

Dynamics of Pesticides in Tropical Conditions. 1. Kinetic Studies of Volatilization, Hydrolysis, and Photolysis of Dieldrin and α - and β -Endosulfan

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Kinetic studies on the degradation of three commonly used pesticides in Jamaica, dieldrin [(1*R*,4*S*,5*S*,8*R*)-1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-*endo*,*exo*-1,4:5,8-dimethanonaphthalene] and α - and β -endosulfan (6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin 3-oxide), were carried out under laboratory conditions that simulated those of tropical agroecosystems. Studies included measurements of rates of volatilization, hydrolysis, and photolysis. Volatility from EC formulations on glass surfaces at 30 °C was in the order α -endosulfan > dieldrin > β -endosulfan. Kinetic data provided first-order plots of $\ln F$ vs t with correlation coefficients ranging from 0.99 to 0.85 (F is the volatilization flux expressed as $\mu\text{g cm}^{-2} \text{day}^{-1}$ and t is the time in days) and $t_{1/2}$ values ranging from 2 to 7 days. Hydrolytic degradation rates of both α - and β -endosulfan at 30 °C decreased with pH in the sequence pH 9.5 ($t_{1/2} = 0.04$ days) > pH 7.0 ($t_{1/2} = 25$ days) > 4.5 ($t_{1/2} = 90$ days) for a first-order model. Hydrolysis of dieldrin ($t_{1/2} = 95$ days) was insensitive to pH over the same range. Photolytic degradation followed a first-order model and the half-lives were in the order dieldrin (2.5 h) < β -endosulfan (3.5 h) < α -endosulfan (20 h) in hexane solution and dieldrin (1.7 h) < β -endosulfan (33 h) < α -endosulfan (48 h) in aqueous solution. Photolysis rates in sunlight were in the same order, but half-lives were between 20 and 40 days in bulk hexane solution, while the average $t_{1/2}$ was 15 h for each compound in a thin layer of hexane solution.

INTRODUCTION

The use of pesticides in developing countries has been increasing rapidly in recent years as the demand for food increases (Pollard, 1981). In Jamaica, although the importation of pesticides during the past 10 years has doubled, this increase has not been accompanied by a parallel growth in scientific data on the environmental fate of these pesticides in tropical agroecosystems. In many cases the economic conditions prevailing in developing countries dictate the use of cheaper broad-spectrum pesticides that are restricted or banned in more developed countries. For example, 30% of the total pesticides used in the Caribbean belong to the organochlorine (OC) class, most of which are banned in developed countries. Some of these OCs may be most effective in tropical conditions because of their environmental stability and persistence, water insolubility, and lipid solubility, but their uncontrolled usage poses a serious threat to man and his environment. Recognizing this dilemma, the joint IAEA-FAO symposium (IAEA-FAO, 1982) strongly recommended a reappraisal of the properties of the persistent pesticides under conditions approximating their use in tropical and subtropical climates. The present study on the physicochemical properties and reactivity of commonly used organochlorine, organophosphorus, and carbamate pesticides was initiated and results of the kinetic studies of volatilization, hydrolysis, and photolysis of three of the so-called "persistent" organochlorines widely used in Jamaica, dieldrin, α -endosulfan, and β -endosulfan (Figure 1), are reported here.

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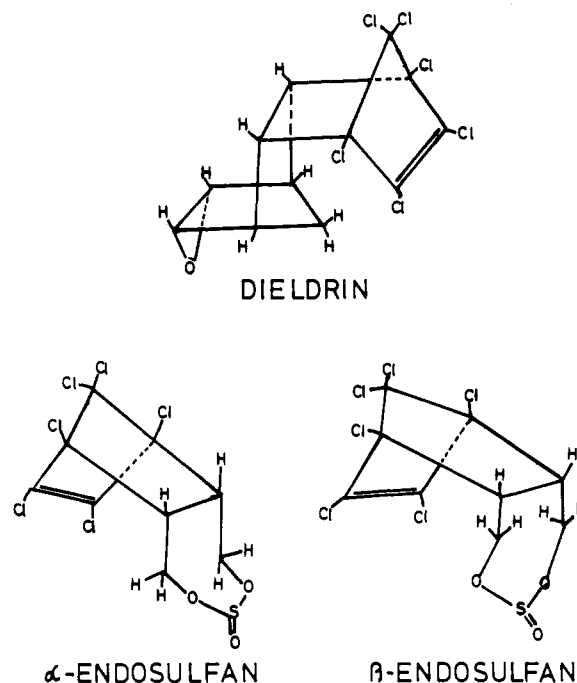


Figure 1. Structure of dieldrin, α -endosulfan, and β -endosulfan.

