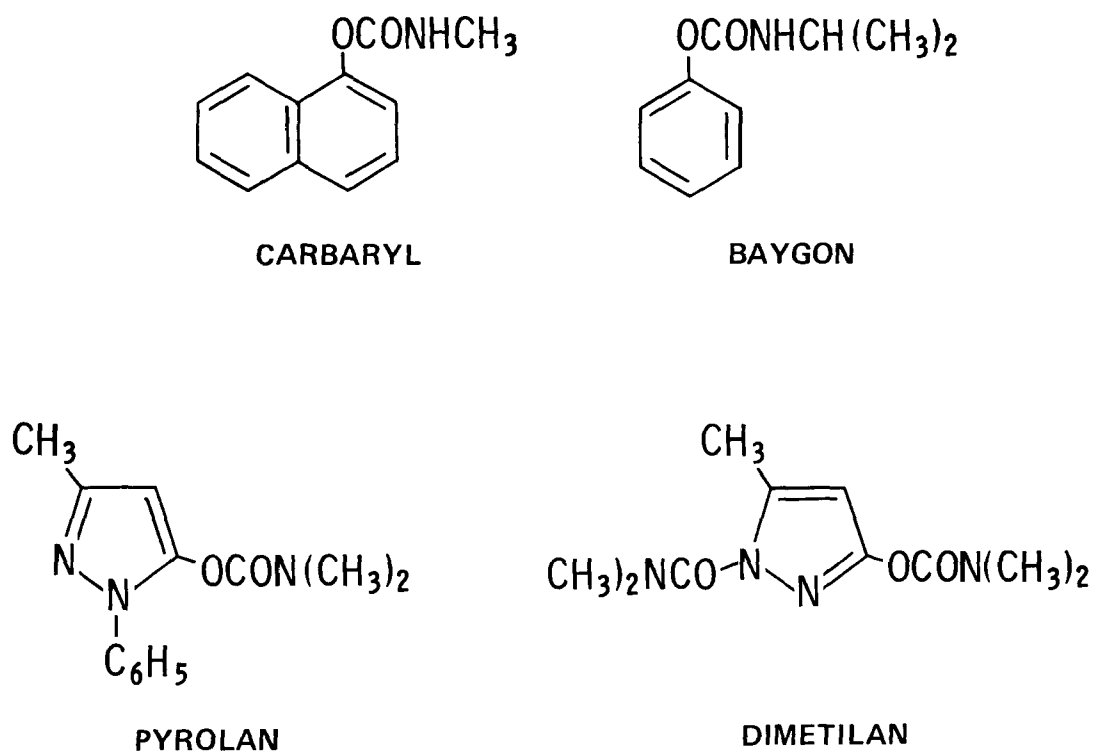


Figure 50. Chemical structures of carbaryl and other carbamate pesticides

Table 24. HYDROLYSIS HALF-LIVES FOR CARBARYL AT pH-VALUES USUALLY FOUND IN THE AQUATIC ENVIRONMENT (27°C) .

pH	Half-life
9	3.2 hrs
8	1.3 days
7	13 days
6	4.4 months
5	3.6 years

OXIDATION

The oxidation of carbaryl under environmental reaction conditions was not anticipated to be significant in view of

its chemical and photochemical reactivity. The product of hydrolysis 1-naphthol, however, would be very readily oxidized.

Wauchope and Hague² reported that the 1-naphthoxide ion (3×10^{-4} M) in room light undergoes photooxidation to give 2-hydroxy-1,4-naphthoquinone.⁶

PHOTOCHEMISTRY

Considering the widespread usage of carbaryl and its reported alteration by sunlight,⁷ we were surprised to find that relatively little is known about its direct photolysis. Crosby and co-workers reported that carbaryl photoproducts include 1-naphthol, methyl isocyanate, and other unidentified cholinesterase inhibitors.^{7,8} Aly and El-Dib reported that some of the photoproducts from carbaryl in water have the same chromatographic retention time as photoproducts of 1-naphthol.⁹ One of the photoproducts from 1-naphthol in air-saturated basic water was found to be 2-hydroxy-1,4-naphthoquinone⁶.

The lack of data concerning carbaryl photoproducts prompted us to look elsewhere for data concerning photolysis of aryl carbamates. Trecker, Foote, and Osborn¹⁰ reported that *p*-tolyl-N-methylcarbamate undergoes a photoreaction similar to the photoFries reaction of aryl esters and anilides¹¹ (Figure 51). Recently, in a series of papers, Silk, Unger, and their co-workers have published results which indicate that the photo-Fries type rearrangement occurs with several carbamate insecticides¹²⁻¹⁵ (Figure 51). These photolyses also yielded brown polymeric substances which were not identified.

The above studies prompted us to synthesize the potential photo-Fries products of carbaryl, N-methyl-1-hydroxy-2-naphthamide and N-methyl-4-hydroxy-1-naphthamide. Careful examination of photolysis mixtures revealed that no more than trace amounts of these products were formed in either methanol or water. Our studies also indicated that 1-naphthol and methyl isocyanate are not products of the direct photolysis (> 290 nm) of carbaryl in either degassed or air-saturated methanol and water (pH 5.5). We analyzed for 1-naphthol by liquid chromatography on a Permaphase ODS column.¹⁶

Control experiments indicated that methyl isocyanate reacts rapidly with methanol to form methyl N-methylcarbamate (eq. 67). However, no methyl N-methyl carbamate was detected (by gas-liquid chromatography), in photolyzed solutions of carbaryl (0.01 M in methanol).

