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INVESTIGATIONS OF THE MECHANISM OF ALKALINE HYDROLYSIS OF ORGANOPHOSPHOROTHIOATE ESTERS.

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ABSTRACT

Three experimental methods were used to investigate the mechanism of organophosphorothioate alkaline hydrolysis. The first method was to obtain a kinetic data base for the hydrolysis of five pesticides over alkaline pH ranges. In the second method, phosphorus 31 NMR was used to attempt to detect the presence of an intermediate in alkaline solution. Finally, the pH of solutions was monitored to detect rapid and excessive decreases in $[OH^-]$ that might result from production of an intermediate.

Extensive data were gathered on the rates of hydrolysis for five organophosphorothioate pesticides over the alkaline region. This data set represents the most accurate and complete compendium of dissappearance rate data available for organphosphorothioate insecticides. The data showed deviations from second order kinetics, which has implications for the prediction of degradation rates over wide pH ranges. The data could not be used to confirm or refute mechanisms involving an intermediate. The phosphorus 31 NMR spectra provided new and potentially valuable data, but did not indicate the presence of an intermediate. This may have been the result of insufficient instrument sensitivity. The pH studies demonstrated that

when thiophosphate triesters are introduced into alkaline solutions, rapid, anomalous decreases in [OH^-] could be detected.

TABLE OF CONTENTS

LIST OF FIGURES

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INTRODUCTION

The purpose of this research was to test the hypothesis that the mechanism of the alkaline hydrolysis of organophosphorothioate pesticides involves the formation of a stable, charged, pentacoordinate intermediate.

Some of the earliest investigations of the alkaline hydrolysis of organophosphate esters were reported by P.W.C. Barnard and co-workers (1961). Their fundamental conclusion was that alkaline hydrolysis of phosphate triesters probably occurs via a one step substitution mechanism with attack by hydroxide at phosphorus (Figure 1a), and not a mechanism that involves a stable intermediate in equilibrium with reactants.

SECOND ORDER MECHANISM (a)

$$O{=}P(OR)_3 + OH^- \xrightarrow{k_2} {}^-O\overset{O}{\overset{\|}{P}}(OR)_2 + HOR$$

INTERMEDIATE MECHANISM (b)

$$O{=}P(OR)_3 + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \left[HO\overset{O}{\overset{|}{P}}(OR)_3 \right]^- \xrightarrow{k_{int}} {}^-O\overset{O}{\overset{\|}{P}}(OR)_2 + HOR$$

Figure 1. Second Order and Intermediate Mechanisms.

They based their conclusion on an experiment involving the alkaline hydrolysis of both trimethyl and triphenyl phosphate in ^{18}O-enriched water. The hydrolysis would be associated with isotopic exchange at the phosphoryl oxygen atom provided that two conditions are met. First, the phosphate triester must be in equilibrium with an intermediate formed from an ^{18}O-enriched hydroxide ion (Figure 1b). Second, all steps must be slower than proton transfers involving the OH and O^- groups of the intermediate (Figure 2). Therefore, non-hydrolyzed phosphate should show an ^{18}O content which increases with reaction time. However, significant amounts of ^{18}O were not found in the unreacted phosphate triester. Therefore, it was concluded that the reaction proceeds via a second order mechanism in which the leaving group is being expelled at the same time the substituting group is entering (Barnard, 1961).

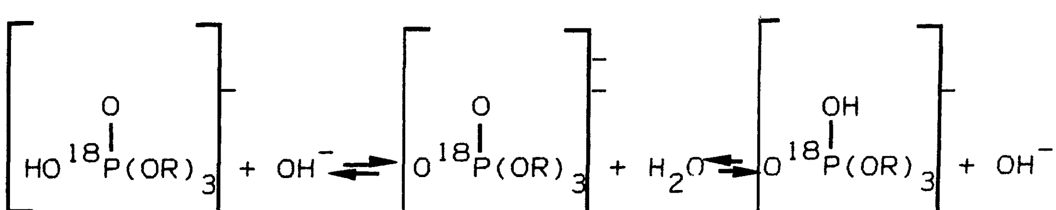
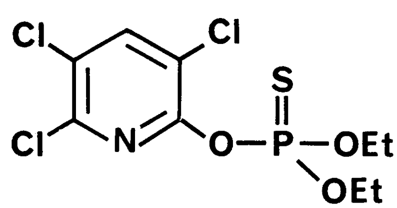


Figure 2. Proton Transfer

However, an alternative explanation for the results, given by Cox and Ramsey (1964), was that the alkaline hydrolysis proceeds by a two-step process in which the intermediate decomposes so rapidly that it does not equilibrate with the reactants. Later, Younas (1973) also suggested the existence of this intermediate. Also, kinetic evidence produced by Macalady and Wolfe (1983) indicated that a intermediate may be involved with the alkaline hydrolysis of a similar but more slowly reacting thiophosphate ester, chlorpyrifos. Chlorpyrifos, has a sulphur atom instead of an oxygen atom bonded to phosphorus (Figure 3).



Structure of Chlorpyrifos

Figure 3

Macalady and Wolfe (1983) plotted the observed pseudo-first order rate constant vs pH. They found the slope to be different from unity, which is inconsistent with second order kinetics.

Second order kinetics for the mechanism Barnard (1961) proposed, implies the following:

$$-d[ester]/dT = k(obs.)[R] = k_2[OH^-][R] \quad (1)$$

Where:

$k(obs.)$ = observed pseudo first order rate constant = $k_2[OH^-]$

k_2 = second order rate constant

$[OH^-]$ = activity of hydroxide ion (pseudo, constant)

$[R]$ = concentration of thiophosphate triester

If one takes the log of k(obs), in equation 1, the following is obtained.

$$\log k(obs.) + \mathbf{\log[R]} = \log k_2 + \log [OH^-] + \mathbf{\log [R]} \quad (2)$$

Because $[OH^-] = K_w/[H^+]$, where $[H^+]$ is the activity of H^+ and K_w is the dissociation constant for water, one can write equation 3:

$$\log k(obs.) = -\log [H^+] + \log k_2 + \log K_w \quad (3)$$

or

$$\log k(obs.) = pH + \log k_2 + \log K_w$$

Therefore, if the reaction is second order, when one plots log k(obs) vs. pH the slope should be unity. For chlorpryifos, Macalady and Wolfe (1983) reported the plot has a slope different than unity and it exhibits deviation from linearity (Figure 4). The line on that graph that shows a linear relationship has a slope of 1.20.

Macalady and Wolfe (1983) solved for the observed rate constant assuming equilibrium between chlorpyrifos and a stable intermediate. The formation of products with time would be the following:

$$d[P]/dT = k_{int}[I] \quad (4)$$

Where:

[P] = activity of products

[I] = activity of intermediate

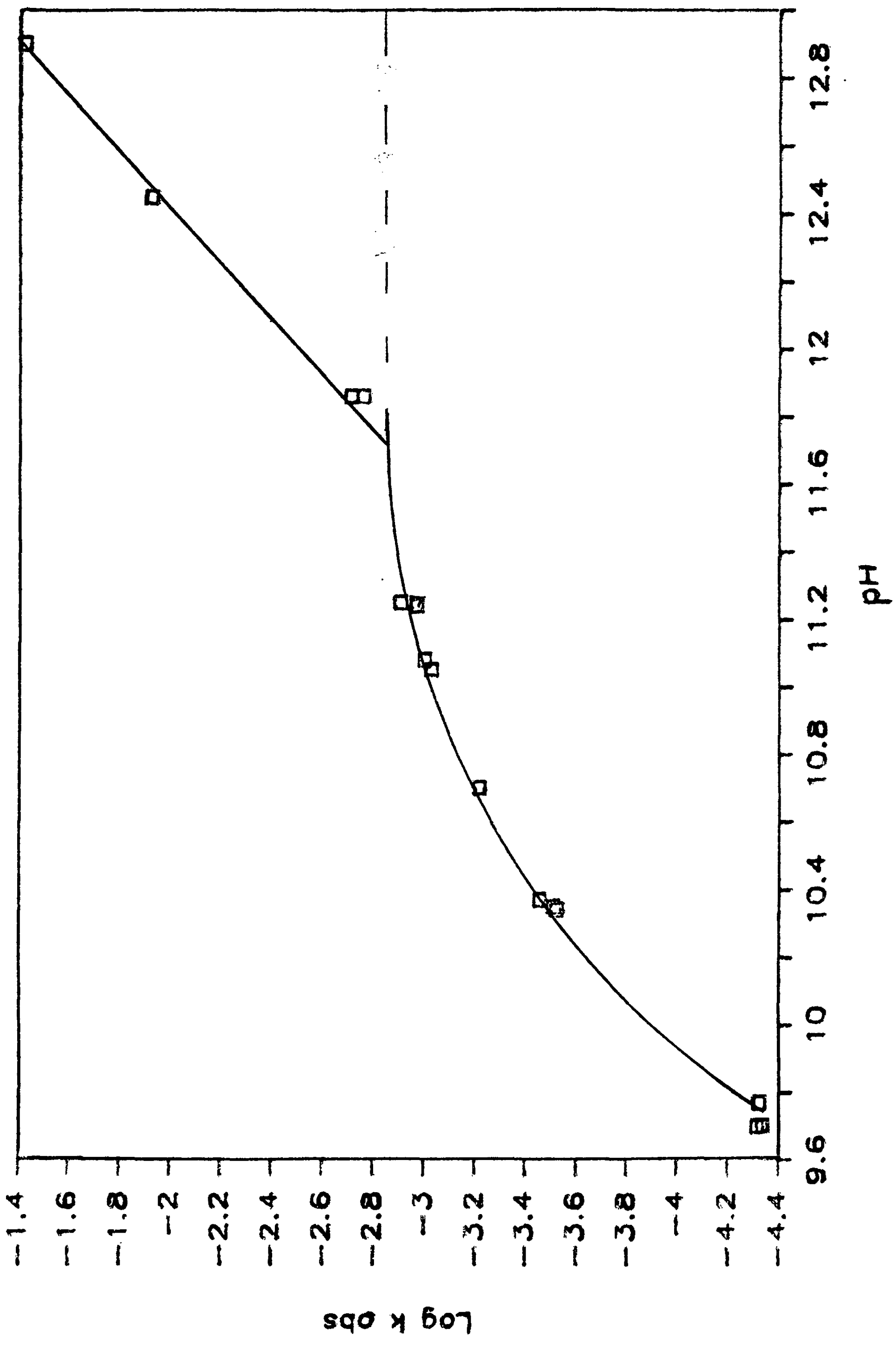
k_{int} = the specific rate at which intermediate decomposes to products

If one assumes equilibrium between reactants and intermediate the following equations can be written. (See Figure 1.)

$$k_1[R][OH^-] = k_{-1}[I] \quad (5)$$

or

Figure 4. Chlorpryifos pH Profile (Macalady, 1983)



$$[I] = k_1[R][OH^-]/k_{-1} = K[R][OH^-]$$

Where: $K = k_1/k_{-1}$

One can also assume the total concentration of reactant is the following.

$$[R_t] = [R] + [I] = [R] + K[R][OH^-] \quad (6)$$

or

$$[R] = [R_t]/(1 + K[OH^-])$$

Equations 5 and 6 can be substituted into 4 to get equation 7 for reactions at constant pH.

$$d[P]/dT = -k_{int}K[OH^-][R_t]/(1 + K[OH^-]) = -k_{obs}[R_t] \quad (7)$$

Equation 7 can be converted to equation 8.

$$1/k_{obs} = 1/k_{int} + 1/k_{int}K[OH^-] \quad (8)$$

Where:

k_{obs} = observed specific rate of hydrolysis

$K = k_1/k_{-1}$

$[OH^-]$ = hydroxide activity

This equation agrees with the chlorpyrifos dissappearance rate over the pH range 9 to 12, but not above pH 12, which provides evidence for the existence of an intermediate in the hydrolysis of chlorpyrifos. Above pH 12 it can be assumed that some other mechanism controls the kinetics.

The purpose of this research was to determine if an intermediate is involved in the general mechanism for hydrolysis of organophosphorothioates. Three different experiments were performed. The first involved obtaining kinetic data on five pesticides that are thiophosphate triesters. The rates of alkaline hydrolysis were determined by using gas chromatographic techniques to observe the pesticides' disappearence in the pH range 10.5 to 14. From this, pH profiles were constructed to attempt to elucidate the mechanism. The second method involved the use of phosphorus 31 NMR to seek evidence for the existence of an intermediate produced from thiophosphate in alkaline solution. Finally, for the third experiment, a pH meter was used to measure the pH of alkaline solutions to which thiophosphate triesters were added. If an intermediate were produced by the triester, OH^- would be bound by it. Therefore, any alteration in pH could be detected by the meter. A drop in pH more rapid than the corresponding increase in product concentration would indicate accumulation of intermediate.

EXPERIMENTAL SECTION

Instrumentation

Kinetic experiments. Gas chromatographic analyses were performed with a Hewlett Packard 5890 gas chromatograph (G.C.) equipped with a Hewlett Packard 3392A integrator. The detectors employed were a ^{63}Ni electron capture detector (ECD) and a nitrogen phosphorus detector (NPD).

The ECD was used with a Hewlett Packard capillary column. The column had an interior diameter of 0.31 mm and a length of 25 meters. The stationary phase was a crosslinked methyl silicone that had a thickness of 0.52 µm.

The operating conditions were the same for the following pesticides: chlorpyrifos, diazinon, isazophos, methyl parathion. They included injector, detector and column-oven temperatures of 250, 325 and 205 degrees Celsius, respectively. Helium was used as a carrier gas with a head pressure of 26 psi. A 5% Argon, 95% methane mixture was used as a make up gas with a flow rate of 30 ml/min.

For the analyses of fenthion the NPD detector was used. The column used in conjunction with the NPD was a Hewlett

Packard 530 μ series. Its length was 10 meters and it had a stationary phase of 50% Phenylmethyl Silicone. The oven temperature was programmed at 185-205 degrees celsius at 15 degrees per minute with a 5 minute final temperature hold. The detector was at 275 degrees and injector was at 200 degrees.

The gases required by the NPD were helium, hydrogen and air. The He acted as the carrier gas. The H_2 and air were delivered to the burner at a rate of 3 ml/min and 100 ml/min, respectively.

P^{31}NMR investigation. The Phosphorus 31 Nuclear Magnetic Resonance studies were performed on JEOL FX 90Q P^{31} spectrometer with an external lithium lock. All runs were at 36.2 megahertz. Phosphoric acid was used as a reference. The P^{31} NMR was made available by the Solar Energy Research Institute, Golden, Colorado.

pH studies. The equipment used for the pH studies included a Beckman 45 pH meter with a Allied Accu-pHast pH probe for the first set of runs and a Sensorex combination pH-reference electrode for the second set of runs. The pH was recorded on a Houston Instruments chart recorder. Experiments were run in a Manostat clear plastic glove box.

All weighing was performed on a Sartorius 1601 MP8 electronic analytical balance.

Compounds

The pesticides used were chlorpyrifos, diazinon, fenthion, isazophos, and methyl parathion. CIBA-GEIGY Corporations' Agricultural Division supplied 88.6% pure diazinon and 93.8% pure isazophos. EPA-Research Triangle Park, N.C., supplied 97.2% fenthion, and 99.9% methyl parathion. All of the following compounds were commercially supplied reagents from Fisher Scientific Company: NaOH, potassium hydrogen phthalate, concentrated nitric acid, $NaHCO_3$, HPLC grade isooctane and HPLC grade methanol. Trimethyl thiophosphate was commercially supplied by ALFA Products.

Experimental procedures

Kinetic experiments. The pesticides were introduced into reaction mixtures as saturated aqueous solutions in all kinetic runs. The saturated solutions were made by using literature values of pesticide solubilities to determine the approximate amount of pesticide per unit volume of water. Based on the solubility information the appropriate amount of pesticide was weighed in a weighing bottle. This amount of pesticide was dissolved in 5 mls of methanol and transferred to a volumetric flask. The weighing bottle was rinsed 4 additional times with 5 mls of methanol and the rinse was transferred to the volumetric flask, which was then brought to volume with water, and stored in a cabinet.

Sodium hydroxide solutions were made up such that a one to one dilution with the saturated pesticide solution would give the desired pH. For example, a solution that was 2 molar in NaOH was made up so that when it was diluted by one half, the pH would be 14. The 2 molar solution was made by adding 2 moles of solid NaOH to a 1 liter, glass, volumetric flask and bringing it to volume with D.I. H_2O. A 0.2 molar NaOH solution was made by diluting the 2 molar solution by a factor 10. A 0.02 M NaOH solution was made by diluting the 0.2 molar NaOH solution by a factor af 10. The above solutions were capped and stored in a cabinet. For pH 11.5 to 10.5 further dilutions were made immediately prior to the reaction to minimize neutralization of hydroxide in solution by CO_2.