EXPERIMENTAL PROCEDURES

Materials. All the reagents used during the study were of reagent grade. Distilled water was further purified by passage through a Milli-Q ultrapure water system (Millipore Co., Bedford, MA) and was used for the hydrolysis and photolysis experiments. Disodium hydrogen phosphate and boric acid were used for making standard buffer solutions. Reference compounds, α - and β -endosulfan and dieldrin (99% purity), were obtained from the Department of Agricultural Chemistry, Oregon State University, Corvallis, OR. Standard safety precautions were observed in handling these compounds due to their toxicity

(oral LD₅₀s to rats: 46, 76, and 240 mg/kg for dieldrin and α - and β -endosulfan, respectively) (Worthing, 1979). Solvents were re-distilled and analyzed for purity by gas chromatography before use.

Endosulfandiols were prepared by dissolving 0.5 g of endosulfan anhydride in THF, and 0.1 g of LiAlH₄ was added gradually to the solution. The reaction mixture was allowed to stand at room temperature for 1 h and then filtered. The solvent from the filtrate was removed under reduced pressure and the residue dissolved in the minimum quantity of acetone. The diol was isolated by preparative layer chromatography on 1.00 mm thick layers of silica gel HF₂₅₄₊₃₆₆ (Merck) using hexane/ethyl acetate/methanol (4:1:1 v/v) as eluant. The purity of the diol was checked spectroscopically.

Instrumentation and Methods. A UV-visible automatic scanning spectrophotometer, Pye Unicam Model SP8-100, and an infrared spectrophotometer, Pye Unicam Model SP8-300, were used for measuring spectra of all organic compounds. NMR spectra of α - and β -endosulfan were recorded on a JEOL PMX 60 spectrometer. Gas chromatographs, Varian 3700 with a CDS 111C data system and Shimadzu 9A with a Chromatopak data system, were used to monitor pesticide concentrations. The Varian 3700 was equipped with a 1.8 m \times 2 mm i.d. glass column packed with 3% SP 2100 on Chromosorb WHP 80/100 or a 0.6 m \times 2 mm i.d. glass column packed with 2.5% DEGS on Chromosorb WHP 80/100. The Shimadzu 9A was fitted with a glass column (1.6 m \times 2 mm i.d.) packed with 3% OV 101 on Chromosorb WHP 80/100. Both gas chromatographs were used with a ⁶³Ni electron capture detector (ECD) and a dual-pen recorder. The carrier gas used was either nitrogen or argon/methane at a flow rate of 4–5 mL/min.

The detection limit for the standard organochlorine compounds was 1 ng/g in each case.

Recovery experiments were carried out for each set of kinetic experiments. The average recoveries of dieldrin, α -endosulfan, and β -endosulfan are 95%, 92%, and 93%, respectively. All the concentrations obtained from the GC experiments for each kinetic run were corrected for 100% recovery.

Volatilization. Volatilization rates were measured gravimetrically by determining the weight loss of the pesticides by using a solvent trap method devised in our laboratory. Five milliliters each of Thiodan 35 EC, Dioldrex 18 EC, and xylene (control) were pipetted separately into small glass Petri dishes in triplicate and weighed on a Mettler analytical balance with a precision of ± 0.2 mg. The dishes were exposed to the open atmosphere on the laboratory roof either under shade or in direct sunlight. Similar experiments were repeated in a fume hood.

The apparatus for the solvent trap method consisted of a filter flask with inlet and outlet tubes for air. Formulations (0.5 mL) of dieldrin and endosulfan were diluted 200-fold with hexane to give solutions of 0.18% and 0.9% ai, respectively, in hexane. Ten milliliters of the final solution was introduced in the flask immersed in a thermostated water bath (30.0 ± 0.1 °C). The outlet tube of the flask was connected to a series (three) of gas bubblers filled with toluene (200 mL). The air flow was adjusted to 120 mL/min. Samples from each bubbler were taken at suitable intervals and analyzed by GC. Before sampling, the volume in each bubbler was adjusted to 200 mL if necessary. Each experiment was duplicated, and the average value was taken.