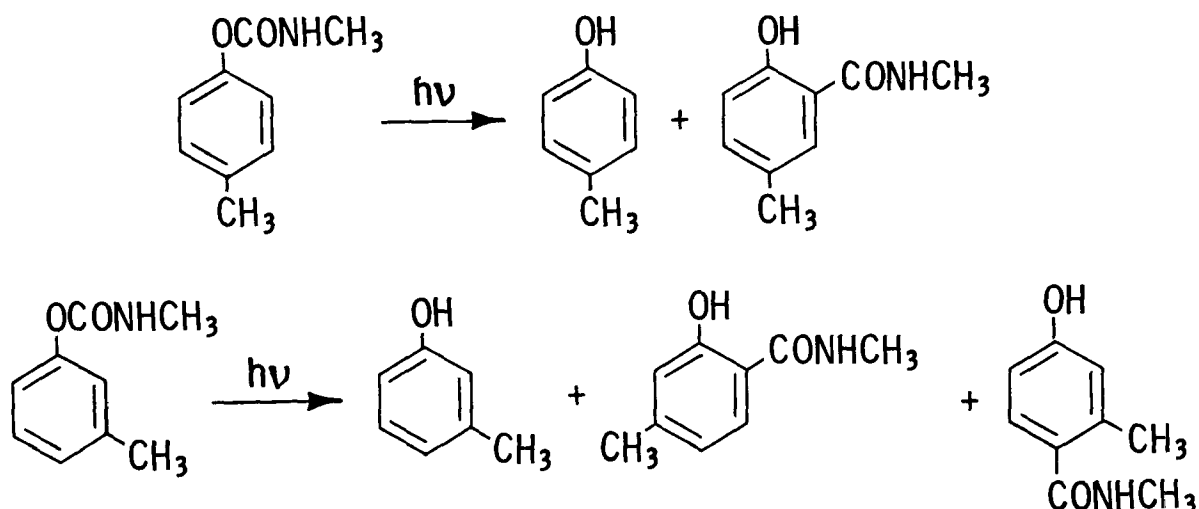
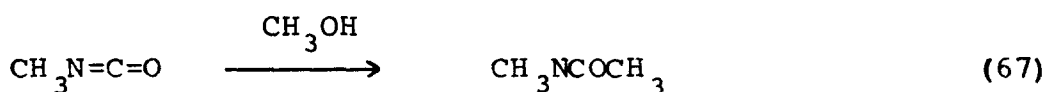


Figure 51. Photoreactions of substituted phenyl N-methyl carbamates



At present, we cannot explain the differences between our results and those reported by others⁷⁻⁹. We did not identify the photoproducts but we have found the following:

- The products from photolysis in methanol and water are non-volatile. Methylation by ethereal diazomethane produces no products detectable by gas chromatography.
- Highly-colored products form in air-saturated water. The colored products do not form in air-free solutions.

Kinetic studies of carbaryl indicated that its photolysis rate under sunlight is rapid compared to other pesticides that we examined. The quantum yields under various reaction conditions are summarized in Table 25. The data indicated that the photolysis is slowed by the presence of oxygen and is pH-independent in the pH 5 to 7 range. Calculated half-lives for the direct photolysis of carbaryl near the surface of a water body are summarized in Table 26. Experiments under midday summer sunlight (June, lat. 34° N) yielded data that were in reasonable agreement with the calculated half-lives for lat 30° and 40° N; the half-life was found to be about 45 hours in distilled water buffered at pH 5.5. Dark controls showed no decomposition. Although the quantum yield for carbaryl photolysis is low, its rapid absorption of sunlight results in facile photoalteration.

Other studies indicated that carbaryl is not readily photooxidized by singlet oxygen in water ($\beta > 37.5$).

Table 25. QUANTUM YIELDS FOR PHOTOLYSIS OF CARBARYL AT 25°C (313nm) IN WATER

Reaction Conditions	Disappearance Quantum Yields
Degassed, pH 5.5	0.016
Air-saturated, pH 5.5	0.0056
Air-saturated, pH 5.2	0.0052
Air-saturated, pH 6.1	0.0058
Air-saturated, pH 6.9	0.0055

Table 26. CALCULATED DIRECT PHOTOLYSIS HALF-LIVES OF CARBARYL AT DIFFERENT SEASONS AND LATITUDES IN THE NORTHERN HEMISPHERE.

Latitude, °N	Half-life, hrs ^a			
	Spring	Summer	Fall	Winter
0	43	45	41	43
30	51	46	68	103
40	64	52	102	200
50	90	61	186	571
70	292	121	1760	43800

^a Calculated for mid-season and for depths of < 10 cm in pure water.

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SECTION XIII

RESULTS AND DISCUSSION: ATRAZINE

HYDROLYSIS

Reports of atrazine hydrolysis in the literature have been primarily concerned with soil degradation studies. Several studies indicate that chemical degradation appears to be a significant breakdown route. Obien and Green¹ found that the rate of degradation of atrazine was dependent on soil pH and temperature and invoked chemical degradation as being more significant than biological degradation. Zimdahl *et al.*² investigated atrazine degradation in soils and postulated that atrazine was first converted non-enzymatically to the 2-hydroxy derivative as the first step in soil degradation. Skipper *et al.*³ evaluated chemical vs. microbial degradation in soils and concluded that chemical degradation of atrazine was largely dependent on chemical hydrolysis to hydroxyatrazine.

