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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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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Kinetic studies on the degradation of three commonly used pesticides in Jamaica, dieldrin [(1R,4S,5R,8R)-1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-endo,exo,endo,exo,1,4,5,8-dimethanophthalene] 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 µg cm⁻² day⁻¹ and t is the time in days) and t½ 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 (t½ = 0.04 days) > pH 7.0 (t½ = 25 days) > 4.5 (t½ = 90 days) for a first-order model. Hydrolysis of dieldrin (t½ = 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 t½ was 15 h for each compound in a thin layer of hexane solution.

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.
to 120 mL/min. Samples from each bubbler were taken at suitable intervals and analyzed by GC. Before sampling, 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+254 (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 × 2 mm i.d. glass column packed with 3% SP 2100 on Chromosorb WHP 80/100 or a 0.6 m × 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 × 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 were 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, Dieldrex 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 α- and β-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 were 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 for a flow rate of 4-5 mL/min.

All the kinetic runs revealed that the volatilization flux (P) or quantity volatilized per unit area per unit time (μg 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 (r²) 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 r² 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).
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 cable to all environmental conditions. Although the plots through this layer. Formation of surface layers, as

The kinetics of hydrolysis or dissipation in aqueous medium of \( \alpha \)- and \( \beta \)-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
The effect of pH on the hydrolysis rates of dieldrin was 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 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 \( k_{\text{OH}^-} \) 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

\[ K_W = [\text{H}_2\text{O}]^2 = \gamma_a [\text{H}^+] [\text{OH}^-] \]

The average activity coefficient, \( \gamma_a \), is calculated from the Debye–Hückel equation (Atkins, 1986), \( \log \gamma_a = -0.509Z^2 \sqrt{\text{ionic strength}} \). The ionic product of water, \( K_W \), at 30 °C and ionic strength, \( I = 0.5 \) M, is calculated to be 1.414 \( \times 10^{-14} \) 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, \( k_{\text{OH}^-} \), for \( \alpha \)-endosulfan was calculated to be 4.52 and 0.64 M⁻¹ 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 \( \beta \)-endosulfan the values for \( k_{\text{OH}^-} \) were found to be 5.5 and 0.77 M⁻¹ 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, endosulfandiol, was quantitatively identified by GC with the synthesized standard as reference (see Experimental Procedures).

The presence of Cu²⁺ 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 IV. Kinetic Data for Hydrolysis of \( \alpha \)- and \( \beta \)-Endosulfan and Dieldrin in Unsterilized (Aqueous) Buffer, pH 7, 30 °C

<table>
<thead>
<tr>
<th>compd</th>
<th>concn</th>
<th>( k/s^{-1} )</th>
<th>( t_{1/2}/\text{days} )</th>
<th>( r^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )-endosulfan</td>
<td>( 2.2 \times 10^{-7} ) (1.13 ± 0.05) \times 10^{-6}</td>
<td>7.04</td>
<td>0.995</td>
<td></td>
</tr>
<tr>
<td>( \beta )-endosulfan</td>
<td>( 2.5 \times 10^{-7} ) (1.10 ± 0.08) \times 10^{-6}</td>
<td>7.30</td>
<td>0.996</td>
<td></td>
</tr>
<tr>
<td>dieldrin</td>
<td>( 2.6 \times 10^{-7} ) (3.38 ± 0.07) \times 10^{-7}</td>
<td>23.76</td>
<td>0.999</td>
<td></td>
</tr>
</tbody>
</table>

Photolysis. The rates of photochemical degradation of \( \alpha \)- and \( \beta \)-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 \( \alpha \)-endosulfan was about twice as inert as either dieldrin or \( \beta \)-endosulfan in hexane solution, and the reactions were distinctly first order in each case (\( r^2 = 0.99 \)). During the photolysis of \( \beta \)-endosulfan there was no indication by gas chromatography that any \( \alpha \)-isomer was formed. The conversion of \( \alpha \)- to \( \beta \)-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 (Durej, 1982). Under our experimental conditions the \( \beta \)-endosulfan degraded faster than the \( \alpha \)-isomer, and hence detection of the \( \beta \)-isomer during the photolysis of the \( \alpha \)-isomer would be unlikely.

The data in Table V indicate that both \( \alpha \)- and \( \beta \)-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 \( \alpha \)- and \( \beta \)-endosulfan by natural 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

### Table V. Kinetic Data for Photolysis of \( \alpha \)- and \( \beta \)-Endosulfan and Dieldrin in Hexane (Temperature 25 °C)

<table>
<thead>
<tr>
<th>compd</th>
<th>( 10^5 k/s^{-1} )</th>
<th>( 10^6 k/s^{-1} )</th>
<th>( t_{1/2}/\text{h} )</th>
<th>( t_{1/2}/\text{sun days} )</th>
<th>( r^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )-endosulfan</td>
<td>( 2.7 \pm 0.2 )</td>
<td>( 4.0 \pm 0.1 )</td>
<td>7.0</td>
<td>47.8</td>
<td>0.990 (0.996)*</td>
</tr>
<tr>
<td>( \beta )-endosulfan</td>
<td>( 6.4 \pm 0.1 )</td>
<td>( 5.9 \pm 0.2 )</td>
<td>3.0</td>
<td>32.9</td>
<td>0.996 (0.996)*</td>
</tr>
<tr>
<td>dieldrin</td>
<td>( 6.2 \pm 0.1 )</td>
<td>( 113 \pm 4 )</td>
<td>3.1</td>
<td>1.7</td>
<td>0.997 (0.997)*</td>
</tr>
</tbody>
</table>

* Photolysis done in water.

### Table VI. Kinetic Data for Photolysis of \( \alpha \)- and \( \beta \)-Endosulfan and Dieldrin in Direct Sunlight

<table>
<thead>
<tr>
<th>compd</th>
<th>( 10^5 k/s^{-1} )</th>
<th>( 10^6 k/s^{-1} )</th>
<th>( t_{1/2}/\text{sun days} )</th>
<th>( r^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )-endosulfan</td>
<td>6.1 ± 2</td>
<td>13.4 (40.3)</td>
<td>0.815</td>
<td></td>
</tr>
<tr>
<td>( \beta )-endosulfan</td>
<td>7.4 ± 2</td>
<td>10.5 (32.6)</td>
<td>0.810</td>
<td></td>
</tr>
<tr>
<td>dieldrin</td>
<td>11.6 ± 2.0</td>
<td>6.3 (20.7)</td>
<td>0.951</td>
<td></td>
</tr>
</tbody>
</table>
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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