Hydrolysis. The rates of hydrolysis of dieldrin and α - and β -endosulfan were measured in aqueous solution at 30 °C and at pH values of 4.5, 7.0, and 9.5. Standard solutions of the pesticides (10 ppm in 1.5 mL of hexane) were pipetted separately in duplicate into 100-mL volumetric flasks. The hexane was evaporated with a gentle stream of nitrogen, and the required amounts of phosphate-citrate buffer (Elving et al., 1956) and KCl solution were added to make up to volume. KCl solution was used to maintain the ionic strength of the final solution. The pH of the solution was measured before and after the kinetic run to ensure that the pH was maintained constant during the run. Aliquots (10 mL) were taken from each flask at zero time and subsequent time intervals and were extracted with hexane in 100-mL separatory funnels. The solution was then passed through beds of Florosil (2 \times 2 cm²) and collected in a 10-mL flask. The separatory funnel was rinsed with hexane (1–2 mL) where necessary, and this was added through the sodium sulfate

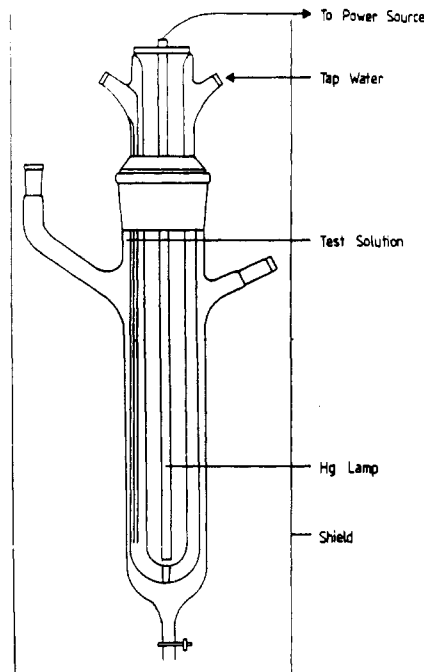


Figure 2. Photochemical apparatus.

bed to make up the final volume to 10 mL. The resultant solution was analyzed by GC. The experiments were repeated at pH 9.0 by using boric acid buffer and with 0.75 ppm Cu²⁺ solution.

Photolysis. Kinetic studies of the photolytic degradation of dieldrin and α - and β -endosulfan were carried out by using a medium-pressure Hg lamp in a photochemical reactor as shown in Figure 2 and in direct sunlight. In the former case, 100 mL of a hexane solution of the pesticide (0.1 ppm) was introduced into the reactor. An aliquot (5 mL) was withdrawn at zero time for analysis and kept in the dark. The UV shield was put in place and the tapwater turned on to maintain the temperature at approximately 25 °C. The 125-W Hg lamp (Applied Photo-physics Ltd.) was switched on and the time noted. Aliquots were taken for analysis at regular intervals after the lamp was switched off and the shield was removed until no further degradation (after 10 measurements) was detectable. Concentrations were measured on the gas chromatograph. The experiments were repeated with aqueous solutions of the pesticides. At least two replicate experiments were performed in each case.

Degradation under sunlight was studied by placing 10 mL of 0.05 ppm hexane solution of each insecticide in a 10-cm³ quartz cell with an airtight stopper and exposing it to sunlight on the laboratory roof. Aliquots (1–2 μ L) were withdrawn in duplicate at suitable intervals and analyzed by GC. In a separate experiment with hexane in the cell, a thermometer was substituted for the airtight stopper with the aid of paper tape and the hourly temperature was noted for 2 days.