Armstrong and co-workers⁴⁻⁵ investigated atrazine hydrolysis in soils and determined the rates of degradation of atrazine under acidic and alkaline conditions. Table 27 contains the pseudo-first-order rate constants calculated from half-life data obtained from the graphs in reference 4. The average value of the second-order rate constant for acid hydrolysis is $3.4 \times 10^{-5} \text{ M}^{-1} \text{ sec}^{-1}$. For alkaline degradation, the average value for the second-order rate constant is $6.5 \times 10^{-5} \text{ M}^{-1} \text{ sec}^{-1}$. It was not possible to evaluate any contribution by water from these data. Based on work by Harrobin⁶, who studied some chloro-1,3,5-triazines, the hydrolysis contributions by water is probably negligible.

Our preliminary studies on the hydrolysis of atrazine were in agreement with the data reported by Armstrong *et al.* For acid and alkaline hydrolysis, the second-order rate constants were $3.9 \times 10^{-5} \text{ M}^{-1} \text{ sec}^{-1}$ and $7.6 \times 10^{-5} \text{ M}^{-1} \text{ sec}^{-1}$, respectively. Thus, it appears that alkaline hydrolysis is about two times more rapid than acidic hydrolysis. The overall reaction is given in Figure 52.

PHOTOCHEMISTRY

Most of the work on direct photolysis of *s*-triazine pesticides has been reported by Zabik and his co-workers⁷⁻⁹.

Table 27. HALF-LIVES AND RATE CONSTANTS FOR HYDROLYSIS OF ATRAZINE^a

pH	Half-life (days)	k_{obsd} (sec ⁻¹) ^{b, c}	k_{H^+} (M ⁻¹ sec ⁻¹) ^d	k_{OH^-} (M ⁻¹ sec ⁻¹) ^d
1.3	5.1	1.6×10^{-6}	3.1×10^{-5}	
2.2	18.4	4.3×10^{-7}	6.9×10^{-5}	
3.1	66.4	1.2×10^{-7}	1.5×10^{-4}	
11.1	81.1	9.9×10^{-8}		7.6×10^{-5}
11.9	15.2	5.3×10^{-7}		6.7×10^{-5}
12.9	12.9	4.2×10^{-6}		5.3×10^{-5}

^aReference 4. ^bpH buffered solution at 25°±2°. ^cObtained from Figure 4 in Reference 4.

^dCalculated from the pseudo-first-order rate constants and pH.

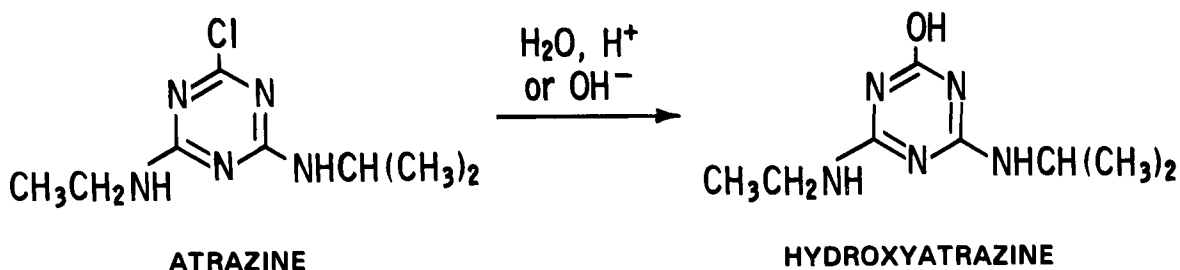


Figure 52. Hydrolysis of atrazine

Photolysis of atrazine in hydroxylic solvents, e.g., water and methanol, results in nucleophilic displacement of the chlorine (Figure 53). Other s-triazines undergo similar photoreactions. The photolysis rates for various s-triazines were found to vary according to the nature of the halogen and alkylamino substituents on the ring⁷. Ruza and co-workers reported surprising differences in the position of the long-wavelength absorption bands of simazine, atrazine, and propazine⁷. Other data published by Sadtler Research Corp. indicate that the ultraviolet absorption spectra of these three pesticides are superimposable¹⁰. Our spectral data are in agreement with the Sadtler spectra. The spectral data indicate that the extremely low direct photolysis rates of atrazine and other s-triazines are due mainly to lack of sunlight absorption. Direct photolysis of atrazine is so slow that it is unlikely to have environmental importance.

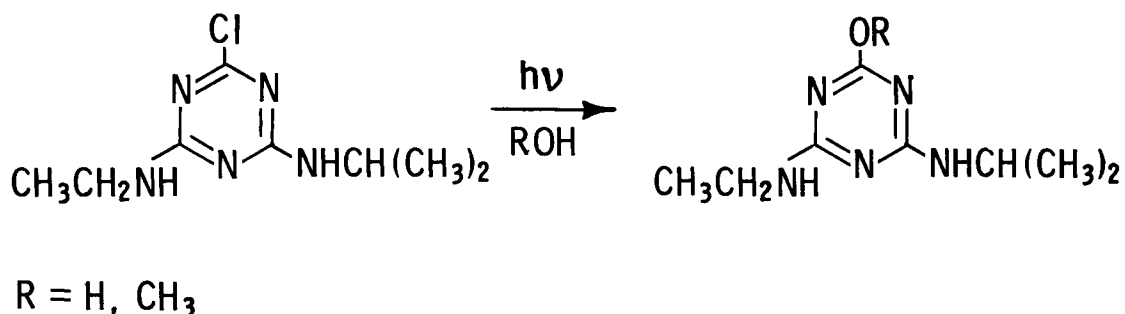


Figure 53. Photoreaction of atrazine

The sensitized photolysis of atrazine was not investigated. Alkylamino substituents of atrazine may be oxidized via the exciplex mechanism discussed earlier in this report (See Section V).