The concentrations of the saturated pesticide solutions were far less than the concentrations of NaOH solutions.

Therefore, when the two solutions were mixed the pH of that mixture would remain constant, because [OH^-] would be essentially constant.

A typical run was initiated by pipetting 50 mls of the NaOH solution into a 250 ml glass stoppered flask. The pesticide was then introduced as 50 mls of the saturated aqueous solution. The mixture was swirled momentarily by hand and then placed in a 25.0ºC water bath. As soon as possible a 5 ml aliquot was taken from the reaction mixture with an automatic pipet, and immediately placed in a glass stoppered test tube which contained isooctane spiked with an internal standard. The internal standard was chlorpyrifos for all experiments except for the hydrolysis of chlorpyrifos itself. Methyl parathion was substituted in this case. The test tube was then mixed on a vortex mixer in order to extract the pesticide from water to isooctane. Fenthion was mixed for 2 minutes. Chlorpyrifos, diazinon, and methyl parathion were mixed 1 minute, and isazophos was mixed 30 seconds. These were the times required for maximum extraction efficiency. This was determined by plotting the concentration extracted versus time of mixing, and finding the time for which further mixing produced no increase in pesticide concentration.

The isooctane and water phases were allowed to separate, and the isooctane layer was analyzed as soon as possible by G.C. This involved pushing the start button on the G.C. and injecting 1 μl of the isooctane layer into the injection port of the G.C. with a 10 μl syringe. The syringe was rinsed 15 times before each injection with the isooctane solution to be analyzed.

After each run the concentration of OH^- was determined for the remaining reaction mixture. This was accomplished by titration with a solution of either 0.05 M or 0.005 M potassium hydrogen phthalate. For runs at pH of 11.0 and 10.5, the titrations were performed at the beginning, during, and after each run. This was done because of the concern that CO_2 or pesticide hydrolysis may have caused a considerable change in $[OH^-]$ at these lower pHs.

Between runs the glassware was cleaned with hot 6 M HNO_3. The glass was then rinsed several times with deionized water, several times with acetone, and allowed to dry at room temperature.

P^{31}NMR investigation. Several different procedures were followed. The first involved determination of the minimum detectable concentration of trimethyl thiophosphate (TMTP). The second was an attempt to observe the formation of TMTP hydrolysis products over a short period of time (hours). In the third procedure the formation of the hydrolysis products was observed over a longer time span (days).

In the first experiment solutions with TMTP concentrations of 1 mM, 5 mM, 10 mM and 20 mM were prepared and placed in separate 5 mm NMR tubes. Concentrations as low as 5 mM were detectable.

In the second experiment a 30 mM TMTP solution was prepared. The solution was then mixed 1 to 1 with the carbonate buffer (0.2M $NaHCO_3$/NaOH) to get a solution of pH 11.0 which was 15 mM in TMTP. Similar, but unbuffered, solutions with pH of 12, 13 and 14 were also prepared. Phosphorus 31 NMR was used to analyze the solutions immediately after mixing. These solutions were then tested periodically to observe any production of products and intermediates using P^{31}NMR.

For the final experiment a 22 mM TMTP solution was made. This was then mixed 1 to 1 with the same 0.2 M $NaHCO_3$/NaOH buffer solution to obtain a solution of pH 11.0. The 22 mM TMTP solution was also mixed with NaOH solutions from the kinetic experiments to obtain solutions with pHs of 14, 13, and 12, and final TMTP concentrations of 11 mM. After a period of 4 days the P^{31}NMR spectra were taken.

pH studies. A weighed quantity of a pesticide was placed in the glove box along with other equipment. The glove box was sealed and purged with N_2 gas overnight. This was done to eliminate the possibility of oxidation of the organothiophoshates.

The next day the pesticide was quantitatively transferred to a 200 ml volumetric flask and brought to volume with N_2-purged deionized water. After mixing, the pesticide solution was transferred to a buret and the buret was suspended over a magnetic stirrer.

Fifty milliliters of NaOH solution was pipetted into a beaker which contained a magnetic stirring bar. The beaker was then placed on the magnetic stirrer. A pH probe was placed in the beaker and the solution was stirred. The pH was recorded on a Houston Instruments chart recorder with the chart speed at 1 cm/hour. When it was clear that the pH was no longer drifting the chart speed was increased to 1 cm/minute and 5 mls of the TMTP solution was buretted into the beaker. For the compounds with low solublity, 50 mls were added. Water was used as a control. The chart speed was reduced to 1 cm/hour shortly after addition of the pesticide solution because major pH changes happened quickly. The pH was recorded until it was stable again. The same process was repeated for each pH of interest.

Calculations

Kinetic experiments. The following method was used to find the concentration of pesticide in solution: An isooctane solution with a known concentration of pesticide and internal standard was injected into the G.C. The only peaks that were produced were the solvent, internal standard, and pesticide peaks. The area of each peak was obtained from the integrator. Using the concentrations and areas of each compound a response factor was determined (Barbato, 1966).

$$F_s = C_i * A_s / C_s * A_i \quad (9)$$

Where:

F_s = response factor

C_i = concentration of internal standard

A_s = peak area of pesticide

C_s = concentration of pesticide

A_i = peak area of internal standard

Using the response factor, the concentration of the extracted pesticides in the reaction mixtures could be found from equation 10, since C_i, A_s, F_s and A_i were known.

$$C_s = C_i*A_s/F_s*A_i*5 \quad (10)$$

(Throughout, the concentration of reactant was used under the assumption that its activity coefficient was constant over the course of the experiment.)

The value was divided by 5 because the pesticide was extracted from five mls water into 1 ml isooctane.

The slope of a plot of ln[pesticide] vs time is equal to the negative of the pseudo-first-order rate constant for the reaction (integrated form of the first-order rate law). The slope was calculated by the following linear regression equation programmed into Lotus software:

$$\text{slope} = [n\Sigma xy-\Sigma x*\Sigma y]/[n\Sigma x^2-(\Sigma x)^2] \quad (11)$$

Where: x = time or pH
y = ln [pesticide] or log k(obs)

The intercept was found using this equation.

$$\text{intercept} = (\Sigma y-\text{slope}*\Sigma x)/n \quad (12)$$

The correlation coefficient and the standard deviation of the slope were found using the following equations: (Neter, 1985)

$$\text{corr coeff} = \frac{n\Sigma xy - \Sigma x * \Sigma y}{[\{n\Sigma x^2 - (\Sigma x)^2\}\{n\Sigma y^2 - (\Sigma y)^2\}]^{0.5}} \quad (13)$$

$$(\text{stand. dev. slope})^2 = \frac{[\Sigma y^2 - \text{intrcpt} * \Sigma y - \text{slope} * \Sigma xy]/n-2}{[\Sigma x^2 - (\Sigma x)^2/n]} \quad (14)$$

When the slope (= $-k_{obs}$) of the ln[] vs time data was determined for each pH of interest the data were handled in two ways. To determine if the data fit second order kinetics a plot of log (k_{obs}) vs pH was made for each pesticide (Equation 3). The pH was calculated using the equation:

$$pH = -\log (K_w/f_{OH}[OH^-]) \quad (15)$$

The activity coefficients of hydroxide, f_{OH}, were calulated from Debye-Huckel for pH 13 and below, and literature values from the 1969 Handbook of Chemistry and Physics were used for pH above 13.

In order to calculate the slope, intercept, correlation coefficient and standard deviation of the slope, equations 11, 12, 13 and 14 were used respectively.

To see if the data were consistent with the intermediate mechanism in Figure 1, a plot of $1/k_{obs}$ vs $1/[OH^-]$ was made. Again equations 11, 12, 13 and 14 were used to evaluate the plot.

pH studies. Only a few calculations were necessary in this section. The change in $[OH^-]$ was calculated from the measured change in pH. The initial and final pH were converted to $[OH^-]$ and the difference between the two was obtained. The final concentrations of intermediate and reactant were calulated assuming that the change in $[OH^-]$ was equal to the [intermediate] produced and the amount of reactant consumed. Using this information K equilibrium was calculated assuming that equilibrium was established much faster than the intermediate was converted to products.

$$K_{eq} = [\text{intermediate}]/[\text{reactants}] = \Delta[OH^-]/\{[OH^-]_{fin}(\text{reactants}-\Delta[OH^-])\} \quad (16)$$

Where:

$\Delta[OH^-]$ = [intermediate]

$[OH^-]_{fin}$ = final activity of OH^-

(reactants $-\Delta[OH^-]$) = final concentration of pesticide

The above assumption, that the $\Delta[OH]$ is equal to intermediate and not product formed, was made because, the final pH was measured after several tens of minutes whereas the formation of products is only significant over periods in the order of days. For example, the amount of product formed for the fastest reacting compound, isazophos, in an hour would not be enough to cause the pH changes observed, as the following calcuation demonstrates (Wolfe, 1980):

$$\ln(c/c_0) = -kt$$

The above equation is the integrated form of the 1st order rate law. Where:

c = concentration remaining at time t

c_0 = the initial concentration

k = observed rate constant

t = time in minutes

The values of c_0 and k for isazophos at pH 10.95 are available in Appendixes B and C. Substituting these values in the equation, the concentration remaining after one hour can be determined.

$$\ln(c/2.2E{-}5M) = -(3.5E{-}4min^{-1})(60min)$$

$$c = 2.15E{-}5 \text{ Molar}$$

Assuming the change in concentration of isazophos is equal to Δ[OH], it is clear that the 5.0E-7 molar drop in isazophos after one hour could not account for the one to three units of pH change observed.

RESULTS AND DISCUSSION

Kinetic experiments. The reason for performing these experiments was to test whether or not the kinetic data could distinquish between a second order mechanism and a mechanism which includes an intermediate for organphosphorothioate alkaline hydrolysis. The results for the hydrolyses of the five pesticides are given in Appendix A. These tables include the time of extraction, the concentration remaining at that time, the natural log of concentration, and the number of half lives throughout the course of each reaction. Also given are the statistical data, such as slope, intercept, correlation coefficient, and standard deviation of the slope.

Summaries of these results for the pesticides chlorpyrifos, diazinon, fenthion, isazophos and methyl parathion are given in Appendix B. The pH and k_{obs} for each run are given along with the calculated values needed for the second order and intermediate plots: log k_{obs}, $1/k_{obs}$ and $1/[OH^-]$. Below these tables the statistical analyses of each of the plots are given. Figures 5 through 9 are the plots of log k_{obs} vs pH for the five pesticides.

The pH profiles were constructed for each pesticide to see if the alkaline hydrolysis reactions followed typical