RESULTS AND DISCUSSION

All the kinetic runs revealed that the volatilization flux (F) or quantity volatilized per unit area per unit time (μ g day⁻¹ cm⁻²) decayed exponentially with time. The linear squares analysis of the data for a first-order plot yields the results presented in Tables I and II. The correlation coefficients (r^2) for a first-order model are generally less than 0.98. There are two exceptions—(i) endosulfan in sunlight and (ii) dieldrin by the solvent trap method—which produce r^2 values greater than 0.98. The low values for the correlation coefficients could be attributed to a higher initial rate than that required for a first-order model; this could be due to (i) direct heating by the sun resulting in a higher initial temperature and (ii) the rapid conversion of dieldrin to photodieldrin, which is a more volatile compound (Rosen, 1968). The rapid decline in volatilization flux could be attributed to

Table I. Kinetic Data for Volatilization by Gravimetric Method

compd	exptl condition	k/s^{-1}	$F_{1/2}/$ days	r^2
endosulfan	lab (mean)	$(1.14 \pm 0.21) \times 10^{-6}$	7.05	0.899
dieldrin	lab (mean)	$(1.52 \pm 0.09) \times 10^{-6}$	5.26	0.989
endosulfan	shade (environ)	$(3.57 \pm 0.04) \times 10^{-6}$	2.24	0.959
endosulfan	sun (environ)	$(4.37 \pm 0.33) \times 10^{-6}$	1.83	0.987
dieldrin	shade (environ)	$(3.21 \pm 0.35) \times 10^{-6}$	2.50	0.966
dieldrin	sun (environ)	$(3.85 \pm 0.59) \times 10^{-6}$	2.08	0.937

Table II. Kinetic Data for Volatilization by the Solvent Trap Method

compd	k/s^{-1}	$F_{1/2}/$ days	r^2
α -endosulfan	$(2.05 \pm 0.15) \times 10^{-6}$	3.92	0.989
β -endosulfan	$(3.90 \pm 1.23) \times 10^{-6}$	2.06	0.852
dieldrin	$(1.82 \pm 0.09) \times 10^{-6}$	4.40	0.991

formation of a thin dark crust, which was observed within a few days in all the dishes exposed to the sun. Further volatilization would have taken place only after diffusion through this layer. Formation of surface layers, as expected, was much slower in the shade and in the laboratory.

The hypothesis that volatilization of pesticides from their formulation might be controlled by diffusion-based processes was suggested by Gueckel et al. (1974) and Hartley et al. (1980). Gueckel found that the quantity of pesticide volatilized was proportional to the square root of the time. However, in the present study, plots of volatilization flux against time resulted in an exponential curve, which suggests that Gueckel's model is not applicable to all environmental conditions. Although the plots of $\ln F$ vs $t_{1/2}$ for our data give a straight line, there is no kinetic justification for the relationship $\ln F = kt^{1/2} + C$. However, this does not preclude the role of diffusion processes in the volatilization mechanism.

Stamper et al. (1979) reported that a log time plot more accurately described the data [correlation coefficient (r^2) = 0.963] for disappearance of organophosphorus pesticides from leaves than a first-order plot ($r^2 = 0.854$). Our data also fit a log F vs log time plot ($r^2 = 0.962$). We prefer a first-order model since this is more easily justified on the basis of kinetic theory. However, the available data do not permit a clear distinction between the two models.

Phillips (1974) demonstrated that the loss of dieldrin as the pure component from cotton leaves was similar to that from glass plates. He also found that the rate of volatilization of the insecticide was slow, showing pronounced curvature, presumably because of the protective action of the wetting agent and adjuvants in the formulation (Phillips, 1971). These curvatures can be explained by the relationship $M = A/(1 + e^{k(t-t')})$, where M is the quantity of compound, A is the area covered, k is a constant, and t is time.

The gravimetric experiments showed a weight loss far greater than the expected loss due to the loss of formulation additives. However, the rate of loss of pure pesticide determined by the solvent trap method should be comparable. The ratio of volatilization fluxes of two compounds, a and b, is given (Hartley, 1969) by

$$F_a/F_b = P_a M_a^{1/2} / P_b M_b^{1/2}$$

where P is the vapor pressure and M is the molecular weight. The relationship gives a value of 1.92 for the ratio of the fluxes of endosulfan and dieldrin, which is in good agreement with our measured mean value of 1.77 obtained by the solvent trap method. The ratios of fluxes from the gravimetric method for the mean weight loss values are