Atrazine was found to be very unreactive towards singlet oxygen. The β value in water was found to be > 37.5 . The lack of reactivity of atrazine may in part be due to its

alkylamino substituents; amines are known to rapidly quench singlet oxygen without reacting¹¹.

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SECTION XIV

RESULTS AND DISCUSSION: DIAZINON

HYDROLYSIS

Melnikov¹ has reported that diazinon is not as resistant to hydrolysis as is parathion. Under acidic conditions, it is reportedly hydrolyzed 12 times faster than parathion. Under alkaline reaction conditions, diazinon hydrolyzes at the same rate as parathion. The hydrolysis reaction is given in Figure 54.

Cowart *et al.*² determined the rates of hydrolysis of several pesticides (low concentration) in water at pH 6.0. Plotting their data as log % conc. remaining of diazinon vs time gives a half-life of 264 hours ($k = 7.3 \times 10^{-7} \text{ sec}^{-1}$). The reaction appears to follow first-order kinetics through one half-life.

Ruzicka *et al.*³ determined the half-life of diazinon in 20% ethanol-water at 70° under buffered reaction conditions (pH 6.0). Based on these data, diazinon has a half-life of 37 hours or a pseudo-first-order rate constant of $1.3 \times 10^{-5} \text{ sec}^{-1}$ at 70°.

Sethunathan and MacRae⁴ reported a diazinon degradative half-life of 43.8 days in sterilized soil at pH 4.7. Konrad *et al.*⁵ observed that diazinon did not hydrolyze in water at pH 6, but was readily hydrolyzed at pH 2.

Mortland and Raman⁶ have reported that copper (II) catalyzes the hydrolysis of diazinon in 50% aqueous ethanol in

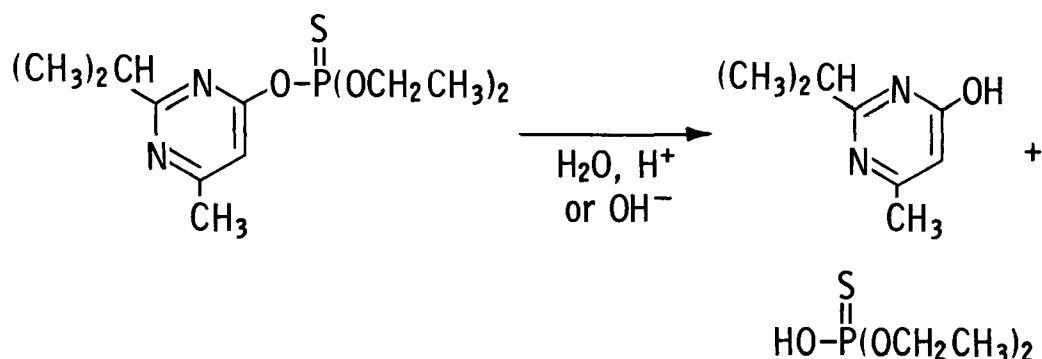


Figure 54. Hydrolysis products of diazinon

the pH range 5-6. Unfortunately, they did not give a rate constant for the uncatalyzed hydrolysis. Lichtenstein *et al.*⁷ determined the effect of sodium azide on the degradation of diazinon in water. Calculation from his data gives a half-life of about 12 days at pH 4.9.

Faust and Gomaa⁸ carried out a study on the effect of pH on the rate of hydrolysis of diazinon and diazoxon. Their data are given in Table 28. The average second-order rate constant (20°) is $5.6 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$ for alkaline hydrolysis and $2.3 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$ for acid degradation. The contribution to hydrolysis by water is apparently too slow to be important. Diazoxon reacts somewhat faster than diazinon. Based on the data of Gomaa and Faust,⁸ the average alkaline and acid second-order rate constants are $6.0 \times 10^{-2} \text{ M}^{-2} \text{ sec}^{-1}$ and $6.4 \times 10^{-1} \text{ M}^{-1} \text{ sec}^{-1}$, respectively. At alkaline pH's, diazinon and diazoxon react at the same rate. Under acidic conditions diazoxon is about 27 times more reactive than diazinon.

In view of these studies, diazinon hydrolysis was not examined in detail. We did carry out a limited investigation with diazinon and based on half-life data calculated the alkaline and acid second-order rate constants (27° C.) as $2.4 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$ and $7.3 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$, respectively. These approximate values are in agreement with Faust and Gomaa.⁸

Table 28. HYDROLYSIS HALF-LIVES AND RATE CONSTANTS FOR DIAZINON AND DIAZOXON AT 20°C.^a

pH	Diazinon		Diazoxon	
	$k_{\text{obsd}} (\text{sec}^{-1})$	$t_{1/2} (\text{days})$	$k_{\text{obsd}} (\text{sec}^{-1})$	$t_{1/2} (\text{days})$
3.1	1.6×10^{-5}	0.49	5.1×10^{-4}	0.017
5.0	2.6×10^{-7}	31	6.3×10^{-6}	1.27
7.5	4.3×10^{-8}	185	2.8×10^{-7}	29
9.0	5.9×10^{-8}	136	4.4×10^{-7}	18
10.4	1.3×10^{-6}	6.0	1.9×10^{-5}	0.42

^aReference 8.

OXIDATION

Ralls *et al.*⁹ reported that diazinon when sprayed on tomatoes give within five days 2-isopropyl-4-methylpyrimidin-6-ol. The authors suggested that diazinon was oxidized to diazoxon which in turn was hydrolyzed to give the above product.