Figure 5. Effect of pH on Specific Rate of Hydrolysis for Chlorpyrifos

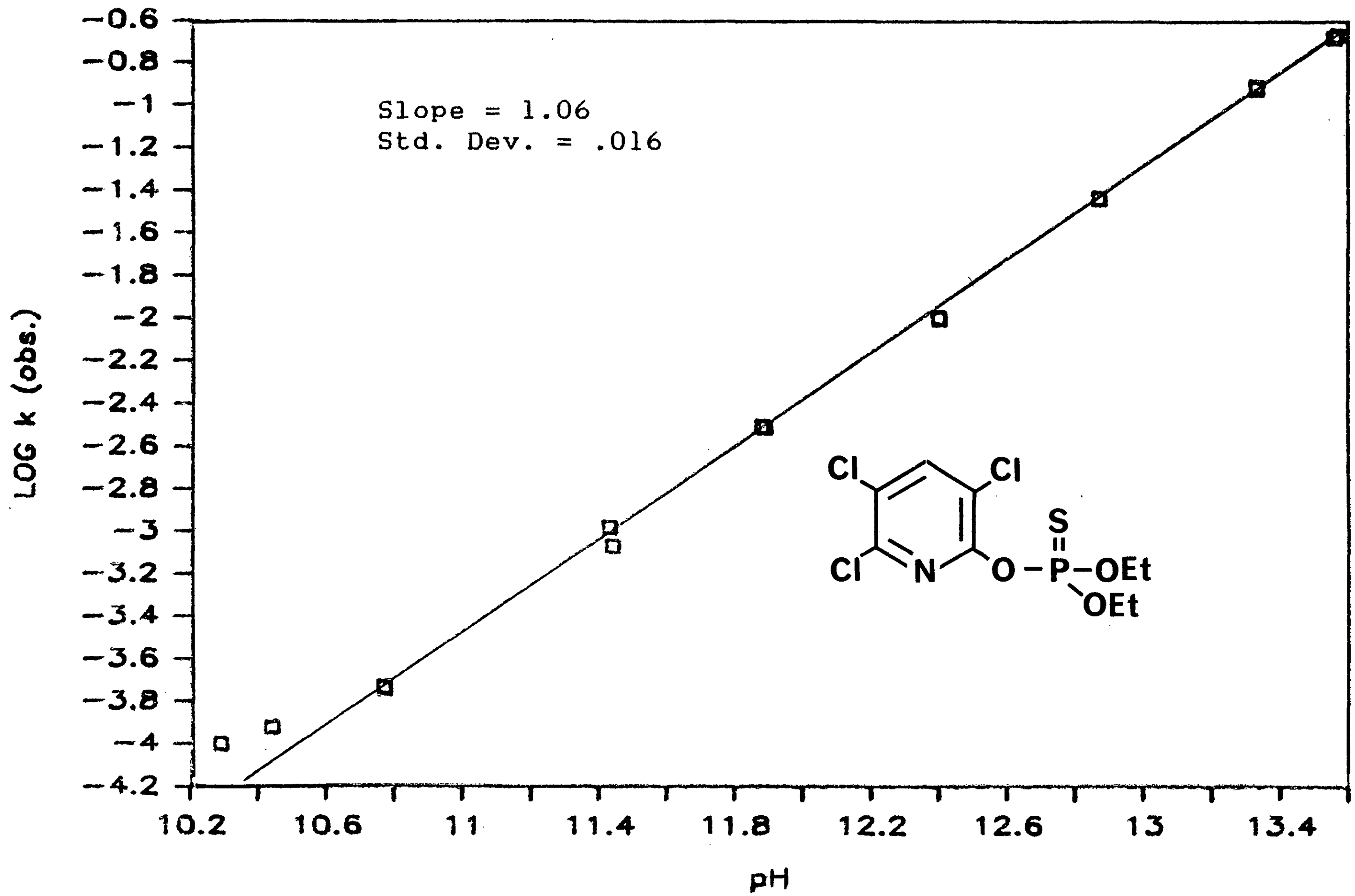


Figure 6. Effect of pH on Specific Rate of Hydrolysis for Diazinon

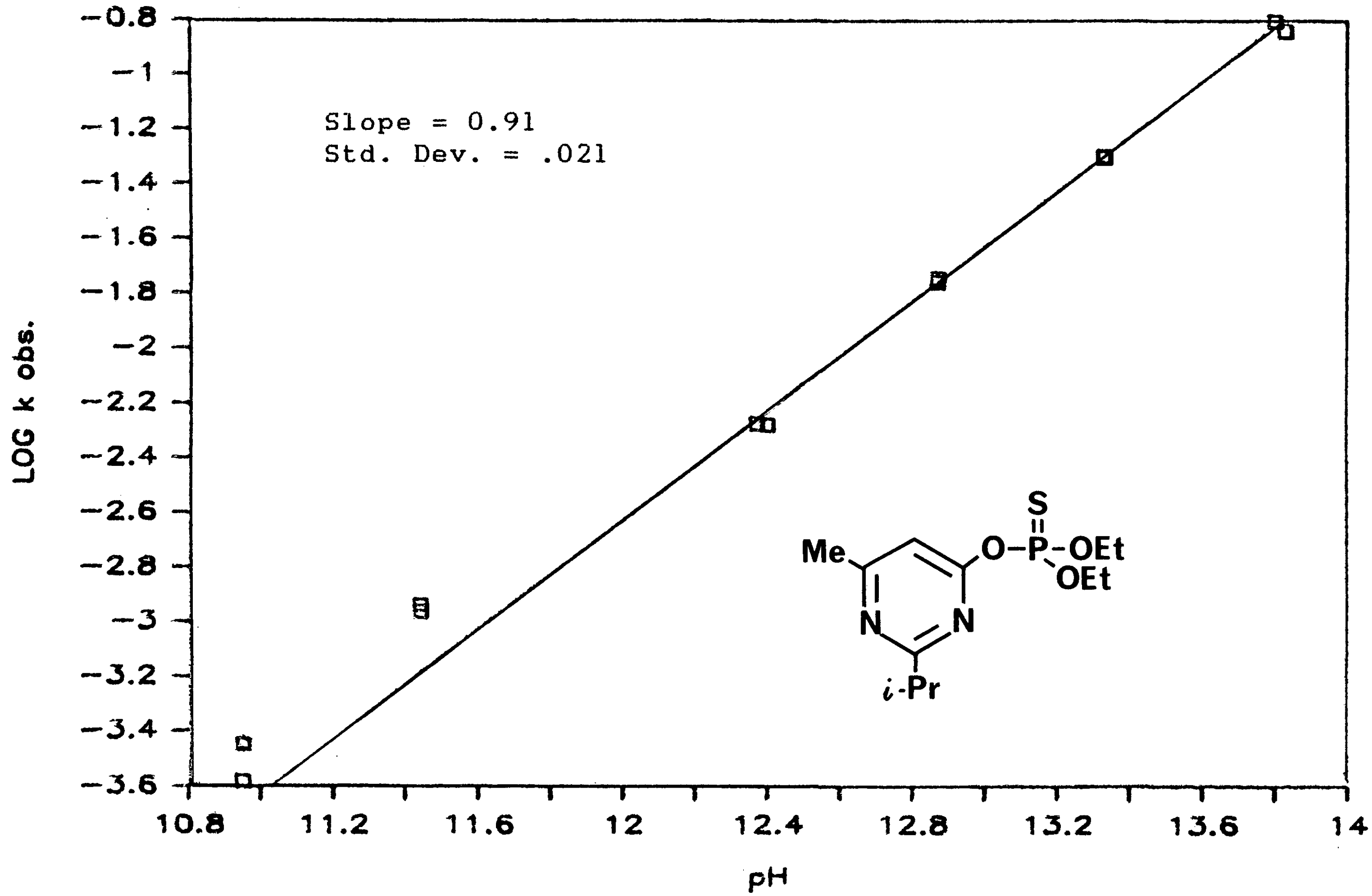


Figure 7. Effect of pH on Specific Rate of Hydrolysis for Fenthion

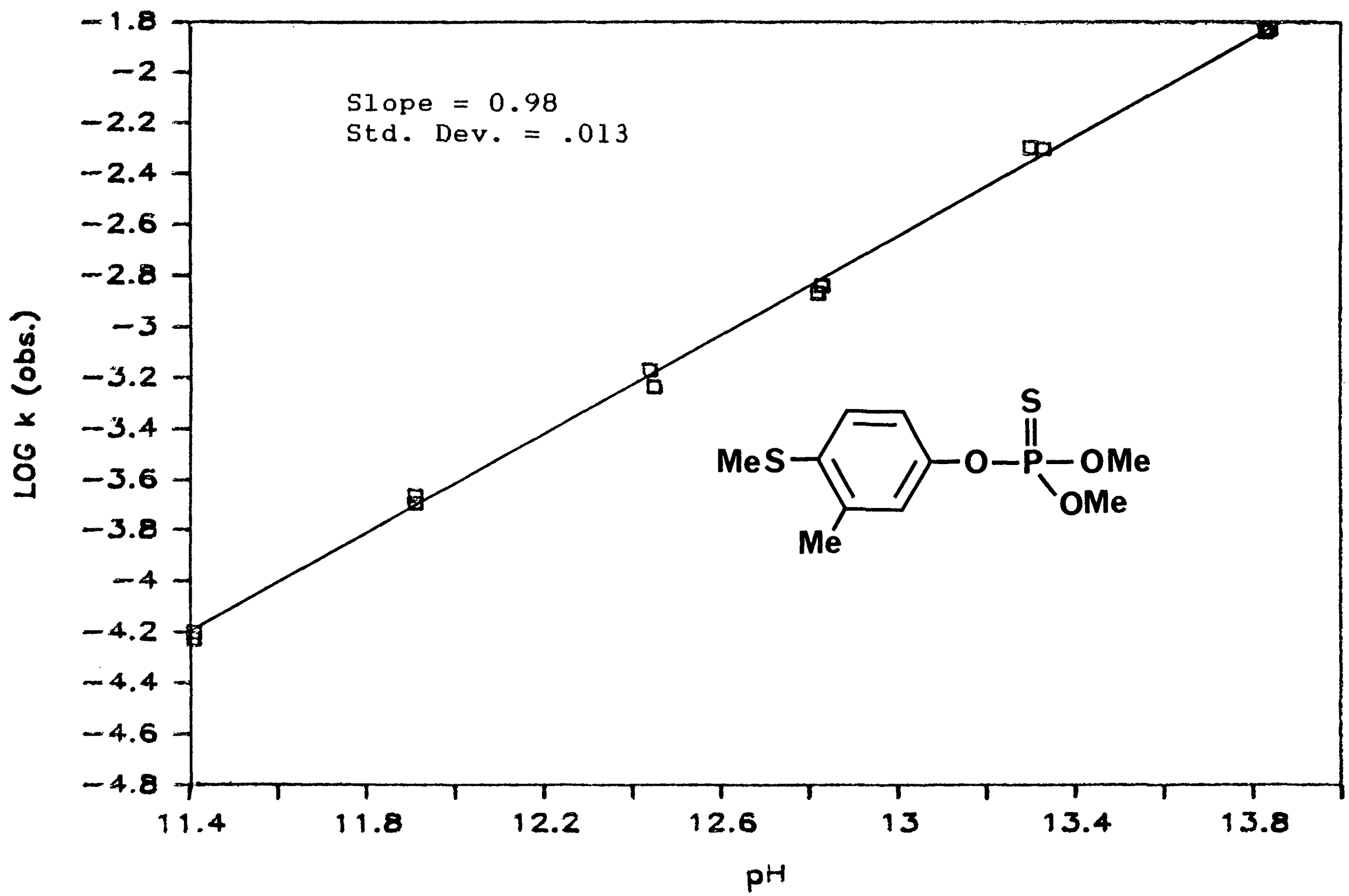


Figure 8. Effect of pH on Specific Rate of Hydrolysis for Isazophos

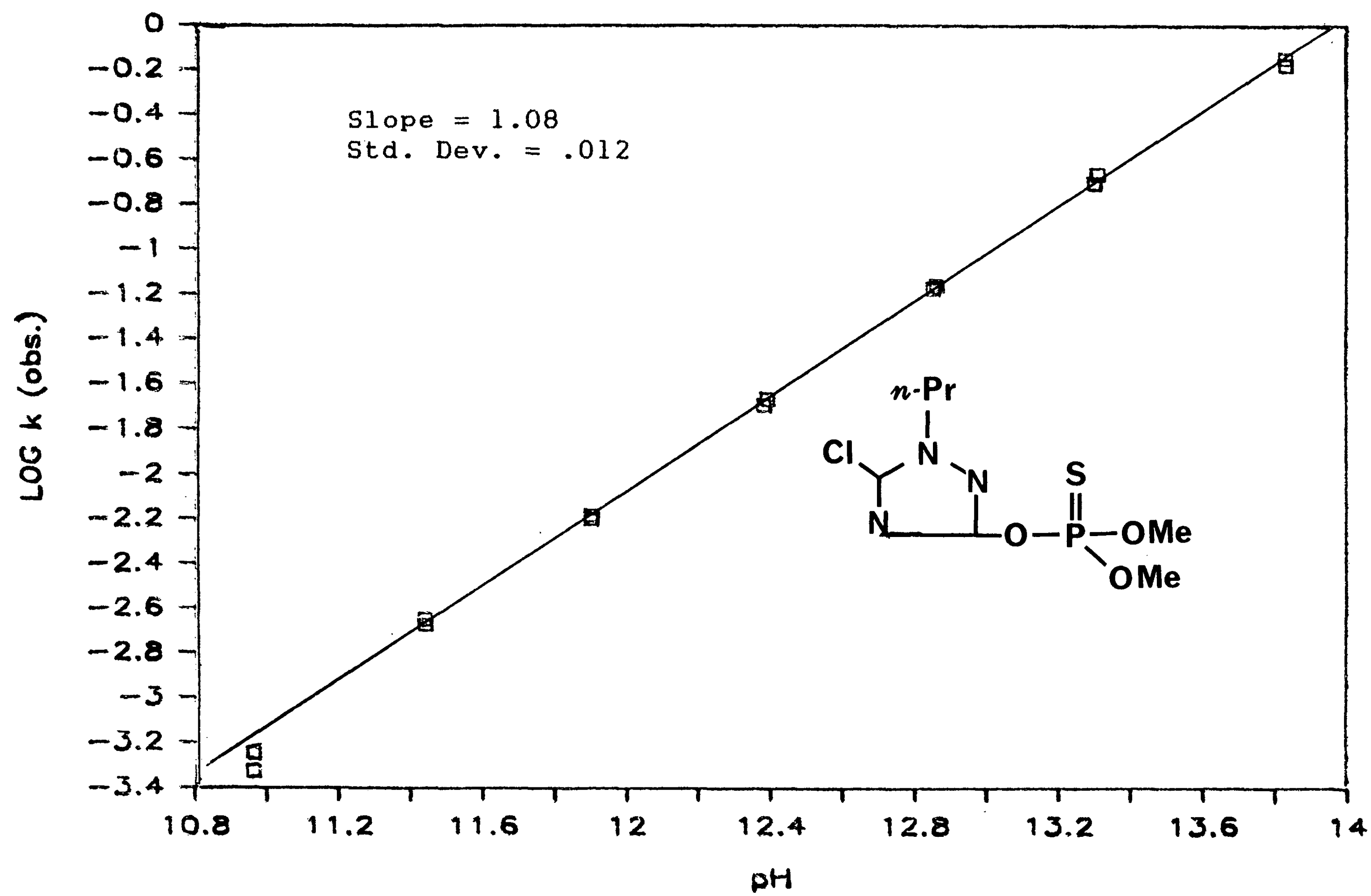
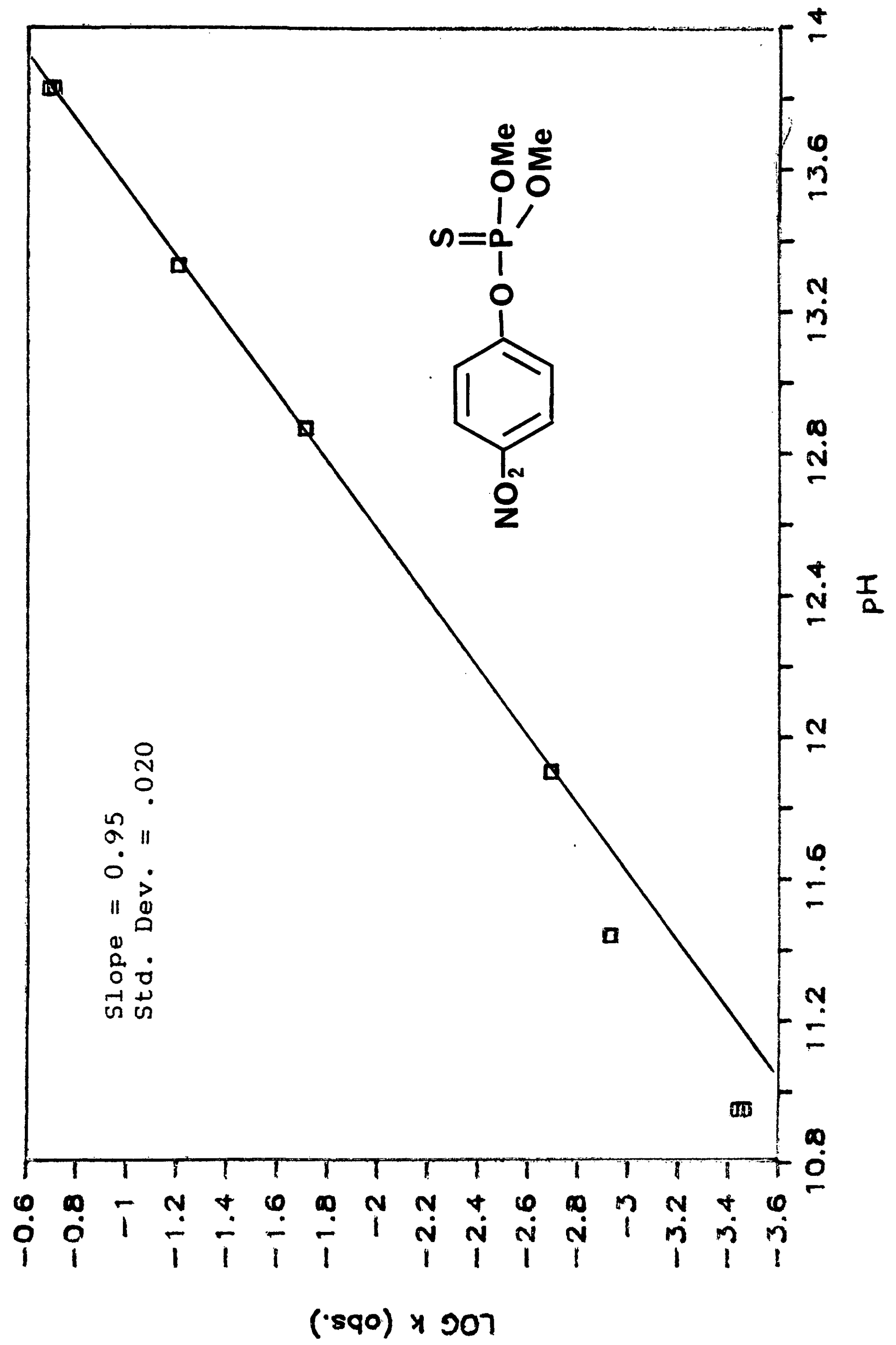


Figure 9. Effect of pH on Specific Rate of Hydrolysis for Methyl Parathion

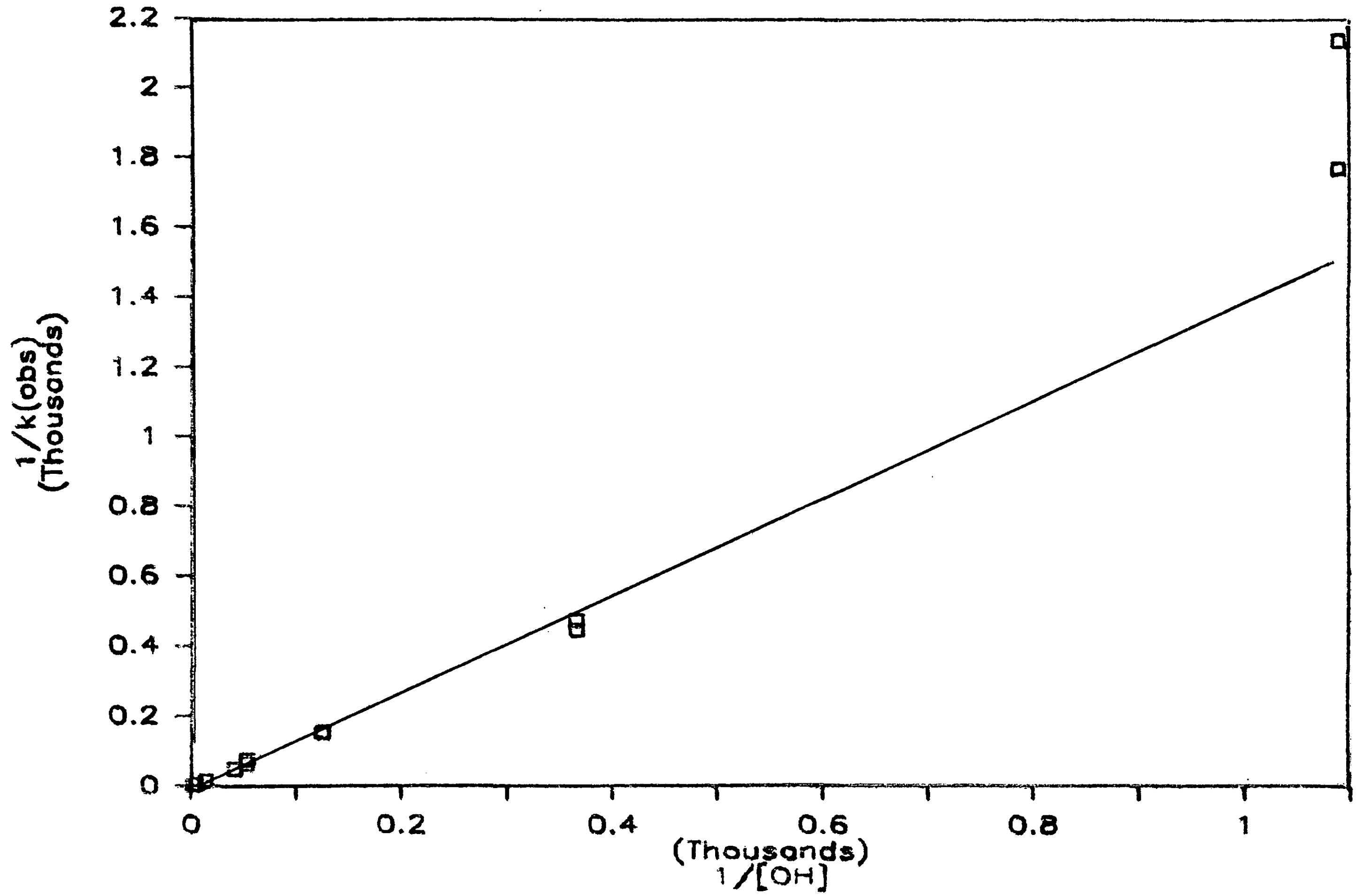


second order kinetics. In all cases the slopes were significantly different from 1.00, indicating the probability of deviation from second order behavior for these pesticides. The slopes for isazophos and chlorpyrifos were above 1.00, and the slopes of the other compounds were below 1.00.