Table III. Kinetic Data for Hydrolysis of Endosulfan and Dieldrin in Sterilized Aqueous Buffer, Temperature 30 °C, $I = 0.5$ M (KCl)

compd	pH	k/s^{-1}	$t_{1/2}/$ days	r^2
α -endosulfan	4.5	$(8.60 \pm 0.18) \times 10^{-8}$	93.3	0.999
α -endosulfan	7.0	$(2.92 \pm 0.04) \times 10^{-7}$	27.5	1.000
α -endosulfan	9.5	$(4.61 \pm 0.31) \times 10^{-4}$	0.043	0.986
β -endosulfan	4.5	$(9.14 \pm 0.09) \times 10^{-8}$	87.7	1.000
β -endosulfan	7.0	$(3.42 \pm 0.09) \times 10^{-7}$	23.5	0.998
β -endosulfan	9.5	$(5.61 \pm 0.47) \times 10^{-4}$	0.036	0.980
dieldrin	4.5	$(7.79 \pm 0.21) \times 10^{-8}$	103	0.998
dieldrin	7.0	$(8.25 \pm 0.12) \times 10^{-6}$	97.2	0.987
dieldrin	9.5	$(9.07 \pm 0.69) \times 10^{-8}$	88.4	0.999

1.58, 2.15, and 1.18 for sun, shade, and laboratory measurements, respectively, with a mean of 1.63, which is in fair agreement with the theoretical value.

The importance of volatilization as a factor in the loss of dieldrin and endosulfan in the field can perhaps be estimated from their flux values (determined by the solvent trap method) at half-time, which are 0.25 and 0.43 $\mu\text{g cm}^{-2} \text{day}^{-1}$, respectively. This would suggest that the rate of loss due to volatilization could be 25 and 43 $\text{g ha}^{-1} \text{day}^{-1}$ or 30% of an applied dose of 1 kg of ai/ha of endosulfan and 20% of a similar dose of dieldrin per week.

Our data reveal that β -endosulfan contributed less than 5% of the total endosulfan flux at any stage during the volatilization process. This is in agreement with other published findings (Beard, 1969). If 50% of an applied dose of endosulfan ($\alpha:\beta = 7.3$) is lost within a week by volatilization, the ratio $\alpha:\beta$ will be 2.4:3, assuming no other disproportionation loss. Hence, β -endosulfan will be the dominant isomer after 1 week. This has in fact been demonstrated in field trials here and elsewhere (Beard, 1969).

Hydrolysis. The kinetics of hydrolysis or dissipation in aqueous medium of α - and β -endosulfan and dieldrin at 30 °C and pH 7.0 in a citric acid/phosphate buffer system were determined. Recoveries were over 90% at or above a concentration of 0.90 ppm and 75–80% at 0.001 ppm of the test insecticides. First-order fits were generally obtained for all the kinetic runs, at the end of which the residual concentrations of the compounds approached minimum quantifiable limits.

The rate constant, k , and half-life ($t_{1/2}$) values obtained from linear least-squares analysis of the data in the form of log concentration vs time plot are shown in Table III. The r^2 values suggest distinct first-order dissipation patterns for all three compounds. However, the half-lives are significantly smaller than the previously published value of $t_{1/2} = 35$ days for aqueous dissipation of endosulfan at pH 7.0 and 20 °C (Greve, 1971). The lower values found in the present study may be attributed to the higher temperatures at which they were measured (30 °C) and also to growth of mold in the flask within a few days of starting the experiment. Though the mold was filtered off before each extraction, some adsorbed or absorbed insecticides would have been lost. There is also a possibility of biotic degradation, which could explain the lower $t_{1/2}$ values. Eichelberger et al. (1971) had also recovered only 30% of the added endosulfan in river water after 1 week, thus emphasizing the significance of our data for the persistence of endosulfan in inland tropical waters where biotic activity is likely to be high.