Studies in our laboratory showed that diazinon was stable to molecular oxygen in air-saturated water for several days at room temperature. Thus, oxidation by molecular oxygen of dilute solutions of diazinon is not likely to be an environmental degradative pathway.

PHOTOCHEMISTRY

No products due to the direct photolysis of diazinon have been reported in the literature. Although this pesticide absorbs sunlight much less strongly than its organophosphorus relative, parathion, our screening studies suggest that it undergoes direct photolysis in water at a similar rate. The slow photolysis rate of diazinon is due principally to weak absorption of sunlight.

Studies by Pardue and co-workers¹⁰ indicate that the isopropyl group of diazinon is susceptible to light-initiated autooxidation. The oxidation product "hydroxydiazinon" that formed upon sunlight irradiation of diazinon-treated kale leaves or ultraviolet irradiation of a diazinon film probably resulted from reduction of a hydroperoxide intermediate that is analogous to the hydroperoxide formed upon autooxidation of isopropyl-benzene¹¹ (Figure 55).

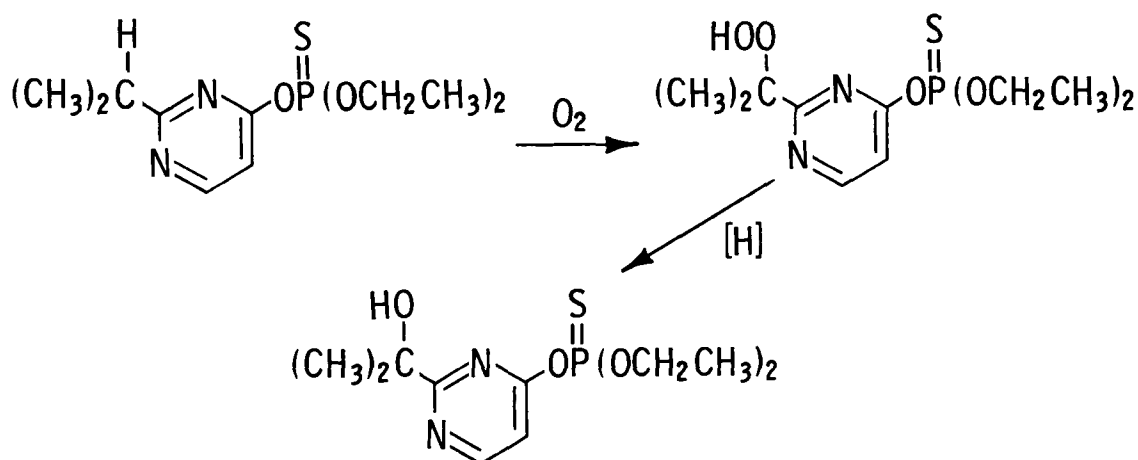


Figure 55. Postulated mechanism for photooxidation of diazinon

Diazinon, like parathion,¹² was unreactive towards singlet oxygen ($\beta > 37.5$ in water). These and Grunwell's data¹² indicate that singlet oxygen is not directly involved in the photochemical conversion of phosphorothionates to the more toxic oxons.

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SECTION XV

RESULTS & DISCUSSION: PARATHION

HYDROLYSIS

Although comprehensive studies concerning the fate of parathion in the environment are not available in the literature, hydrolysis is believed to be the most important process for degradation even though the rate of hydrolysis is slow in water. In addition, two other compounds, the oxygen analog, paraoxon and the isomer O-*p*-nitrophenyl phosphothiolate (Figure 56) are associated with the biological effects and therefore their hydrolytic data, when available, is worth scrutiny.

Thermal stability of parathion was investigated by Metcalf and March¹. When heated to 150° for 24 hours parathion was 85% degraded and gave O,*S*-diethyl-O-*p*-nitrophenyl phosphorothiolate as the major product. Although these compounds might be found as impurities in parathion as a result of manufacturing or storage it is not likely that they will be formed at most environmental temperatures.

Ruzika *et al.*² in laboratory studies investigated the half-life of parathion along with 36 other pesticides. Parathion was determined to have a half-life of 43.0 hours at 70° in 20% ethanol-water buffered at pH 6.0. The oxygen analog paraoxon had a half-life of 28.0 hours. Parathion

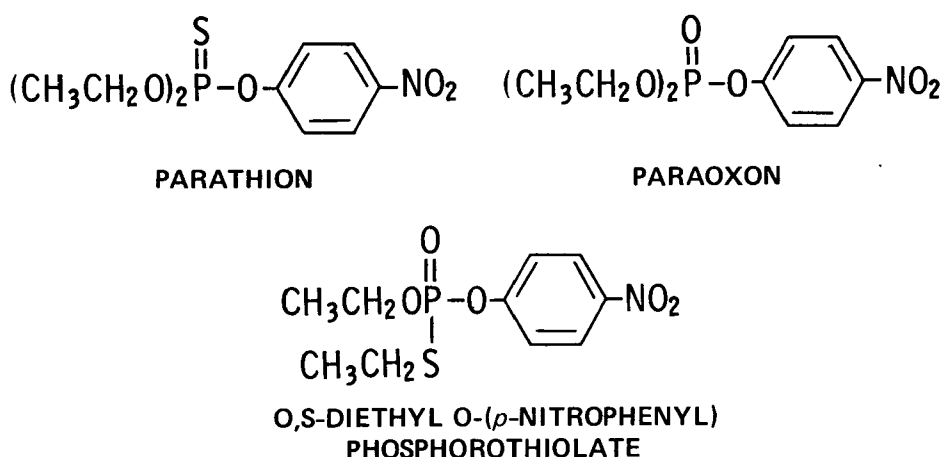


Figure 56. Structures of parathion and some products derived from its chemical transformations

half-life was also determined in two river water samples containing 20% ethanol. Parathion had a half-life of 65 hours in River Thames water (pH 8.0) and 68 hours in River Irthing water (pH 7.5).