Attempts were made to see if the data were indicative of a mechanism involving an intermediate by constructing plots of $1/k_{obs}$ vs. $1/[OH^-]$. A straight line would indicate agreement with equation 8, that is the kinetic model describing a mechanism involving an intermediate. However, the plot was not used because the close proximity of the points at high pH concealed any curvature or poor correlations, as illustrated by Figure 10. At low pH, errors would be amplified. Therefore, it would be in error to make strong conclusions on the basis of these plots.

Since these plots were not very promising, attempts were made to discern the mechanism by using the plots of $\log k_{obs}$ vs pH. The five pH profiles of this research were compared to the one for chlorpyrifos obtained by Macalady and Wolfe (1983). None of the five profiles demonstrated as much deviation from linearity as the Macalady-Wolfe profile of chlorpyrifos, including the chlorpyrifos profile from this research.

Figure 10. Kinetic Model of an Intermediate Mechanism for Isazophos

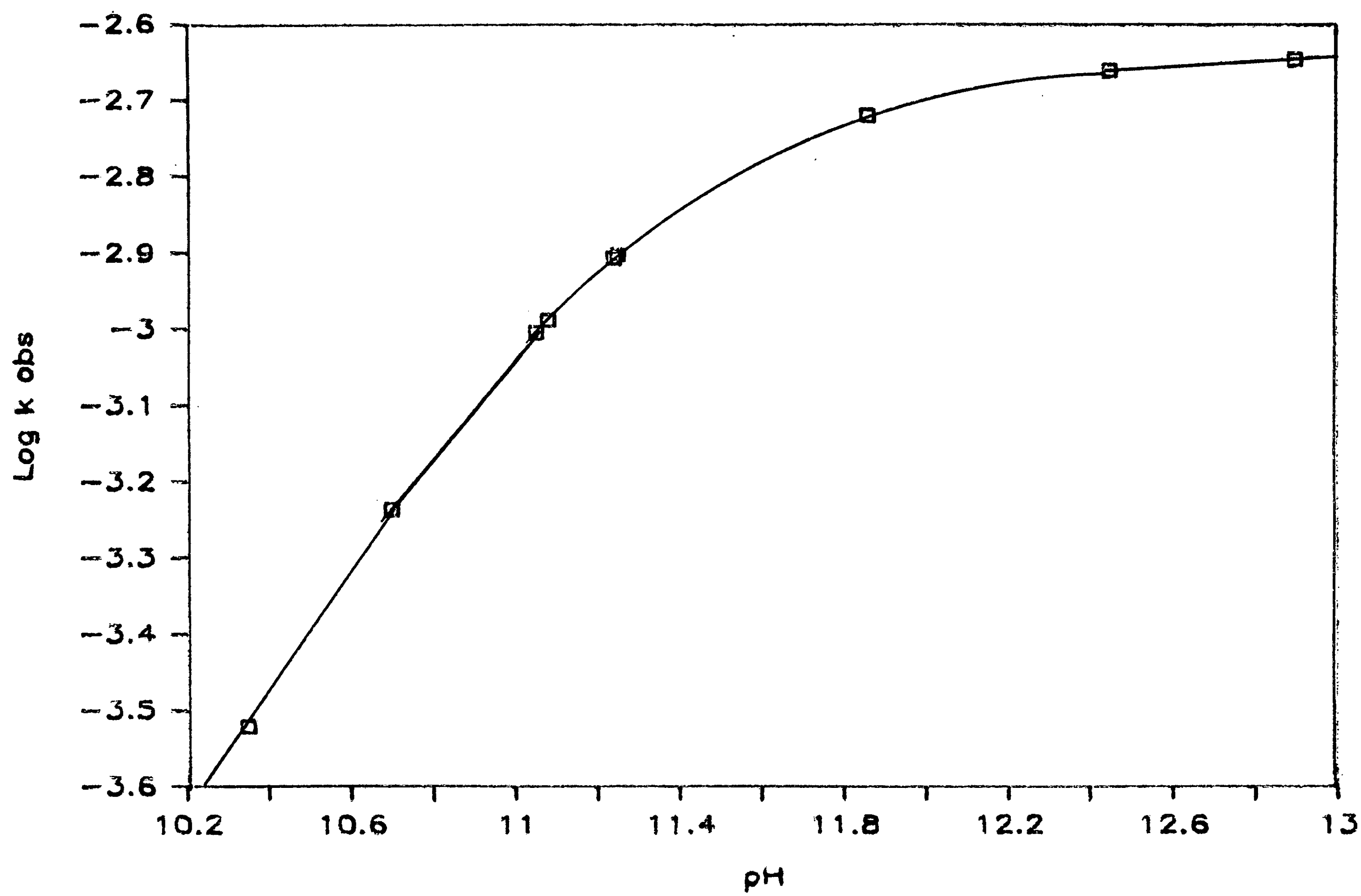


The discrepancy between the two sets of chlorpyrifos data is believed to be due to the difference in methods of pH measurement. At pH 12 and above the hyroxide ion concentrations in both sets of data were obtained by titration with potassium hydrogen phthalate (KHP), and the data are in agreement. Below pH 12, Macalady and Wolfe (1983) determined pH using a pH meter and probe. However, KHP was used to measure hydroxide ion concentration in this research. It is in this pH region that the discrepancies in the data sets arise. It is believed that the KHP titrations are more reliable.

Even though the large inflection in the Macalady-Wolfe pH profile of chlorpyrifos can partly be ascribed to experimental procedure, the slopes of the log k(obs) vs pH graphs still differ from 1.00 for the 5 pesticides studied. A slight inflection is also observed for chlorpyrifos, diazinon, and methyl parathion. Therefore, the efforts to see if these irregularities in the profiles are caused by an intermediate were continued.

The five pesticide pH profiles were compared to another profile constructed by Macalady and Wolfe (Figure 11). This profile was made by calculating what the k_{obs} would be for each pH using equation 8. The constants in equation 8, k_{int} and K, were derived from observed rate constants

Figure 11. pH Profile Calculated From Equation 8



obtained by Macalady and Wolfe (k_{int} = 2.3E-4 min^{-1}, K = 674).

Comparison of Figure 11 with Figures 4, 5, 6, 7, and 8, could lead to three conflicting conclusions. The first is that an intermediate does not exist in the alkaline hydrolysis of thiophosphate triesters. The second is that the k_i calculated by Macalady and Wolfe (1983) is far smaller than the actual k_i, in which case the kinetic data cannot be used to distinguish between the second order and intermediate mechanisms. And finally, there may be another mechanism controlling the kinetics at higher pHs, while the intermediate mechanism is prevalent at lower alkaline pHs. This last conclusion was suggested in the Macalady and Wolfe paper and subsequently supported by P^{31} NMR data for fenthion (Lui, 1984).

The additional mechanism that may be responsible for the continued increase in k_{obs} at high pHs is nucleophilic attack by OH^- at the carbon of the methyl or ethyl groups. It has been shown by Barnard (1961) that fission of the C-O bond by OH^- does not occur for phosphate triesters. Since then, the same has been assumed for the phosphorothioates, but this has never been demonstrated.

Therefore, under the assumption that attack at carbon is possible, a mathematic model was formulated to include all the kinetic contributions, considered thus far.

$$dP/dt = k_0[R] + k_2[OH^-][R] + k_iK[OH^-][R]/(1 + K[OH^-]) = k_{obs}[R] \quad (17)$$

or

$$k_{obs} = k_0 + k_2[OH^-] + k_iK[OH^-]/(1 + K[OH^-])$$

Where:

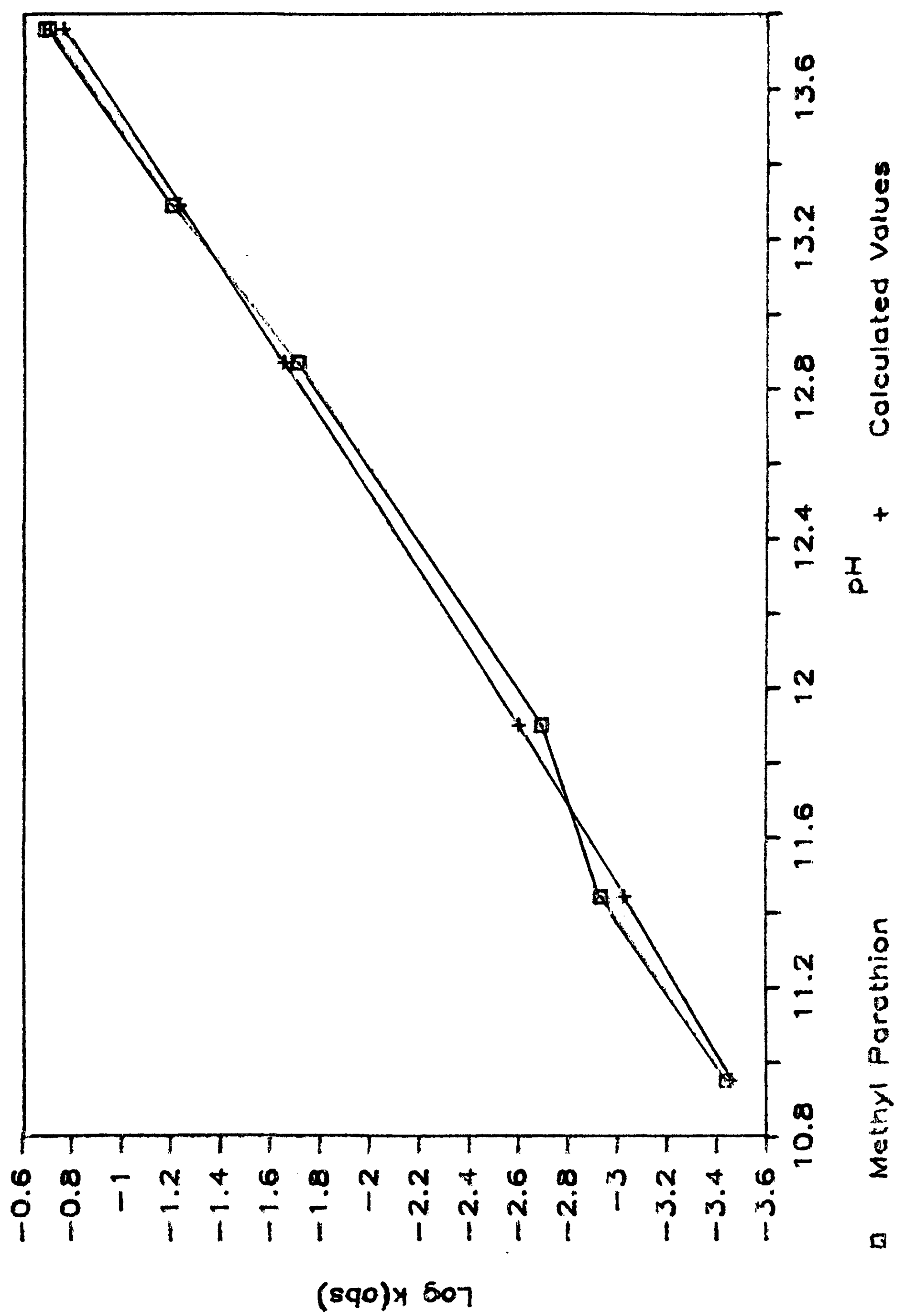
k_0 = neutral hydrolysis rate constant,

k_2 = alkaline hydrolysis by OH^- attack at carbon,

$k_iK[OH^-]/(1+K[OH^-])$ = alkaline hydrolysis via an intermediate mechanism

Measured values of k_0 are available, and using arbitrary values for k_2, k_{int}, and K, a plot of log k_{obs} vs pH (Figure 12) was constructed (k_0=0.00001, k_2=0.3, K=1000, k_i=0.00015). The slope of the plot of calculated rate constants showed good agreement with the slope of the actual data for methyl parathion. But there is no obvious way to obtain good estimates of k_2, k_i or K. Even if there were, and the result of a calculated pH profile showed a good relationship with the experimental profiles, one still could not eliminate the other mechanistic possibilities. Therefore, one can conclude that disappearance kinetics is

Figure 12. Methyl Parathion and Calculated pH Profile



not a sufficient tool to discern the mechanism of the alkaline hydrolysis for these organophosphorothioates.

Phosphorus 31 NMR. The purpose of these experiments was to determine if the formation of a thiophosphate triester intermediate could be detected by P^{31} NMR. The results show that the peak of the reactant, trimethyl thiophosphate (TMTP), is detectable at concentrations as low as 5 mM and is located at 71 parts per million up field from phosphoric acid. Upon reacting with hydroxide ion two peaks formed at 3 ppm and 58 ppm upfield.

The peak at 3 ppm formed shortly after mixing TMTP with the basic solution, which lead to the initial belief that it may be due to the intermediate. The peak at 58 ppm forms at a slower rate than the peak at 3 ppm. Therefore, it was concluded that the 58 ppm peak is a product peak.

However, upon letting the reaction continue the peak at 58 ppm continues to grow as expected but the peak at 3 ppm never diminishes. The temperature of a pH 14 reaction mixture was brought to 80 degrees Celcius for 72 hours but this had little effect on the 3 ppm peak height. One would expect the peak of an intermediate that is in equilibrium with the reactant to diminish as the reactant peak diminishes. From this information it was concluded that the peak at 3 ppm was another product peak.

The peak at 3 ppm was later discovered in solution of neutral pH. Therefore, it was postulated to be an oxidation product of TMTP. This speculation was never substantiated.

Even though an intermediate was not discovered by P^{31} NMR it is possible that if the intermediate does exist, it is at a concentration below the detectable limit of the P^{31} NMR used.

pH Meter Study. This experiment was performed under the assumption that if there is an rapid equilibrium established between an intermediate and thiophospate triesters during alkaline hydrolysis, then it would immobilize hydroxide ion and would thereby lower the detectable concentration of OH^-.

The results of these experiments (Appendix C) were erratic and irreproducible. However, it is believed that the pH drops that were obtained were not caused by a dilution effect or the result of neutralization by CO_2.

CONCLUSIONS AND RECOMMENDATIONS

A complete and accurate kinetic data base was established for the alkaline hydrolysis of five organophosphorothioate pesticides (cf. Macalady, 1983; Wolfe, 1980; Lui, 1984). The pH profiles of the five organophosphorothioates studied indicate deviations from second order behavior in that each profile has a slope which is different from 1.00. Thus, if one assumes second order behavior for the above compounds in order to predict alkaline hydrolysis rates, errors can be incurred. It is advised that rate constants be measured for a range of pH instead of using the rate constant at one pH to make predictions over a wide alkaline range.

The disappearance kinetics for the five pesticides do not unequivocally define the hydrolysis mechanism. The models for two mechanisms fit the data depending on the rate constants used. The first involves only a intermediate and the second an intermediate along with nucleophilic attack at the aliphatic carbon atom which leads to a different product. In order to determine the mechanism, product determinations should be made and, if possible, production rates should be obtained for each product to help confirm the mechanism.

Finally, the pH decreases caused by the organophosphorothioates indicate that a mechanism other than a direct substitution is involved in the alkaline hydrolysis, but no quantitative information was obtained because of the irreproducible results. But, this method has the potential of obtaining equilibrium constants for a mechanism involving an intermediate that establishes rapid equilibrium with reactants. This constant could be used as evidence for such mechanisms and help predict disappearance kinetics.

It is important that the research be continued. Eight pesticide disposal plants in the U.S. currently use high pH as a method of degrading these esters (Jett, 1983). It is assumed that there is attack solely at phosphorus, therefore only a dimethyl or diethyl thiophosphate and an alcohol are being produced. But if there is C-O bond fission there is a possibility that toxic by-products are formed (Wolfe, 1986). One possible method of establishing whether or not there is fission of the C-O bond is by further NMR studies on compounds that have two or three different ester groups linked to phosphorus. These compounds will produce several products if there is attack both at carbon and at phosphorus.