Studies on the rate of hydrolysis of the two isomers of endosulfan and of dieldrin in sterilized aqueous buffered media at fixed ionic strength (0.5 M KCl), 30 °C, and different pH values were carried out, and the values obtained for the first-order rate constants are presented in Table IV. The results show that the rates of hydrolysis

Table IV. Kinetic Data for Hydrolysis of α - and β -Endosulfan and Dieldrin in Unsterilized (Aqueous) Buffer, pH 7, 30 °C

compd	concn	k/s^{-1}	$t_{1/2}/\text{days}$	r^2
α -endosulfan	2.2×10^{-7}	$(1.13 \pm 0.05) \times 10^{-6}$	7.04	0.995
β -endosulfan	2.5×10^{-7}	$(1.10 \pm 0.05) \times 10^{-6}$	7.30	0.995
dieldrin	2.6×10^{-7}	$(3.38 \pm 0.07) \times 10^{-7}$	23.76	0.999

of the endosulfan isomers are pH dependent. The isomers become much more resistant to hydrolysis as the pH is lowered from 9.5 to 4.5. The half-lives reported for endosulfan (presumably $\alpha:\beta = 7:3$) at 20 °C were 35 days at pH 7.0 and 150 days at pH 5.5 (Greve, 1971). These data are comparable to the present finding when the temperature difference is taken into account. The rapid rates of degradation observed at high pH suggest possible base-catalyzed hydrolysis, in which case the observed first-order rate constant can be defined as

$$k_{\text{obs}} = k_{\text{H}_2\text{O}} + k_{\text{OH}^-}[\text{OH}^-]$$

where $k_{\text{H}_2\text{O}}$ is the first-order solvolytic rate constant and k_{OH^-} is the second-order rate constant for base hydrolysis. The rate constant is similar to that used for the hydrolysis of methoxychlor and DDT (Wolfe, 1977). The hydroxide ion concentration, $[\text{OH}^-]$, has been calculated from the relationship

$$K_{\text{W}} = (a_{\text{H}^+})(a_{\text{OH}^-}) = \gamma_{\pm}^2[\text{H}^+][\text{OH}^-]$$

The average activity coefficient, γ_{\pm} , is calculated from the Debye-Hückel equation (Atkins, 1986), $\log \gamma_{\pm} = -0.509Z_+Z_-I^{1/2}$. The ionic product of water, K_{W} , at 30 °C and ionic strength, $I = 0.5 \text{ M}$, is calculated to be 1.414×10^{-14} as described previously (Harned, 1963). Assuming the rate constant at pH 4.5 to be the water-catalyzed rate constant, $k_{\text{H}_2\text{O}}$, the base-catalyzed rate constant, k_{OH^-} , for α -endosulfan was calculated to be 4.52 and $0.64 \text{ M}^{-1} \text{ s}^{-1}$ at pH 9.5 and 7.0, respectively. A discrepancy of this magnitude is to be expected since the values were calculated from only two pH values which differ by 2.5 pH units. Similarly, for β -endosulfan the values for k_{OH^-} were found to be 5.5 and $0.77 \text{ M}^{-1} \text{ s}^{-1}$ at pH 9.5 and 7.0, respectively.

Mechanisms of acid- and base-catalyzed hydrolysis of a number of organic sulfites have been proposed (Van Woerden, 1963) on the basis of detailed kinetic studies. A similar mechanism can also be proposed for the water- and base-catalyzed hydrolysis of endosulfan. This involves simultaneous nucleophilic attack by water and hydroxide ion at the sulfur moiety of the endosulfan followed by the rapid cleavage of the S-O bond, leading to the formation of the diol and inorganic sulfite. The main end product, endosulfandiols, was quantitatively identified by GC with the synthesized standard as reference (see Experimental Procedures).

The effect of pH on the hydrolysis rates of dieldrin was negligibly small. The rate constants for hydrolysis of dieldrin in neutral and alkaline media are much lower than those of α - and β -endosulfan at similar pH values but perhaps not as low as is to be expected from the unreactive nature of dieldrin. The most likely hydrolytic transformation product of dieldrin is 6,7-*trans*-dihydroxydieldrin, which is a well-known environmental metabolite.

The presence of Cu^{2+} at 0.75 ppm did not affect the hydrolysis rates of any of the organochlorines discussed above at pH 7.0. This concentration of copper was chosen to match the endosulfan:Cu ratios used in insecticide-fungicide mixtures routinely applied to coffee plants in Jamaica.