Cowart *et al.*³ investigated the hydrolysis of seven organophosphate pesticides. Using these data, a semilog plot of parathion concentration vs. time gives a straight line through only one half-life and then deviates.

Muhlman and Schrader⁴ determined the rate of hydrolysis of parathion over the temperature range of 0-70° in the pH range 1-5 and reported a pseudo-first-order rate constant (k_{H_2O}) of $1.2 \times 10^{-8} \text{ sec}^{-1}$ at 20°.

Aldridge and Davison⁵ reported a first-order hydrolysis rate constant (k_{obsd}) of $1.6 \times 10^{-8} \text{ sec}^{-1}$ at pH 7.6 at 37° and $1.8 \times 10^{-5} \text{ sec}^{-1}$ for the S-ethyl isomer of parathion under the same conditions.

In more detailed laboratory studies Hassan *et al.*⁶ investigated the hydrolysis of parathion and paraoxon over the pH range 3.1 to 10.4 at 20°. Their data shows no pH dependence below pH 7 which corresponds to a hydrolysis contribution by water with a pseudo-first-order rate constant (k_{H_2O}) of about $5 \times 10^{-8} \text{ sec}^{-1}$ for both parathion and paraoxon. Based on rate data at pH 10.4 parathion has an alkaline second-order rate constant (k_{OH^-}) of $2.3 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$ compared to $1.3 \times 10^{-1} \text{ M}^{-1} \text{ sec}^{-1}$ for paraoxon.

Pet⁷ reported rate data for parathion hydrolysis at 25° and 35°. Extrapolation of his data to 20° gives a pseudo-first order rate constant for water (k_{H_2O}) of $3.3 \times 10^{-8} \text{ sec}^{-1}$ and a secondorder rate constant for alkaline hydrolysis (k_{OH^-}) of $4.6 \times 10^{-4} \text{ M}^{-1} \text{ sec}^{-1}$.

Ketelaar^{8,9} also studied alkaline hydrolysis of paration and methyl parathion in water. They found the second-order alkaline hydrolysis rate constant (k_{OH^-}), extrapolated to 20°, was $5.9 \times 10^{-4} \text{ M}^{-1} \text{ sec}^{-1}$ while for methyl parathion it was $2.4 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$.

Scrutiny of the above data reveals that the second-order rate constant for water hydrolysis (k_{H_2O}) is about $(3-4) \times 10^{-8} \text{ sec}^{-1}$ and the second-order alkaline hydrolysis rate constant (k_{OH^-}) is $(4.6-5.9) \times 10^{-4} \text{ M}^{-1} \text{ sec}^{-1}$. The rate data of Hassan *et al.*⁶ for alkaline hydrolysis is out of line with the other data. It is also noted that at alkaline pH's their data does not appear to follow second-order kinetics, contrary to other reports. Products of the hydrolysis are shown in Figure 57.

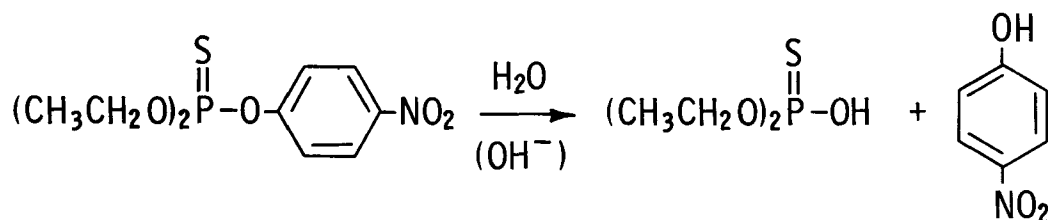


Figure 57. Hydrolysis of parathion

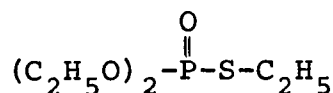
OXIDATION

Hassan *et al.* have reported the oxidation of parathion and paraoxon in water by Cl_2 , ClO_2 , and KMnO_4 .⁶ The oxidation of parathion by KMnO_4 at neutral pH's gave paraoxon as the product. Also at pH 7.4, Cl_2 and ClO_2 oxidized parathion to paraoxon. Gunther has shown that parathion is oxidized by ozone to paraoxon.¹⁰ However, it is not anticipated that these processes will be important in most aquatic ecosystems.

Koivistoninen and Meriläinen¹¹ showed that parathion as a thin film on glass gave paraoxon as a product in the dark. The effect of uv radiation was to increase the amount of paraoxon. An explanation for these results might well be autooxidation where the effect of uv radiation is to provide free radical initiation.