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Appendix A

Kinetic Data

HYDROLYSIS OF CHLORPYRIFOS AT PH 14 RUN A

TIME(MIN)	CONC. (M)	LN [M]	
**********	**********	***********	SLOPE = -k (obs)
5.00E-01	2.05E-07	-1.54E+01	-2.10E-01
5.00E-01	2.05E-07	-1.54E+01	
1.75E+00	1.68E-07	-1.56E+01	INTERCEPT
1.75E+00	1.68E-07	-1.56E+01	-1.53E+01
2.75E+00	1.24E-07	-1.59E+01	
2.75E+00	1.24E-07	-1.59E+01	CORR COEFF
3.75E+00	1.13E-07	-1.60E+01	-9.97E-01
3.75E+00	1.13E-07	-1.60E+01	
4.75E+00	8.34E-08	-1.63E+01	STD. OF SLOPE
4.75E+00	8.34E-08	-1.63E+01	4.33E-03
5.75E+00	6.83E-08	-1.65E+01	
5.75E+00	6.83E-08	-1.65E+01	NO. OF POINTS
6.85E+00	5.59E-08	-1.67E+01	1.60E+01
6.85E+00	5.59E-08	-1.67E+01	
8.00E+00	4.14E-08	-1.70E+01	NO. OF 1/2 LIVES
8.00E+00	4.58E-08	-1.69E+01	2.16E+00

HYDROLYSIS OF CHLORPYRIFOS AT PH 14 RUN B

TIME(MIN)	CONC. (M)	LN [M]	
**********	**********	***********	SLOPE = -k (obs)
2.00E-01	2.27E-07	-1.53E+01	-2.15E-01
2.00E-01	2.05E-07	-1.54E+01	
1.20E+00	1.68E-07	-1.56E+01	INTERCEPT
1.20E+00	1.68E-07	-1.56E+01	-1.53E+01
2.20E+00	1.37E-07	-1.58E+01	
2.20E+00	1.37E-07	-1.58E+01	CORR COEFF
3.20E+00	1.24E-07	-1.59E+01	-9.95E-01
3.20E+00	1.24E-07	-1.59E+01	
4.25E+00	9.21E-08	-1.62E+01	STD. OF SLOPE
4.25E+00	9.21E-08	-1.62E+01	5.98E-03
5.25E+00	6.83E-08	-1.65E+01	
5.25E+00	6.83E-08	-1.65E+01	NO. OF POINTS
6.25E+00	6.18E-08	-1.66E+01	1.60E+01
6.25E+00	6.18E-08	-1.66E+01	
7.25E+00	4.58E-08	-1.69E+01	NO. OF 1/2 LIVES
7.25E+00	4.58E-08	-1.69E+01	2.31E+00

HYDROLYSIS OF CHLORPYRIFOS AT PH 13.5 RUN A

TIME(MIN)	CONC. (M)	LN [M]	
**********	**********	***********	SLOPE = -k (obs)
4.50E+00	2.01E-07	-1.54E+01	-1.20E-01
4.50E+00	2.09E-07	-1.54E+01	
7.50E+00	1.33E-07	-1.58E+01	INTERCEPT
7.50E+00	1.36E-07	-1.58E+01	-1.49E+01
1.12E+01	9.12E-08	-1.62E+01	
1.12E+01	9.12E-08	-1.62E+01	CORR COEFF
1.42E+01	6.24E-08	-1.66E+01	-9.99E-01
1.42E+01	6.36E-08	-1.66E+01	
1.72E+01	4.35E-08	-1.70E+01	STD. OF SLOPE
1.72E+01	4.27E-08	-1.70E+01	1.65E-03
2.02E+01	2.89E-08	-1.74E+01	
2.02E+01	3.39E-08	-1.72E+01	NO. OF POINTS
2.32E+01	2.16E-08	-1.77E+01	1.60E+01
2.32E+01	2.14E-08	-1.77E+01	
2.62E+01	1.36E-08	-1.81E+01	NO. OF 1/2 LIVES
2.62E+01	1.57E-08	-1.80E+01	3.68E+00

HYDROLYSIS OF CHLORPYRIFOS AT PH 13.5 RUN B

TIME(MIN)	CONC. (M)	LN [M]	
**********	**********	***********	SLOPE = -k (obs)
4.50E+00	1.91E-07	-1.55E+01	-1.24E-01
4.50E+00	2.05E-07	-1.54E+01	
7.50E+00	1.43E-07	-1.58E+01	INTERCEPT
7.50E+00	1.43E-07	-1.58E+01	-1.48E+01
1.12E+01	8.59E-08	-1.63E+01	
1.12E+01	9.03E-08	-1.62E+01	CORR COEFF
1.42E+01	6.24E-08	-1.66E+01	-9.98E-01
1.42E+01	6.43E-08	-1.66E+01	
1.72E+01	4.40E-08	-1.69E+01	STD. OF SLOPE
1.72E+01	4.35E-08	-1.70E+01	2.03E-03
2.02E+01	2.83E-08	-1.74E+01	
2.02E+01	2.98E-08	-1.73E+01	NO. OF POINTS
2.32E+01	1.70E-08	-1.79E+01	1.60E+01
2.32E+01	2.12E-08	-1.77E+01	
2.62E+01	1.46E-08	-1.80E+01	NO. OF 1/2 LIVES
2.62E+01	1.36E-08	-1.81E+01	3.81E+00

HYDROLYSIS OF CHLORPYRIFOS AT PH 13 RUN A

TIME(MIN)	CONC. (M)	LN [M]	
**********	**********	***********	SLOPE = -k obs.
5.000E-01	2.010E-07	-1.542E+01	-3.714E-02
5.000E-01	2.071E-07	-1.539E+01	
9.550E+00	1.375E-07	-1.580E+01	INTERCEPT
9.550E+00	1.361E-07	-1.581E+01	-1.543E+01
1.850E+01	9.783E-08	-1.614E+01	
1.850E+01	9.783E-08	-1.614E+01	CORR
2.800E+01	7.033E-08	-1.647E+01	-9.984E-01
2.800E+01	7.248E-08	-1.644E+01	
3.620E+01	4.907E-08	-1.683E+01	STD. OF SLOPE
3.620E+01	5.107E-08	-1.679E+01	5.554E-04
4.620E+01	3.257E-08	-1.724E+01	
4.620E+01	3.599E-08	-1.714E+01	NO. OF POINTS
5.325E+01	2.693E-08	-1.743E+01	1.600E+01
5.325E+01	2.747E-08	-1.741E+01	
6.250E+01	1.995E-08	-1.773E+01	NO. OF 1/2 LIVES
6.250E+01	2.140E-08	-1.766E+01	3.232E+00

HYDROLYSIS OF CHLORPYRIFOS AT PH 13 RUN B

TIME(MIN)	CONC. (M)	LN [M]	
**********	**********	***********	SLOPE = -k obs.
5.000E-01	1.893E-07	-1.548E+01	-3.677E-02
5.000E-01	1.874E-07	-1.549E+01	
9.550E+00	1.416E-07	-1.577E+01	INTERCEPT
9.550E+00	1.445E-07	-1.575E+01	-1.544E+01
1.850E+01	9.783E-08	-1.614E+01	
1.850E+01	1.028E-07	-1.609E+01	CORR
2.800E+01	7.033E-08	-1.647E+01	-9.982E-01
2.800E+01	7.248E-08	-1.644E+01	
3.620E+01	5.057E-08	-1.680E+01	STD. OF SLOPE
3.620E+01	5.423E-08	-1.673E+01	5.887E-04
4.620E+01	3.493E-08	-1.717E+01	
4.620E+01	3.389E-08	-1.720E+01	NO. OF POINTS
5.325E+01	2.486E-08	-1.751E+01	1.600E+01
5.325E+01	2.831E-08	-1.738E+01	
6.250E+01	2.056E-08	-1.770E+01	NO. OF 1/2 LIVES
6.250E+01	2.118E-08	-1.767E+01	3.160E+00

HYDROLYSIS OF CHLORPYRIFOS AT PH 12.5 RUN A

TIME(MIN)	CONC. (M)	LN [M]	
**********	**********	***********	SLOPE = -k obs.
0.000E+00	1.874E-07	-1.549E+01	-1.015E-02
0.000E+00	1.951E-07	-1.545E+01	
3.000E+01	1.361E-07	-1.581E+01	INTERCEPT
3.000E+01	1.334E-07	-1.583E+01	-1.548E+01
7.100E+01	9.306E-08	-1.619E+01	
7.100E+01	9.686E-08	-1.615E+01	CORR
9.000E+01	7.321E-08	-1.643E+01	-9.991E-01
9.000E+01	7.851E-08	-1.636E+01	
1.100E+02	6.176E-08	-1.660E+01	STD. OF SLOPE
1.100E+02	6.054E-08	-1.662E+01	1.176E-04
1.350E+02	4.668E-08	-1.688E+01	
1.350E+02	4.907E-08	-1.683E+01	NO. OF POINTS
1.600E+02	3.746E-08	-1.710E+01	1.600E+01
1.600E+02	3.746E-08	-1.710E+01	
1.850E+02	2.888E-08	-1.736E+01	NO. OF 1/2 LIVES
1.850E+02	2.860E-08	-1.737E+01	2.713E+00

HYDROLYSIS OF CHLORPYRIFOS AT PH 12.5 RUN B

TIME(MIN)	CONC. (M)	LN [M]	
**********	**********	***********	SLOPE = -k obs.
0.000E+00	1.819E-07	-1.552E+01	-9.949E-03
0.000E+00	1.855E-07	-1.550E+01	
3.000E+01	1.445E-07	-1.575E+01	INTERCEPT
3.000E+01	1.445E-07	-1.575E+01	-1.549E+01
7.100E+01	9.590E-08	-1.616E+01	
7.100E+01	9.122E-08	-1.621E+01	CORR
9.000E+01	7.773E-08	-1.637E+01	-9.985E-01
9.000E+01	7.696E-08	-1.638E+01	
1.100E+02	6.238E-08	-1.659E+01	STD. OF SLOPE
1.100E+02	6.301E-08	-1.658E+01	1.443E-04
1.350E+02	4.715E-08	-1.687E+01	
1.350E+02	4.810E-08	-1.685E+01	NO. OF POINTS
1.600E+02	3.746E-08	-1.710E+01	1.600E+01
1.600E+02	3.599E-08	-1.714E+01	
1.850E+02	3.160E-08	-1.727E+01	NO. OF 1/2 LIVES
1.850E+02	3.098E-08	-1.729E+01	2.554E+00

HYDROLYSIS OF CHLORPYRIFOS AT PH 12 RUN A

TIME(MIN)	CONC. (M)	LN [M]	
**********	**********	***********	SLOPE = -k obs.
0.000E+00	1.783E-07	-1.554E+01	-3.145E-03
0.000E+00	1.747E-07	-1.556E+01	
7.000E+01	1.402E-07	-1.578E+01	INTERCEPT
7.000E+01	1.416E-07	-1.577E+01	-1.561E+01
1.750E+02	9.686E-08	-1.615E+01	
1.750E+02	9.783E-08	-1.614E+01	CORR
2.750E+02	6.301E-08	-1.658E+01	-9.957E-01
2.750E+02	6.115E-08	-1.661E+01	
3.300E+02	5.701E-08	-1.668E+01	STD. OF LINE
3.300E+02	5.588E-08	-1.670E+01	7.794E-05
4.150E+02	4.224E-08	-1.698E+01	
4.150E+02	4.309E-08	-1.696E+01	NO. OF POINTS
5.800E+02	2.803E-08	-1.739E+01	1.600E+01
5.800E+02	2.747E-08	-1.741E+01	
6.800E+02	2.140E-08	-1.766E+01	NO. OF 1/2 LIVES
6.800E+02	2.076E-08	-1.769E+01	3.102E+00

HYDROLYSIS OF CHLORPYRIFOS AT PH 12 RUN B

TIME(MIN)	CONC. (M)	LN [M]	
**********	**********	***********	SLOPE = -k obs.
0.000E+00	1.931E-07	-1.546E+01	-3.090E-03
0.000E+00	1.801E-07	-1.553E+01	
7.000E+01	1.256E-07	-1.589E+01	INTERCEPT
7.000E+01	1.307E-07	-1.585E+01	-1.560E+01
1.750E+02	9.590E-08	-1.616E+01	
1.750E+02	1.018E-07	-1.610E+01	CORR
2.750E+02	6.963E-08	-1.648E+01	-9.961E-01
2.750E+02	6.624E-08	-1.653E+01	
3.300E+02	5.994E-08	-1.663E+01	STD. OF LINE
3.300E+02	5.994E-08	-1.663E+01	7.318E-05
4.150E+02	4.309E-08	-1.696E+01	
4.150E+02	4.485E-08	-1.692E+01	NO. OF POINTS
5.800E+02	2.775E-08	-1.740E+01	1.600E+01
5.800E+02	2.803E-08	-1.739E+01	
6.800E+02	2.249E-08	-1.761E+01	NO. OF 1/2 LIVES
6.800E+02	2.161E-08	-1.765E+01	3.160E+00

HYDROLYSIS OF CHLORPYRIFOS AT PH 11.5 RUN A

TIME(MIN)	CONC. (M)	LN [M]	
**********	**********	***********	SLOPE = -k obs.
0.000E+00	3.812E-07	-1.478E+01	-1.051E-03
0.000E+00	3.736E-07	-1.480E+01	
8.000E+01	3.449E-07	-1.488E+01	INTERCEPT
8.000E+01	3.484E-07	-1.487E+01	-1.480E+01
2.750E+02	2.686E-07	-1.513E+01	
2.750E+02	2.713E-07	-1.512E+01	CORR
5.150E+02	2.289E-07	-1.529E+01	-9.986E-01
5.150E+02	2.312E-07	-1.528E+01	
6.600E+02	1.855E-07	-1.550E+01	STD. OF LINE
6.600E+02	1.819E-07	-1.552E+01	1.500E-05
1.345E+03	8.337E-08	-1.630E+01	
1.345E+03	8.941E-08	-1.623E+01	NO. OF POINTS
1.585E+03	7.033E-08	-1.647E+01	1.600E+01
1.585E+03	6.963E-08	-1.648E+01	
1.835E+03	5.644E-08	-1.669E+01	NO. OF 1/2 LIVES
1.835E+03	5.701E-08	-1.668E+01	2.741E+00

HYDROLYSIS OF CHLORPYRIFOS AT PH 11.5 RUN B

TIME(MIN)	CONC. (M)	LN [M]	
**********	**********	***********	SLOPE = -k obs.
0.000E+00	1.819E-07	-1.552E+01	-8.547E-04
0.000E+00	1.855E-07	-1.550E+01	
8.000E+01	1.445E-07	-1.575E+01	INTERCEPT
8.000E+01	1.445E-07	-1.575E+01	-1.579E+01
2.750E+02	9.590E-08	-1.616E+01	
2.750E+02	9.122E-08	-1.621E+01	CORR
5.150E+02	7.773E-08	-1.637E+01	-9.625E-01
5.150E+02	7.696E-08	-1.638E+01	
6.600E+02	6.238E-08	-1.659E+01	STD. OF LINE
6.600E+02	6.301E-08	-1.658E+01	6.441E-05
1.345E+03	4.715E-08	-1.687E+01	
1.345E+03	4.810E-08	-1.685E+01	NO. OF POINTS
1.585E+03	3.746E-08	-1.710E+01	1.600E+01
1.585E+03	3.599E-08	-1.714E+01	
1.835E+03	3.160E-08	-1.727E+01	NO. OF 1/2 LIVES
1.835E+03	3.098E-08	-1.729E+01	2.554E+00

HYDROLYSIS OF CHLORPYRIFOS AT PH 11 RUN A

TIME(MIN)	CONC. (M)	LN [M]
**********	**********	***********
0.000E+00	1.674E-06	-1.330E+01
0.000E+00	1.658E-06	-1.331E+01
1.440E+03	1.204E-06	-1.363E+01
1.440E+03	1.134E-06	-1.369E+01
2.820E+03	7.302E-07	-1.413E+01
2.820E+03	7.015E-07	-1.417E+01
4.080E+03	5.518E-07	-1.441E+01
4.080E+03	5.518E-07	-1.441E+01
5.820E+03	4.846E-07	-1.454E+01
5.820E+03	4.703E-07	-1.457E+01
8.430E+03	3.059E-07	-1.500E+01
8.430E+03	3.121E-07	-1.498E+01
9.870E+03	2.382E-07	-1.525E+01
9.870E+03	2.382E-07	-1.525E+01