Table V. Kinetic Data for Photolysis of α - and β -Endosulfan and Dieldrin in Hexane (Temperature 25 °C)

compd	$10^5k/s^{-1}$	$10^6k'/s^{-1}$	$t_{1/2}/\text{h}$	$t'_{1/2}/\text{h}$	r^2
α -endosulfan	2.7 ± 0.2	4.0 ± 0.1	7.0	47.8	0.990 (0.996) ^a
β -endosulfan	6.4 ± 0.1	5.9 ± 0.2	3.0	32.9	0.996 (0.996) ^a
dieldrin	6.2 ± 0.1	113 ± 4	3.1	1.7	0.997 (0.997) ^a

^a Photolysis done in water.

Table VI. Kinetic Data for Photolysis of α - and β -Endosulfan and Dieldrin in Direct Sunlight

compd	$10^7k/s^{-1}$	$t_{1/2}/\text{sun days (days)}$	r^2
α -endosulfan	6.1 ± 2	13.4 (40.3)	0.815
β -endosulfan	7.4 ± 2	10.9 (32.6)	0.810
dieldrin	11.6 ± 2.0	6.9 (20.7)	0.951

Photolysis. The rates of photochemical degradation of α - and β -endosulfan and dieldrin in hexane solution were measured by analyzing the irradiated solution by GC. The determination of the exact intensity of light and quantum yields at specific wavelength was not attempted; hence, the results presented here must be considered as only semiquantitative indices of relative photochemical stability.

The rate constants, half-lives, and correlation coefficients obtained by linear least-squares analysis of first-order plots of the photolysis data are presented in Table V. The data show that α -endosulfan was about twice as inert as either dieldrin or β -endosulfan in hexane solution, and the reactions were distinctly first order in each case ($r^2 = 0.99$). During the photolysis of β -endosulfan there was no indication by gas chromatography that any α -isomer was formed. The conversion of α - to β -endosulfan on plant leaves by sunlight and by UV radiation (high-intensity Hg lamp) in hexane/acetone (4:1 v/v) for 12 h was reported (Dureja, 1982). Under our experimental conditions the β -endosulfan degraded faster than the α -isomer, and hence detection of the β -isomer during the photolysis of the α -isomer would be unlikely.

The data in Table V indicate that both α - and β -endosulfan were relatively more inert to UV radiation in aqueous solution than in hexane solution. Dieldrin, on the other hand, was quite labile in aqueous solution. A point of interest here is that the rapid rate of photolysis of dieldrin in water permitted the measurement of its concentration over 10 half-lives. The results show a longer "tail" in concentration than expected for a perfect first-order model. A similar but much more pronounced effect was observed by Benson (1971) during the UV photolysis of solid dieldrin. In fact, this type of behavior, in which only the early part of the pesticide dissipation process is first order followed by a slower rate, is quite common. The relatively high stability to ultraviolet radiation combined with its high resistance to hydrolysis in acidic water would enable it to show long persistence in water bodies, endangering fish and aquatic fauna. The rates of photodegradation of α - and β -endosulfan by natural sunlight in bulk hexane solution in a quartz cell follow a first-order model with lower r^2 values. However, the data for dieldrin gave a fair fit to the first-order model. The half-life in continuous sunlight time (sun days) was much longer than that obtained with the lamp because the proportion of UV radiation of appropriate intensity and wavelength for photodegradation is relatively low. The results of linear least-squares analysis of the data points on the apparent "first-order" part of the curves for the three pesticides used are presented in Table VI. Photolysis of dieldrin and the endosulfan isomers by sunlight in a 2-mm hexane solution layer in a quartz cell, which might more closely resemble the situation on a leaf surface, produced results

dramatically different from those in bulk hexane solution in sunlight. The observed decay processes are fairly well described by first-order kinetics, but the half-lives are now in hours compared to days for the bulk measurements (Table VI). This sharp decrease in persistence is probably due to increased incident intensity and more efficient transfer of radiant energy to each pesticide molecule within the thin layer of solution. Temperature fluctuation of the solution in the quartz cell was pronounced in all the experiments carried out in normal sunlight on the laboratory roof. The mean temperature in the cell was 29 °C at 8:30 a.m. rising to 39 °C by 10 a.m., remaining at 39 °C until 2:00 p.m., and then declining to 29 °C by 4:30 p.m. No change in concentration of pesticide occurred during the night. This temperature fluctuation will of course affect the kinetics of thermal degradation and, hence, the overall reaction rate. No attempt was therefore made to extend the study of photodegradation in the quartz cell in open sunlight.

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