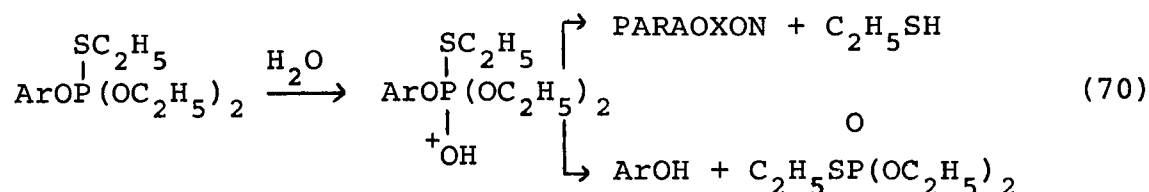
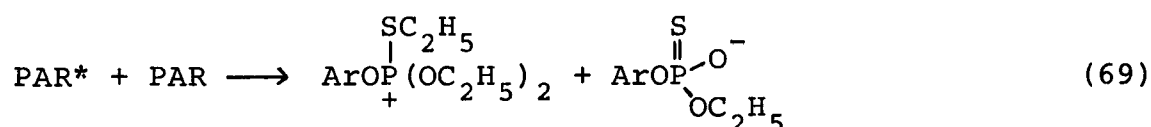
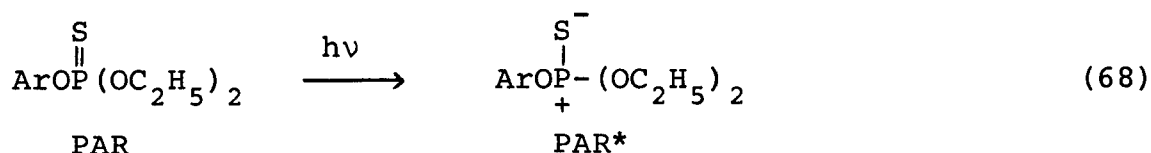
PHOTOCHEMISTRY

Interest in the photolysis of parathion has stemmed primarily from observations that its photoproducts are cholinesterase inhibitors. These observations were first recorded by Payton¹² and were later corroborated by Frawley and Cook.¹³ Early work by Cook and Pugh indicated that one of the cholinesterase inhibitors was paraoxon.¹⁴ Koivistoninen and Meriläinen¹¹ exposed parathion to uv light and sunlight and reported paraoxon, S-ethyl and S-phenyl isomers of parathion and other unidentified products. Methyl parathion on the other hand gave only methyl paraoxon. El-Refai and Hopkins¹⁵ observed paraoxon as one of the products when parathion was deposited on bean plant leaves and glass plates and irradiated by light. Recently, Joiner and co-workers have reported that parathion forms numerous products upon exposure to high intensity ultraviolet light¹⁶⁻¹⁸ (Figure 58). Several of these products were found in field studies conducted by Joiner and Baetke;¹⁸ paraoxon was the major product found in these studies. Grunwell and Erickson¹⁹ have reported that O,O,S-triethylthiophosphate (shown below) is the major photoproduct from parathion at high concentrations in dioxane-water.



Products reported by Joiner and Grunwell are summarized in Figure 58.

Most of the above product data were obtained from photolysis of parathion films or high concentrations of parathion in aqueous emulsion or organic solvents. According to Grunwell,¹⁹ the presence of water is essential to the formation of paraoxon in solution; no photolysis occurred in dry organic solvents. Grunwell has suggested that the mechanism shown below accounts for the photoalteration products at high concentrations²⁰ (eq. 68-70). This mechanism suggests that formation of paraoxon may be less important at lower concentrations and that the photolysis rate of parathion may increase with increasing concentration.



Our studies of the direct photolysis of parathion were not detailed. They did establish that photoalteration of parathion at wavelengths > 280 nm is very slow in water (pH 5.5) at dilute concentrations (2.8 ppm). The slow rate was not due to lack of light absorption at wavelengths > 300 nm. Parathion absorbs sunlight much more rapidly than the other