SLOPE = -k obs.
-1.880E-04

INTERCEPT
-1.346E+01

CORR
-9.830E-01

STD. OF SLOPE
1.015E-05

NO. OF POINTS
1.400E+01

NO. OF 1/2 LIVES
2.814E+00

HYDROLYSIS OF CHLORPYRIFOS AT PH 11 RUN B

TIME(MIN)	CONC. (M)	LN [M]
**********	**********	***********
0.000E+00	1.641E-06	-1.332E+01
0.000E+00	1.577E-06	-1.336E+01
1.440E+03	1.100E-06	-1.372E+01
1.440E+03	1.216E-06	-1.362E+01
2.820E+03	7.524E-07	-1.410E+01
2.820E+03	7.375E-07	-1.412E+01
4.080E+03	5.409E-07	-1.443E+01
4.080E+03	5.249E-07	-1.446E+01
5.820E+03	4.993E-07	-1.451E+01
5.820E+03	4.993E-07	-1.451E+01
8.430E+03	3.216E-07	-1.495E+01
8.430E+03	3.347E-07	-1.491E+01
9.870E+03	2.430E-07	-1.523E+01
9.870E+03	2.312E-07	-1.528E+01

SLOPE = -k obs.
-1.830E-04

INTERCEPT
-1.347E+01

CORR
-9.814E-01

STD. OF SLOPE
1.033E-05

NO. OF POINTS
1.400E+01

NO. OF 1/2 LIVES
2.828E+00

HYDROLYSIS OF CHLORPYRIFOS AT PH 10.5 RUN A

TIME(MIN)	CONC. (M)	LN [M]	
**********	**********	***********	SLOPE = -k obs.
0.000E+00	1.674E-06	-1.330E+01	-9.939E-05
0.000E+00	1.658E-06	-1.331E+01	
2.820E+03	9.856E-07	-1.383E+01	INTERCEPT
2.820E+03	9.856E-07	-1.383E+01	-1.340E+01
5.820E+03	8.569E-07	-1.397E+01	
5.820E+03	8.399E-07	-1.399E+01	CORR
8.430E+03	6.876E-07	-1.419E+01	-9.860E-01
8.430E+03	6.740E-07	-1.421E+01	
9.870E+03	5.801E-07	-1.436E+01	STD. OF SLOPE
9.870E+03	5.744E-07	-1.437E+01	5.315E-06
1.344E+04	4.007E-07	-1.473E+01	
1.344E+04	3.889E-07	-1.476E+01	NO. OF POINTS
			1.200E+01
			NO. OF 1/2 LIVES
			2.107E+00

HYDROLYSIS OF CHLORPYRIFOS AT PH 10.5 RUN B

TIME(MIN)	CONC. (M)	LN [M]	
**********	**********	***********	SLOPE = -k obs.
0.000E+00	1.641E-06	-1.332E+01	-1.192E-04
0.000E+00	1.674E-06	-1.330E+01	
2.820E+03	1.006E-06	-1.381E+01	INTERCEPT
2.820E+03	9.661E-07	-1.385E+01	-1.339E+01
5.820E+03	7.676E-07	-1.408E+01	
5.820E+03	7.449E-07	-1.411E+01	CORR
8.430E+03	5.919E-07	-1.434E+01	-9.935E-01
8.430E+03	5.744E-07	-1.437E+01	
9.870E+03	4.518E-07	-1.461E+01	STD. OF SLOPE
9.870E+03	4.656E-07	-1.458E+01	4.323E-06
1.344E+04	3.248E-07	-1.494E+01	
1.344E+04	3.059E-07	-1.500E+01	NO. OF POINTS
			1.200E+01
			NO. OF 1/2 LIVES
			2.424E+00

HYDROLYSIS OF DIAZINON AT PH 14 RUN A

TIME(MIN)	CONC.(mM)	LN[mM]
**********	**********	***********
0.000E+00	4.410E-03	-5.424E+00
0.000E+00	4.410E-03	-5.424E+00
2.300E+01	1.030E-04	-9.181E+00
2.300E+01	1.020E-04	-9.191E+00
2.800E+01	8.660E-05	-9.354E+00
2.800E+01	8.660E-05	-9.354E+00
3.100E+01	4.740E-05	-9.957E+00
3.100E+01	4.740E-05	-9.957E+00
3.500E+01	2.800E-05	-1.048E+01
3.500E+01	2.800E-05	-1.048E+01

SLOPE =(-k obs)
-1.441E-01

INTERCEPT
-5.508E+00

CORR. COEFF.
-9.944E-01

STD. OF SLOPE
5.432E-03

NO. OF POINTS
1.000E+01

NO. OF 1/2 LIFES
7.300E+00

HYDROLYSIS OF DIAZINON AT PH 14 RUN B

TIME(MIN)	CONC.(mM)	LN[mM]
**********	**********	***********
0.000E+00	4.160E-02	-3.180E+00
0.000E+00	4.230E-02	-3.163E+00
3.200E+00	2.390E-02	-3.734E+00
3.200E+00	2.550E-02	-3.669E+00
6.000E+00	1.600E-02	-4.135E+00
6.000E+00	1.570E-02	-4.154E+00
9.000E+00	9.050E-03	-4.705E+00
9.000E+00	9.220E-03	-4.686E+00
1.200E+01	6.480E-03	-5.039E+00
1.200E+01	6.350E-03	-5.059E+00
1.500E+01	3.740E-03	-5.589E+00
1.500E+01	4.100E-03	-5.497E+00
1.800E+01	2.650E-03	-5.933E+00
1.800E+01	2.280E-03	-6.084E+00
2.115E+01	1.510E-03	-6.496E+00
2.115E+01	1.460E-03	-6.529E+00

SLOPE =(-k obs)
-1.566E-01

INTERCEPT
-3.202E+00

CORR. COEFF.
-9.990E-01

STD. OF SLOPE
1.882E-03

NO. OF POINTS
1.600E+01

NO. OF 1/2 LIFES
4.833E+00

HYDROLYSIS OF DIAZINON AT PH 13.5 RUN A

TIME(MIN)	CONC.(mM)	LN[mM]	
**********	**********	***********	SLOPE =(-k obs)
0.000E+00	4.950E-02	-3.006E+00	-5.009E-02
0.000E+00	4.770E-02	-3.043E+00	
8.500E+00	3.500E-02	-3.352E+00	INTERCEPT
8.500E+00	3.400E-02	-3.381E+00	-2.957E+00
1.800E+01	2.000E-02	-3.912E+00	
1.800E+01	2.200E-02	-3.817E+00	CORR. COEFF.
2.500E+01	1.500E-02	-4.200E+00	-9.988E-01
2.500E+01	1.600E-02	-4.135E+00	
3.030E+01	1.200E-02	-4.423E+00	STD. OF SLOPE
3.030E+01	1.200E-02	-4.423E+00	6.475E-04
3.900E+01	7.700E-03	-4.867E+00	
3.900E+01	7.500E-03	-4.893E+00	NO. OF POINTS
5.000E+01	4.000E-03	-5.521E+00	1.600E+01
5.000E+01	4.200E-03	-5.473E+00	
6.200E+01	2.200E-03	-6.119E+00	NO. OF 1/2 LIVES
6.200E+01	2.300E-03	-6.075E+00	4.428E+00

HYDROLYSIS OF DIAZINON AT PH 13.5 RUN B

TIME(MIN)	CONC.(mM)	LN[mM]	
**********	**********	***********	SLOPE =(-k obs)
0.000E+00	5.300E-02	-2.937E+00	-5.043E-02
0.000E+00	5.400E-02	-2.919E+00	
8.500E+00	3.200E-02	-3.442E+00	INTERCEPT
8.500E+00	3.300E-02	-3.411E+00	-2.979E+00
1.800E+01	1.980E-02	-3.922E+00	
1.800E+01	2.090E-02	-3.868E+00	CORR. COEFF.
2.500E+01	1.390E-02	-4.276E+00	-9.992E-01
2.500E+01	1.390E-02	-4.276E+00	
3.030E+01	1.100E-02	-4.510E+00	STD. OF SLOPE
3.030E+01	1.100E-02	-4.510E+00	5.256E-04
3.900E+01	7.300E-03	-4.920E+00	
3.900E+01	7.100E-03	-4.948E+00	NO. OF POINTS
5.000E+01	3.800E-03	-5.573E+00	1.600E+01
5.000E+01	4.000E-03	-5.521E+00	
6.200E+01	2.400E-03	-6.032E+00	NO. OF 1/2 LIVES
6.200E+01	2.300E-03	-6.075E+00	4.527E+00

HYDROLYSIS OF DIAZINON AT PH 13 RUN A

TIME(MIN)	CONC.(mM)	LN[mM]
0.000E+00	5.930E-02	-2.825E+00
0.000E+00	5.400E-02	-2.919E+00
6.670E+00	4.180E-02	-3.175E+00
6.670E+00	4.700E-02	-3.058E+00
1.367E+01	3.950E-02	-3.231E+00
1.367E+01	3.950E-02	-3.231E+00
2.141E+01	3.590E-02	-3.327E+00
2.141E+01	3.590E-02	-3.327E+00
2.850E+01	2.890E-02	-3.544E+00
2.850E+01	3.080E-02	-3.480E+00
4.425E+01	2.400E-02	-3.730E+00
4.425E+01	2.400E-02	-3.730E+00
7.525E+01	1.320E-02	-4.328E+00
7.525E+01	1.390E-02	-4.276E+00
1.163E+02	7.630E-03	-4.876E+00
1.163E+02	6.390E-03	-5.053E+00

SLOPE =(-k obs)
-1.745E-02

INTERCEPT
-2.964E+00

CORR. COEFF.
-9.955E-01

STD. OF SLOPE
4.420E-04

NO. OF POINTS
1.600E+01

NO. OF 1/2 LIVES
3.214E+00

HYDROLYSIS OF DIAZINON AT PH 13 RUN B

TIME(MIN)	CONC.(mM)	LN[mM]
0.000E+00	6.350E-02	-2.757E+00
0.000E+00	4.650E-02	-3.068E+00
6.670E+00	5.420E-02	-2.915E+00
6.670E+00	5.110E-02	-2.974E+00
1.367E+01	4.200E-02	-3.170E+00
1.367E+01	4.220E-02	-3.165E+00
2.141E+01	4.000E-02	-3.219E+00
2.141E+01	4.000E-02	-3.219E+00
2.850E+01	3.390E-02	-3.384E+00
2.850E+01	3.390E-02	-3.384E+00
4.425E+01	2.200E-02	-3.817E+00
4.425E+01	2.540E-02	-3.673E+00
7.525E+01	1.370E-02	-4.290E+00
7.525E+01	1.320E-02	-4.328E+00
1.163E+02	7.190E-03	-4.935E+00
1.163E+02	7.190E-03	-4.935E+00

SLOPE =(-k obs)
-1.805E-02

INTERCEPT
-2.887E+00

CORR. COEFF.
-9.931E-01

STD. OF SLOPE
5.702E-04

NO. OF POINTS
1.600E+01

NO. OF 1/2 LIVES
3.143E+00

HYDROLYSIS OF DIAZINON AT PH 12.5 RUN A

TIME(MIN)	CONC. (mM)	LN [mM]	
*************************************			SLOPE =(-k obs)
0.000E+00	6.000E-02	-2.813E+00	-5.330E-03
0.000E+00	5.800E-02	-2.847E+00	
4.400E+01	4.700E-02	-3.058E+00	INTERCEPT
4.400E+01	4.700E-02	-3.058E+00	-2.910E+00
1.390E+02	2.500E-02	-3.689E+00	
1.390E+02	2.400E-02	-3.730E+00	CORR. COEFF.
2.190E+02	1.600E-02	-4.135E+00	-9.961E-01
2.190E+02	1.500E-02	-4.200E+00	
2.790E+02	1.100E-02	-4.510E+00	STD. OF SLOPE
2.790E+02	1.200E-02	-4.423E+00	1.260E-04
3.390E+02	8.300E-03	-4.791E+00	
3.390E+02	8.100E-03	-4.816E+00	NO. OF POINTS
4.790E+02	4.400E-03	-5.426E+00	1.600E+01
4.790E+02	4.200E-03	-5.473E+00	
5.330E+02	3.600E-03	-5.627E+00	NO. OF 1/2 LIVES
5.330E+02	3.600E-03	-5.627E+00	4.059E+00

HYDROLYSIS OF DIAZINON AT PH 12.5 RUN B

TIME(MIN)	CONC. (mM)	LN [mM]	
*************************************			SLOPE =(-k obs)
0.000E+00	6.100E-02	-2.797E+00	-5.262E-03
0.000E+00	5.900E-02	-2.830E+00	
4.400E+01	5.000E-02	-2.996E+00	INTERCEPT
4.400E+01	4.700E-02	-3.058E+00	-2.882E+00
1.390E+02	2.400E-02	-3.730E+00	
1.390E+02	2.500E-02	-3.689E+00	CORR. COEFF.
2.190E+02	1.700E-02	-4.075E+00	-9.970E-01
2.190E+02	1.700E-02	-4.075E+00	
2.790E+02	1.200E-02	-4.423E+00	STD. OF SLOPE
2.790E+02	1.200E-02	-4.423E+00	1.086E-04
3.390E+02	8.800E-03	-4.733E+00	
3.390E+02	8.800E-03	-4.733E+00	NO. OF POINTS
4.790E+02	4.800E-03	-5.339E+00	1.600E+01
4.790E+02	4.800E-03	-5.339E+00	
5.330E+02	3.700E-03	-5.599E+00	NO. OF 1/2 LIVES
5.330E+02	3.500E-03	-5.655E+00	4.124E+00

HYDROLYSIS OF DIAZINON AT PH 11.5 RUN A

TIME(MIN)	CONC. (M)	LN [M]	
**********	**********	***********	SLOPE =(-k obs)
0.000E+00	3.132E-05	-1.037E+01	-1.089E-03
0.000E+00	3.715E-05	-1.020E+01	
8.500E+02	1.738E-05	-1.096E+01	INTERCEPT
8.500E+02	1.862E-05	-1.089E+01	-1.028E+01
1.300E+03	5.888E-06	-1.204E+01	
1.300E+03	6.310E-06	-1.197E+01	CORR. COEFF.
2.400E+03	2.399E-06	-1.294E+01	-9.941E-01
2.400E+03	2.399E-06	-1.294E+01	
3.000E+03	1.349E-06	-1.352E+01	STD. OF SLOPE
3.000E+03	1.349E-06	-1.352E+01	3.436E-05
3.880E+03	4.467E-07	-1.462E+01	
3.880E+03	5.888E-07	-1.435E+01	NO. OF POINTS
4.570E+03	2.818E-07	-1.508E+01	1.400E+01
4.570E+03	2.042E-07	-1.540E+01	
			NO. OF 1/2 LIVES
			7.262E+00

HYDROLYSIS OF DIAZINON AT PH 11.5 RUN B

TIME(MIN)	CONC. (M)	LN [M]	
**********	**********	***********	SLOPE =(-k obs)
0.000E+00	2.630E-05	-1.055E+01	-1.152E-03
0.000E+00	3.467E-05	-1.027E+01	
8.500E+02	1.318E-05	-1.124E+01	INTERCEPT
8.500E+02	1.585E-05	-1.105E+01	-1.044E+01
1.300E+03	5.012E-06	-1.220E+01	
1.300E+03	4.786E-06	-1.225E+01	CORR. COEFF.
2.400E+03	1.698E-06	-1.329E+01	-9.959E-01
2.400E+03	1.413E-06	-1.347E+01	
3.000E+03	8.710E-07	-1.395E+01	STD. OF SLOPE
3.000E+03	9.772E-07	-1.384E+01	2.791E-05
3.880E+03	4.266E-07	-1.467E+01	
3.880E+03	3.890E-07	-1.476E+01	NO. OF POINTS
4.570E+03	1.479E-07	-1.573E+01	1.600E+01
4.570E+03	1.380E-07	-1.580E+01	
5.470E+03	5.623E-08	-1.669E+01	NO. OF 1/2 LIVES
5.470E+03	5.129E-08	-1.679E+01	9.003E+00

HYDROLYSIS OF DIAZINON AT PH 11 RUN A

TIME(MIN)	CONC. (M)	LN [M]	
**********	**********	***********	SLOPE =(-k obs)
0.000E+00	4.169E-05	-1.009E+01	-3.568E-04
0.000E+00	4.571E-05	-9.993E+00	
8.500E+02	2.512E-05	-1.059E+01	INTERCEPT
8.500E+02	2.630E-05	-1.055E+01	-1.025E+01
2.375E+03	1.413E-05	-1.117E+01	
2.375E+03	1.230E-05	-1.131E+01	CORR. COEFF.
3.730E+03	9.333E-06	-1.158E+01	-9.903E-01
3.730E+03	9.333E-06	-1.158E+01	
4.540E+03	6.457E-06	-1.195E+01	STD. OF SLOPE
4.540E+03	5.370E-06	-1.213E+01	1.337E-05
5.440E+03	4.467E-06	-1.232E+01	
5.440E+03	4.467E-06	-1.232E+01	NO. OF POINTS
7.030E+03	3.162E-06	-1.266E+01	1.600E+01
7.030E+03	2.951E-06	-1.273E+01	
8.530E+03	1.950E-06	-1.315E+01	NO. OF 1/2 LIVES
8.530E+03	1.950E-06	-1.315E+01	4.419E+00

HYDROLYSIS OF DIAZINON AT PH 11 RUN B

TIME(MIN)	CONC. (M)	LN [M]	
**********	**********	***********	SLOPE =(-k obs)
0.000E+00	2.884E-05	-1.045E+01	-2.618E-04
0.000E+00	2.692E-05	-1.052E+01	
8.500E+02	2.818E-05	-1.048E+01	INTERCEPT
8.500E+02	2.818E-05	-1.048E+01	-1.041E+01
2.375E+03	1.445E-05	-1.114E+01	
2.375E+03	1.738E-05	-1.096E+01	CORR. COEFF.
3.730E+03	1.230E-05	-1.131E+01	-9.892E-01
3.730E+03	1.148E-05	-1.137E+01	
4.540E+03	9.772E-06	-1.154E+01	STD. OF SLOPE
4.540E+03	8.710E-06	-1.165E+01	1.038E-05
5.440E+03	5.888E-06	-1.204E+01	
5.440E+03	6.761E-06	-1.190E+01	NO. OF POINTS
7.030E+03	4.677E-06	-1.227E+01	1.600E+01
7.030E+03	4.365E-06	-1.234E+01	
8.530E+03	3.802E-06	-1.248E+01	NO. OF 1/2 LIVES
8.530E+03	3.467E-06	-1.257E+01	3.057E+00

HYDROLYSIS OF FENTHION AT PH 14 RUN A

TIME(MIN)	CONC. (mM)	LN [mM]
0.000E+00	1.110E-02	-4.501E+00
0.000E+00	1.070E-02	-4.538E+00
3.000E+01	6.780E-03	-4.994E+00
3.000E+01	7.070E-03	-4.952E+00
6.000E+01	4.410E-03	-5.424E+00
6.000E+01	4.060E-03	-5.507E+00
8.000E+01	3.190E-03	-5.748E+00
8.000E+01	2.890E-03	-5.846E+00
1.000E+02	2.110E-03	-6.161E+00
1.000E+02	2.160E-03	-6.138E+00
1.200E+02	2.150E-03	-6.142E+00
1.200E+02	2.180E-03	-6.128E+00
1.500E+02	1.100E-03	-6.812E+00
1.500E+02	1.040E-03	-6.869E+00

SLOPE = -k obs.
-1.497E-02

INTERCEPT
-4.542E+00

CORR. COEFF.
-9.909E-01

STD. OF SLOPE
5.877E-04

NO. OF POINTS
1.400E+01

NO. OF 1/2 LIVES
3.416E+00

HYDROLYSIS OF FENTHION AT PH 14 RUN B

TIME(MIN)	CONC. (mM)	LN [mM]
0.000E+00	1.650E-02	-4.104E+00
0.000E+00	1.520E-02	-4.186E+00
2.000E+01	1.100E-02	-4.510E+00
2.000E+01	1.030E-02	-4.576E+00
4.000E+01	7.900E-03	-4.841E+00
4.000E+01	8.200E-03	-4.804E+00
6.000E+01	6.140E-03	-5.093E+00
6.000E+01	5.820E-03	-5.146E+00
8.000E+01	4.330E-03	-5.442E+00
8.000E+01	4.100E-03	-5.497E+00
1.000E+02	3.230E-03	-5.735E+00
1.000E+02	2.960E-03	-5.823E+00
1.500E+02	1.990E-03	-6.220E+00
1.500E+02	1.630E-03	-6.419E+00

SLOPE = -k obs.
-1.460E-02

INTERCEPT
-4.233E+00

CORR. COEFF.
-9.929E-01

STD. OF SLOPE
5.035E-04

NO. OF POINTS
1.400E+01

NO. OF 1/2 LIVES
3.340E+00

HYDROLYSIS OF FENTHION AT PH 13.5 RUN A

TIME(MIN)	CONC. (mM)	LN [mM]
0.000E+00	1.940E-02	-3.942E+00
0.000E+00	1.900E-02	-3.963E+00
6.000E+01	1.500E-02	-4.200E+00
6.000E+01	1.580E-02	-4.148E+00
1.200E+02	1.200E-02	-4.423E+00
1.200E+02	1.190E-02	-4.431E+00
1.800E+02	8.660E-03	-4.749E+00
1.800E+02	8.900E-03	-4.722E+00
2.400E+02	6.030E-03	-5.111E+00
2.400E+02	5.930E-03	-5.128E+00
3.000E+02	4.640E-03	-5.373E+00
3.000E+02	4.490E-03	-5.406E+00
4.100E+02	2.470E-03	-6.004E+00
4.100E+02	2.510E-03	-5.987E+00

SLOPE = -k obs.
-5.073E-03

INTERCEPT
-3.878E+00

CORR. COEFF.
-9.975E-01

STD. OF SLOPE
1.045E-04

NO. OF POINTS
1.400E+01

NO. OF 1/2 LIVES
2.951E+00

HYDROLYSIS OF FENTHION AT PH 13.5 RUN B

TIME(MIN)	CONC. (mM)	LN [mM]
0.000E+00	1.870E-02	-3.979E+00
0.000E+00	1.730E-02	-4.057E+00
6.000E+01	1.400E-02	-4.269E+00
6.000E+01	1.380E-02	-4.283E+00
1.200E+02	1.090E-02	-4.519E+00
1.200E+02	1.100E-02	-4.510E+00
1.800E+02	8.010E-03	-4.827E+00
1.800E+02	7.898E-03	-4.841E+00
2.400E+02	6.110E-03	-5.098E+00
2.400E+02	5.560E-03	-5.192E+00
3.000E+02	3.990E-03	-5.524E+00
3.000E+02	4.220E-03	-5.468E+00
4.100E+02	2.420E-03	-6.024E+00
4.100E+02	2.280E-03	-6.084E+00

SLOPE = -k obs.
-5.028E-03

INTERCEPT
-3.964E+00

CORR. COEFF.
-9.976E-01

STD. OF SLOPE
1.003E-04

NO. OF POINTS
1.400E+01

NO. OF 1/2 LIVES
3.036E+00

HYDROLYSIS OF FENTHION AT PH 13 RUN A

TIME(MIN)	CONC. (mM)	LN [mM]	
***********************		***********	SLOPE = -k obs.
0.000E+00	1.470E-02	-4.220E+00	-1.361E-03
0.000E+00	1.460E-02	-4.227E+00	
6.450E+01	1.040E-02	-4.566E+00	INTERCEPT
6.450E+01	1.060E-02	-4.547E+00	-4.350E+00
5.100E+02	6.900E-03	-4.976E+00	
5.100E+02	6.400E-03	-5.051E+00	CORR. COEFF.
7.920E+02	4.800E-03	-5.339E+00	-9.837E-01
7.920E+02	4.700E-03	-5.360E+00	
1.332E+03	1.400E-03	-6.571E+00	STD. OF SLOPE
1.332E+03	1.400E-03	-6.571E+00	6.652E-05
1.580E+03	1.700E-03	-6.377E+00	
1.580E+03	1.700E-03	-6.377E+00	NO. OF POINTS
1.770E+03	1.500E-03	-6.502E+00	1.600E+01
1.770E+03	1.400E-03	-6.571E+00	
2.112E+03	7.000E-04	-7.264E+00	NO. OF 1/2 LIVES
2.112E+03	6.800E-04	-7.293E+00	4.435E+00

HYDROLYSIS OF FENTHION AT PH 13 RUN B

TIME(MIN)	CONC. (mM)	LN [mM]	
*************************************			SLOPE = -k obs.
0.000E+00	1.500E-02	-4.200E+00	-1.453E-03
0.000E+00	1.500E-02	-4.200E+00	
5.000E+01	1.480E-02	-4.213E+00	INTERCEPT
5.000E+01	1.480E-02	-4.213E+00	-4.139E+00
1.667E+02	1.300E-02	-4.343E+00	
1.667E+02	1.300E-02	-4.343E+00	CORR. COEFF.
4.500E+02	8.400E-03	-4.780E+00	-9.984E-01
4.500E+02	8.400E-03	-4.780E+00	
6.600E+02	6.460E-03	-5.042E+00	STD. OF SLOPE
6.600E+02	6.460E-03	-5.042E+00	2.361E-05
8.700E+02	4.370E-03	-5.433E+00	
8.700E+02	4.370E-03	-5.433E+00	NO. OF POINTS
1.350E+03	2.200E-03	-6.119E+00	1.400E+01
1.350E+03	2.200E-03	-6.119E+00	
			NO. OF 1/2 LIVES
			2.770E+00

HYDROLYSIS OF FENTHION AT PH 12.5 RUN A

TIME(MIN)	CONC. (mM)	LN [mM]
0.000E+00	1.390E-02	-4.276E+00
0.000E+00	1.370E-02	-4.290E+00
6.150E+02	1.004E-02	-4.601E+00
6.150E+02	9.770E-03	-4.628E+00
1.395E+03	6.010E-03	-5.114E+00
1.395E+03	5.860E-03	-5.140E+00
2.055E+03	3.990E-03	-5.524E+00
2.055E+03	3.940E-03	-5.537E+00
2.835E+03	2.360E-03	-6.049E+00
2.835E+03	2.300E-03	-6.075E+00
3.525E+03	1.390E-03	-6.578E+00
3.525E+03	1.310E-03	-6.638E+00
4.285E+03	8.140E-04	-7.114E+00
4.285E+03	7.090E-04	-7.252E+00

SLOPE = -k obs.
-6.777E-04

INTERCEPT
-4.206E+00

CORR. COEFF.
-9.980E-01

STD. OF SLOPE
1.253E-05

NO. OF POINTS
1.400E+01

NO. OF 1/2 LIVES
4.294E+00

HYDROLYSIS OF FENTHION AT PH 12.5 RUN B

TIME(MIN)	CONC. (mM)	LN [mM]
0.000E+00	1.780E-02	-4.029E+00
0.000E+00	1.760E-02	-4.040E+00
6.150E+02	1.350E-02	-4.305E+00
6.150E+02	1.330E-02	-4.320E+00
1.395E+03	8.840E-03	-4.728E+00
1.395E+03	7.880E-03	-4.843E+00
2.055E+03	6.190E-03	-5.085E+00
2.055E+03	6.190E-03	-5.085E+00
2.835E+03	3.960E-03	-5.532E+00
2.835E+03	3.770E-03	-5.581E+00
3.525E+03	2.430E-03	-6.020E+00
3.525E+03	2.350E-03	-6.053E+00
4.285E+03	1.540E-03	-6.476E+00
4.285E+03	1.390E-03	-6.578E+00

SLOPE = - k obs.
-5.821E-04

INTERCEPT
-3.968E+00

CORR. COEFF.
-9.973E-01

STD. OF SLOPE
1.228E-05

NO. OF POINTS
1.400E+01

NO. OF 1/2 LIVES
3.679E+00

HYDROLYSIS OF FENTHION AT PH 12 RUN A

TIME(MIN)	CONC. (mM)	LN [mM]
0.000E+00	1.500E-02	-4.200E+00
0.000E+00	1.470E-02	-4.220E+00
1.285E+03	1.090E-02	-4.519E+00
1.285E+03	1.040E-02	-4.566E+00
2.805E+03	8.290E-03	-4.793E+00
2.805E+03	7.990E-03	-4.830E+00
4.260E+03	5.720E-03	-5.164E+00
4.260E+03	5.510E-03	-5.201E+00
7.155E+03	3.240E-03	-5.732E+00
7.155E+03	3.120E-03	-5.770E+00
8.595E+03	1.968E-03	-6.231E+00
8.505E+03	2.063E-03	-6.184E+00
1.007E+04	1.718E-03	-6.367E+00
1.007E+04	1.833E-03	-6.302E+00

SLOPE = -k obs.
-2.167E-04

INTERCEPT
-4.235E+00

CORR. COEFF.
-9.966E-01

STD. OF SLOPE
5.209E-06

NO. OF POINTS
1.400E+01

NO. OF 1/2 LIVES
3.033E+00

HYDROLYSIS OF FENTHION AT PH 12 RUN B

TIME(MIN)	CONC. (mM)	LN [mM]
0.000E+00	1.260E-02	-4.374E+00
0.000E+00	1.250E-02	-4.382E+00
1.285E+03	1.080E-02	-4.528E+00
1.285E+03	1.060E-02	-4.547E+00
2.805E+03	8.010E-03	-4.827E+00
2.805E+03	7.890E-03	-4.842E+00
4.260E+03	6.605E-03	-5.020E+00
4.260E+03	6.750E-03	-4.998E+00
7.155E+03	3.330E-03	-5.705E+00
7.155E+03	3.180E-03	-5.751E+00
8.595E+03	2.394E-03	-6.035E+00
8.505E+03	2.316E-03	-6.068E+00
1.007E+04	1.817E-03	-6.311E+00
1.007E+04	1.701E-03	-6.377E+00

SLOPE = -k obs.
-2.015E-04

INTERCEPT
-4.287E+00

CORR. COEFF.
-9.955E-01

STD. OF SLOPE
5.560E-06

NO. OF POINTS
1.400E+01

NO. OF 1/2 LIVES
2.889E+00

HYDROLYSIS OF FENTHION AT PH 11.5 RUN A

TIME(MIN)	CONC. (mM)	LN [mM]	
*************************************			SLOPE = -k obs.
0.000E+00	1.460E-02	-4.227E+00	-6.289E-05
0.000E+00	1.450E-02	-4.234E+00	
1.260E+03	1.380E-02	-4.283E+00	INTERCEPT
1.260E+03	1.400E-02	-4.269E+00	-4.237E+00
7.170E+03	8.780E-03	-4.735E+00	
7.170E+03	8.870E-03	-4.725E+00	CORR. COEFF.
1.137E+04	6.620E-03	-5.018E+00	-9.971E-01
1.137E+04	7.030E-03	-4.958E+00	
1.728E+04	4.780E-03	-5.343E+00	STD. OF SLOPE
1.728E+04	4.940E-03	-5.310E+00	1.526E-06
2.154E+04	3.700E-03	-5.599E+00	
2.154E+04	4.010E-03	-5.519E+00	NO. OF POINTS
			1.200E+01
			NO. OF 1/2 LIVES
			1.864E+00

HYDROLYSIS OF FENTHION AT PH 11.5 RUN B

TIME(MIN)	CONC. (mM)	LN [mM]	
*************************************			SLOPE = -k obs.
0.000E+00	1.530E-02	-4.180E+00	-5.943E-05
0.000E+00	1.480E-02	-4.213E+00	
1.260E+03	1.390E-02	-4.276E+00	INTERCEPT
1.260E+03	1.370E-02	-4.290E+00	-4.215E+00
7.170E+03	9.480E-03	-4.659E+00	
7.170E+03	9.410E-03	-4.666E+00	CORR. COEFF.
1.137E+04	7.360E-03	-4.912E+00	-9.989E-01
1.137E+04	7.290E-03	-4.921E+00	
1.728E+04	5.278E-03	-5.244E+00	STD. OF SLOPE
1.728E+04	5.410E-03	-5.220E+00	8.759E-07
2.154E+04	4.060E-03	-5.507E+00	
2.154E+04	4.260E-03	-5.458E+00	NO. OF POINTS
			1.200E+01
			NO. OF 1/2 LIVES
			1.845E+00

HYDROLYSIS OF ISAZOPHOS AT PH 14 RUN A

TIME(MIN)	CONC. (mM)	LN [mM]	
			SLOPE = -k obs.
0.000E+00	4.860E-03	-5.327E+00	-6.642E-01
0.000E+00	4.220E-03	-5.468E+00	
5.000E-01	3.040E-03	-5.796E+00	INTERCEPT
5.000E-01	3.100E-03	-5.776E+00	-5.370E+00
1.000E+00	2.600E-03	-5.952E+00	
1.000E+00	2.600E-03	-5.952E+00	CORR. COEFF.
1.500E+00	1.770E-03	-6.337E+00	-9.957E-01
1.500E+00	1.760E-03	-6.342E+00	
2.000E+00	1.270E-03	-6.669E+00	STD. OF SLOPE
2.000E+00	1.190E-03	-6.734E+00	1.652E-02
2.500E+00	9.290E-04	-6.981E+00	
2.500E+00	9.670E-04	-6.941E+00	NO. OF POINTS
3.000E+00	6.740E-04	-7.302E+00	1.600E+01
3.000E+00	6.450E-04	-7.346E+00	
3.500E+00	4.200E-04	-7.775E+00	NO. OF 1/2 LIVES
3.500E+00	4.000E-04	-7.824E+00	3.603E+00