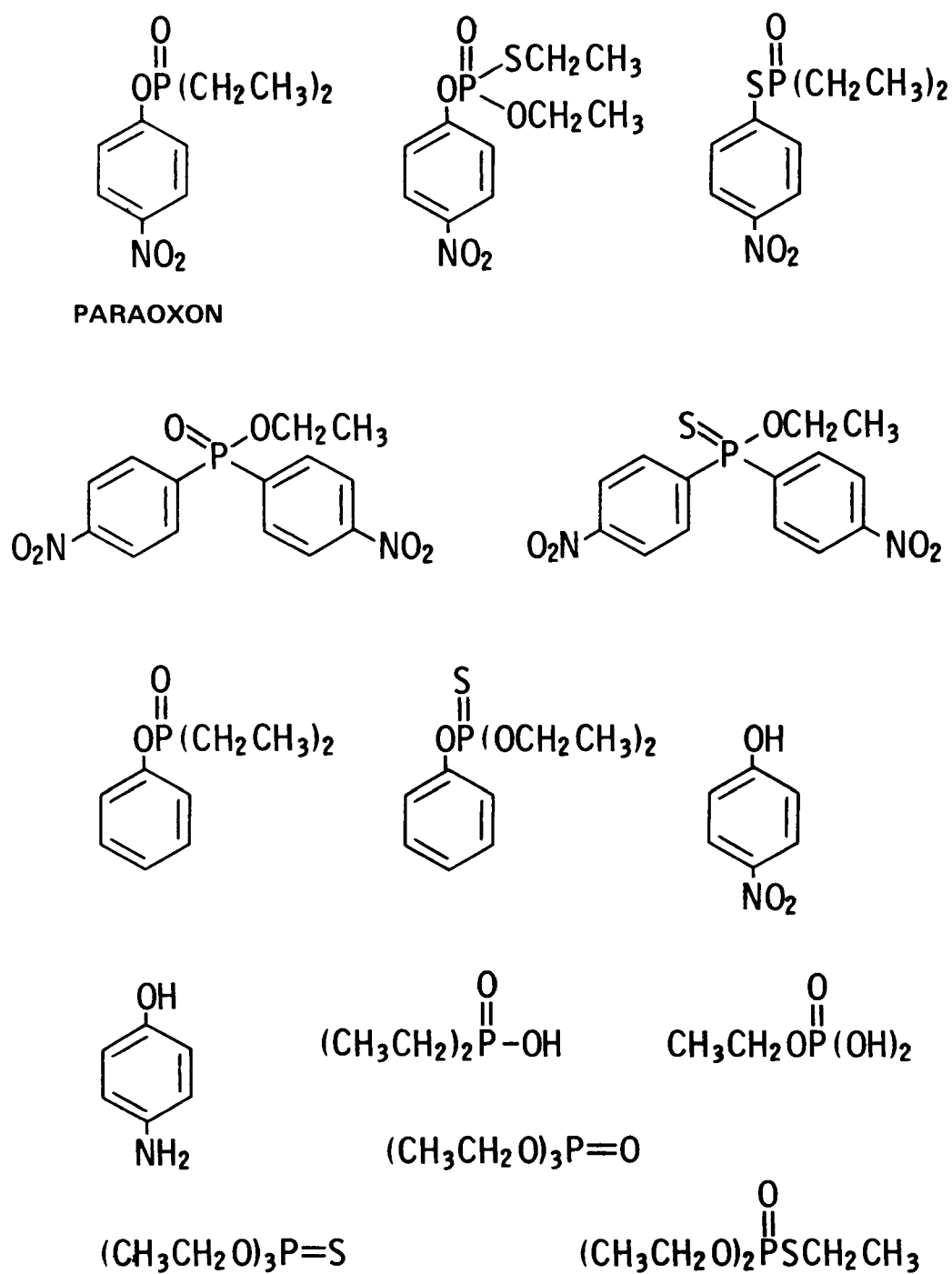


Figure 58. Reported photoalteration products of parathion

pesticides that were included in this report (Table 29). The quantum yield for parathion photolysis must be very low, certainly less than 0.001. Other workers have also reported that the quantum yield for photoinduced hydrolysis of *p*-nitrophenylphosphate is very low,²¹⁻²² although *m*-nitrophenylphosphate photohydrolyzes very efficiently.

Grunwell has concluded that parathion and other thiophosphates are unreactive toward singlet oxygen.¹⁹⁻²⁰ Our data are consistent with his observations.

Table 29. SPECIFIC SUNLIGHT ABSORPTION RATES OF PARATHION AND OTHER SELECTED PESTICIDES DURING MIDSUMMER AND MIDDAY AT LATITUDE 40°N

Pesticide	$k_a \times 10^6 (\text{sec}^{-1})$	Relative k_a
Parathion	6,930	8,000
Carbaryl	623	720
2,4-D Ester	194	22
Atrazine	6.6	7.6
Diazinon	6.2	7.1
Malathion	1.2	1.3
Methoxychlor	0.87	1

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SECTION XVI

RESULTS & DISCUSSION: TOXAPHENE

HYDROLYSIS AND OXIDATION

The persistence of toxaphene, when applied to lakes and rivers, has been related to the time required for detoxification of the water body. This persistence has been suggested to be dependent on such factors as pH, alkalinity, temperature, sunlight and dissolved oxygen. The subject has been recently reviewed by Hughes¹ and there does not appear to be an understanding of the relationship of environmental factors to toxaphene persistence.

Toxaphene is dehydrohalogenated in strong alkaline medium. Archer and Crosby² reported partial dehydrochlorination in approximately 2 M alcoholic KOH in 15 min. at 75-80°.

It is reported that toxaphene is stable to sulfuric acid and a 1:1 mixture of sulfuric-nitric acid.¹ However, it is surprising that any double bonds in the toxaphene are not protonated by the strongly acidic medium.

In our studies toxaphene was found to be stable in air-saturated dilute acidic and alkaline medium at 65°. After two days under these reaction conditions, there was no detectable change in the gas chromatographic fingerprint. These results indicate that under environmental reaction conditions the degradation of toxaphene by oxygen, acid or alkali would be too slow to be environmentally significant.

PHOTOCHEMISTRY

Our screening studies indicated that photolysis of toxaphene under sunlight is a very slow process in pure water. Also, it is not readily oxidized by photochemically-generated singlet oxygen ($\beta > 37.5$ in water). Thus, no detailed studies were carried out.

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TECHNICAL REPORT DATA <i>(Please read Instructions on the reverse before completing)</i>		
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		11. CONTRACT/GRANT NO.
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		14. SPONSORING AGENCY CODE EPA-ORD
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16. ABSTRACT <p>This report presents the results of laboratory studies to quantitatively predict chemical and photochemical transformation rates and products of pesticides in water. It includes a general discussion of relevant transformation processes and associated kinetic expressions. The processes treated in most detail are hydrolysis, direct photolysis, and reaction with singlet oxygen. Implications of other processes such as oxidation and sensitized photolysis are also discussed.</p> <p>Results of detailed studies are included for the pesticides, malathion, carbaryl, methoxychlor, captan, and 2,4-D esters. The measured rate constants and half-lives indicate that chemical and/or photochemical processes of these compounds are likely to be important in the aquatic environment.</p> <p>Less extensive data is presented for the pesticides, atrazine, diazinon, parathion, and toxaphene, along with a discussion of available literature data.</p>		
17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pesticides Hydrolysis Photolysis		6F 7C 7E
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