HYDROLYSIS OF ISAZOPHOS AT PH 14 RUN B

TIME(MIN)	CONC. (mM)	LN [mM]	
			SLOPE = -k obs.
0.000E+00	5.070E-03	-5.284E+00	-7.095E-01
0.000E+00	4.950E-03	-5.308E+00	
5.000E-01	3.560E-03	-5.638E+00	INTERCEPT
5.000E-01	3.800E-03	-5.573E+00	-5.234E+00
1.000E+00	2.620E-03	-5.945E+00	
1.000E+00	2.650E-03	-5.933E+00	CORR. COEFF.
1.500E+00	2.040E-03	-6.195E+00	-9.973E-01
1.500E+00	1.950E-03	-6.240E+00	
2.000E+00	1.390E-03	-6.578E+00	STD. OF SLOPE
2.000E+00	1.420E-03	-6.557E+00	1.392E-02
2.500E+00	9.020E-04	-7.011E+00	
2.500E+00	9.000E-04	-7.013E+00	NO. OF POINTS
3.000E+00	6.100E-04	-7.402E+00	1.600E+01
3.000E+00	6.000E-04	-7.419E+00	
3.500E+00	4.000E-04	-7.824E+00	NO. OF 1/2 LIVES
3.500E+00	4.600E-04	-7.684E+00	3.463E+00

HYDROLYSIS OF ISAZOPHOS AT PH 13.5 RUN A

TIME(MIN)	CONC. (mM)	LN [mM]
0.000E+00	4.840E-03	-5.331E+00
0.000E+00	4.950E-03	-5.308E+00
2.500E+00	2.890E-03	-5.846E+00
2.500E+00	2.890E-03	-5.846E+00
5.000E+00	1.760E-03	-6.342E+00
5.000E+00	1.760E-03	-6.342E+00
7.500E+00	9.870E-04	-6.921E+00
7.500E+00	1.070E-03	-6.840E+00
1.000E+01	6.400E-04	-7.354E+00
1.000E+01	5.500E-04	-7.506E+00
1.200E+01	4.420E-04	-7.724E+00
1.200E+01	3.760E-04	-7.886E+00
1.500E+01	2.130E-04	-8.454E+00
1.500E+01	1.460E-04	-8.832E+00

SLOPE = -k obs.
-2.173E-01

INTERCEPT
-5.281E+00

CORR. COEFF.
-9.956E-01

STD. OF SLOPE
5.909E-03

NO. OF POINTS
1.400E+01

NO. OF 1/2 LIVES
5.051E+00

HYDROLYSIS OF ISAZOPHOS AT PH 13.5 RUN B

TIME(MIN)	CONC. (mM)	LN [mM]
0.000E+00	5.060E-03	-5.286E+00
0.000E+00	4.970E-03	-5.304E+00
2.500E+00	3.220E-03	-5.738E+00
2.500E+00	3.120E-03	-5.770E+00
5.000E+00	1.930E-03	-6.250E+00
5.000E+00	1.850E-03	-6.293E+00
7.500E+00	1.120E-03	-6.794E+00
7.500E+00	1.090E-03	-6.822E+00
1.000E+01	6.990E-04	-7.266E+00
1.000E+01	6.130E-04	-7.397E+00
1.200E+01	4.570E-04	-7.691E+00
1.200E+01	4.840E-04	-7.633E+00
1.350E+01	3.830E-04	-7.867E+00
1.350E+01	3.450E-04	-7.972E+00

SLOPE = -k obs.
-1.981E-01

INTERCEPT
-5.291E+00

CORR. COEFF.
-9.986E-01

STD. OF SLOPE
3.044E-03

NO. OF POINTS
1.400E+01

NO. OF 1/2 LIVES
3.875E+00

HYDROLYSIS OF ISAZOPHOS AT PH 13 RUN A

TIME(MIN)	CONC. (mM)	LN [mM]
0.000E+00	5.420E-03	-5.218E+00
0.000E+00	5.440E-03	-5.214E+00
2.000E+00	4.790E-03	-5.341E+00
2.000E+00	4.930E-03	-5.312E+00
4.500E+00	4.140E-03	-5.487E+00
4.500E+00	4.110E-03	-5.494E+00
1.033E+01	2.940E-03	-5.829E+00
1.033E+01	2.860E-03	-5.857E+00
1.600E+01	2.040E-03	-6.195E+00
1.600E+01	2.060E-03	-6.185E+00
2.400E+01	1.100E-03	-6.812E+00
2.400E+01	1.130E-03	-6.786E+00
3.300E+01	6.000E-04	-7.419E+00
3.300E+01	5.840E-04	-7.446E+00
3.825E+01	4.400E-04	-7.729E+00

SLOPE = -k obs.
-6.696E-02

INTERCEPT
-5.182E+00

CORR. COEFF.
-9.992E-01

STD. OF SLOPE
7.557E-04

NO. OF POINTS
1.500E+01

NO. OF 1/2 LIVES
3.623E+00

HYDROLYSIS OF ISAZOPHOS AT PH 13 RUN B

TIME(MIN)	CONC. (mM)	LN [mM]
0.000E+00	5.670E-03	-5.173E+00
0.000E+00	5.600E-03	-5.185E+00
2.000E+00	5.080E-03	-5.282E+00
2.000E+00	5.080E-03	-5.282E+00
4.500E+00	4.290E-03	-5.451E+00
4.500E+00	4.250E-03	-5.461E+00
1.033E+01	2.750E-03	-5.896E+00
1.033E+01	2.780E-03	-5.885E+00
1.600E+01	1.950E-03	-6.240E+00
1.600E+01	1.860E-03	-6.287E+00
2.400E+01	1.120E-03	-6.794E+00
2.400E+01	1.080E-03	-6.831E+00
3.300E+01	6.680E-04	-7.311E+00
3.300E+01	5.280E-04	-7.546E+00
3.825E+01	3.790E-04	-7.878E+00
3.825E+01	4.380E-04	-7.733E+00

SLOPE = -k obs.
-6.897E-02

INTERCEPT
-5.161E+00

CORR. COEFF.
-9.985E-01

STD. OF SLOPE
1.019E-03

NO. OF POINTS
1.600E+01

NO. OF 1/2 LIVES
3.903E+00

HYDROLYSIS OF ISAZOPHOS AT PH 12.5 RUN A

TIME(MIN)	CONC. (mM)	LN [mM]	
**************************************			SLOPE = -k obs.
0.000E+00	5.940E-03	-5.126E+00	-2.022E-02
0.000E+00	5.910E-03	-5.131E+00	
2.000E+01	4.420E-03	-5.422E+00	INTERCEPT
2.000E+01	4.450E-03	-5.415E+00	-5.049E+00
3.400E+01	3.310E-03	-5.711E+00	
3.400E+01	3.330E-03	-5.705E+00	CORR. COEFF.
5.400E+01	2.190E-03	-6.124E+00	-9.980E-01
5.400E+01	2.290E-03	-6.079E+00	
6.900E+01	1.620E-03	-6.425E+00	STD. OF SLOPE
6.900E+01	1.680E-03	-6.389E+00	3.408E-04
8.000E+01	1.320E-03	-6.630E+00	
8.000E+01	1.260E-03	-6.677E+00	NO. OF POINTS
9.400E+01	8.820E-04	-7.033E+00	1.600E+01
9.400E+01	9.350E-04	-6.975E+00	
1.150E+02	6.200E-04	-7.386E+00	NO. OF 1/2 LIVES
1.150E+02	6.100E-04	-7.402E+00	3.260E+00

HYDROLYSIS OF ISAZOPHOS AT PH 12.5 RUN B

TIME(MIN)	CONC. (mM)	LN [mM]	
**************************************			SLOPE = -k obs.
0.000E+00	6.250E-03	-5.075E+00	-2.158E-02
0.000E+00	6.130E-03	-5.095E+00	
2.000E+01	4.590E-03	-5.384E+00	INTERCEPT
2.000E+01	4.480E-03	-5.408E+00	-4.988E+00
3.400E+01	3.370E-03	-5.693E+00	
3.400E+01	3.380E-03	-5.690E+00	CORR. COEFF.
5.400E+01	2.290E-03	-6.079E+00	-9.974E-01
5.400E+01	2.270E-03	-6.088E+00	
6.900E+01	1.540E-03	-6.476E+00	STD. OF SLOPE
6.900E+01	1.650E-03	-6.407E+00	4.194E-04
8.000E+01	1.280E-03	-6.661E+00	
8.000E+01	1.220E-03	-6.709E+00	NO. OF POINTS
9.400E+01	8.400E-04	-7.082E+00	1.600E+01
9.400E+01	8.970E-04	-7.016E+00	
1.150E+02	5.330E-04	-7.537E+00	NO. OF 1/2 LIVES
1.150E+02	5.380E-04	-7.528E+00	3.552E+00

HYDROLYSIS OF ISAZOPHOS AT PH 12 RUN A

TIME(MIN)	CONC. (mM)	LN [mM]
0.000E+00	6.060E-03	-5.106E+00
0.000E+00	6.180E-03	-5.086E+00
5.000E+01	4.640E-03	-5.373E+00
5.000E+01	4.680E-03	-5.364E+00
1.310E+02	2.390E-03	-6.036E+00
1.310E+02	2.540E-03	-5.976E+00
2.100E+02	1.580E-03	-6.450E+00
2.100E+02	1.570E-03	-6.457E+00
2.620E+02	1.080E-03	-6.831E+00
2.620E+02	1.170E-03	-6.751E+00
3.040E+02	9.620E-04	-6.946E+00
3.040E+02	1.070E-03	-6.840E+00
3.610E+02	5.720E-04	-7.466E+00

SLOPE = -k obs.
-6.303E-03

INTERCEPT
-5.103E+00

CORR. COEFF.
-9.951E-01

STD. OF SLOPE
1.889E-04

NO. OF POINTS
1.300E+01

NO. OF 1/2 LIVES
3.406E+00

HYDROLYSIS OF ISAZOPHOS AT PH 12 RUN B

TIME(MIN)	CONC. (mM)	LN [mM]
0.000E+00	6.590E-03	-5.022E+00
0.000E+00	6.520E-03	-5.033E+00
5.000E+01	4.590E-03	-5.384E+00
5.000E+01	4.630E-03	-5.375E+00
1.310E+02	2.650E-03	-5.933E+00
1.310E+02	2.620E-03	-5.945E+00
2.100E+02	1.530E-03	-6.482E+00
2.100E+02	1.530E-03	-6.482E+00
2.620E+02	1.150E-03	-6.768E+00
2.620E+02	1.130E-03	-6.786E+00
3.040E+02	9.400E-04	-6.970E+00
3.040E+02	1.050E-03	-6.859E+00
3.610E+02	5.880E-04	-7.439E+00
3.610E+02	5.190E-04	-7.564E+00
4.270E+02	4.140E-04	-7.790E+00

SLOPE = -k obs.
-6.531E-03

INTERCEPT
-5.055E+00

CORR. COEFF.
-9.968E-01

STD. OF SLOPE
1.462E-04

NO. OF POINTS
1.500E+01

NO. OF 1/2 LIVES
3.993E+00

HYDROLYSIS OF ISAZOPHOS AT PH 11.5 RUN A

TIME(MIN)	CONC. (M)	LN [M]	
************************************			SLOPE = -k obs.
0.000E+00	5.030E-06	-1.220E+01	-2.234E-03
0.000E+00	5.560E-06	-1.210E+01	
2.200E+02	3.372E-06	-1.260E+01	INTERCEPT
2.200E+02	3.372E-06	-1.260E+01	-1.211E+01
3.400E+02	2.761E-06	-1.280E+01	
3.400E+02	2.761E-06	-1.280E+01	CORR. COEFF.
4.600E+02	2.045E-06	-1.310E+01	-9.975E-01
4.600E+02	2.045E-06	-1.310E+01	
1.360E+03	2.505E-07	-1.520E+01	STD. OF SLOPE
1.360E+03	2.505E-07	-1.520E+01	4.245E-05
1.480E+03	2.051E-07	-1.540E+01	
1.480E+03	1.855E-07	-1.550E+01	NO. OF POINTS
1.660E+03	1.125E-07	-1.600E+01	1.600E+01
1.660E+03	1.125E-07	-1.600E+01	
1.920E+03	8.337E-08	-1.630E+01	NO. OF 1/2 LIVES
1.920E+03	1.018E-07	-1.610E+01	5.627E+00

HYDROLYSIS OF ISAZOPHOS AT PH 11.5 RUN B

TIME(MIN)	CONC. (M)	LN [M]	
************************************			SLOPE = -k obs.
0.000E+00	5.560E-06	-1.210E+01	-2.106E-03
0.000E+00	5.030E-06	-1.220E+01	
2.200E+02	3.372E-06	-1.260E+01	INTERCEPT
2.200E+02	3.727E-06	-1.250E+01	-1.212E+01
3.400E+02	2.761E-06	-1.280E+01	
3.400E+02	2.761E-06	-1.280E+01	CORR. COEFF.
4.600E+02	2.045E-06	-1.310E+01	-9.976E-01
4.600E+02	2.260E-06	-1.300E+01	
1.360E+03	3.059E-07	-1.500E+01	STD. OF SLOPE
1.360E+03	3.059E-07	-1.500E+01	3.871E-05
1.480E+03	2.051E-07	-1.540E+01	
1.480E+03	1.855E-07	-1.550E+01	NO. OF POINTS
1.660E+03	1.855E-07	-1.550E+01	1.600E+01
1.660E+03	1.679E-07	-1.560E+01	
1.920E+03	1.018E-07	-1.610E+01	NO. OF 1/2 LIVES
1.920E+03	1.125E-07	-1.600E+01	5.627E+00

HYDROLYSIS OF ISAZOPHOS AT PH 11 RUN A

TIME(MIN)	CONC. (M)	LN [M]	
			SLOPE = -k obs.
0.000E+00	5.560E-06	-1.210E+01	-5.647E-04
0.000E+00	5.030E-06	-1.220E+01	
6.000E+02	4.552E-06	-1.230E+01	INTERCEPT
6.000E+02	4.119E-06	-1.240E+01	-1.210E+01
1.500E+03	2.498E-06	-1.290E+01	
1.500E+03	2.260E-06	-1.300E+01	CORR. COEFF.
1.830E+03	2.260E-06	-1.300E+01	-9.887E-01
1.830E+03	1.851E-06	-1.320E+01	
2.070E+03	1.674E-06	-1.330E+01	STD. OF SLOPE
2.070E+03	1.515E-06	-1.340E+01	2.702E-05
2.970E+03	1.122E-06	-1.370E+01	
2.970E+03	1.016E-06	-1.380E+01	NO. OF POINTS
			1.200E+01
			NO OF 1/2 LIVES
			2.453E+00

HYDROLYSIS OF ISAZOPHOS AT PH 11 RUN B

TIME(MIN)	CONC. (M)	LN [M]	
			SLOPE = -k obs.
0.000E+00	5.560E-06	-1.210E+01	-4.677E-04
0.000E+00	5.560E-06	-1.210E+01	
6.000E+02	4.119E-06	-1.240E+01	INTERCEPT
6.000E+02	4.119E-06	-1.240E+01	-1.211E+01
1.500E+03	2.761E-06	-1.280E+01	
1.500E+03	2.761E-06	-1.280E+01	CORR. COEFF.
1.830E+03	2.260E-06	-1.300E+01	-9.964E-01
1.830E+03	2.260E-06	-1.300E+01	
2.070E+03	2.260E-06	-1.300E+01	STD. OF SLOPE
2.070E+03	2.045E-06	-1.310E+01	1.399E-05
			NO. OF POINTS
			1.000E+01
			NO OF 1/2 LIVES
			1.443E+00

HYDROLYSIS OF METHYL PARATHION AT PH 14 RUN A

TIME(MIN)	CONC. (mM)	LN [mM]	
**********	**********	***********	SLOPE = -k(obs)
0.000E+00	1.165E-02	-4.452E+00	-2.062E-01
0.000E+00	1.147E-02	-4.468E+00	
1.330E+00	9.060E-03	-4.704E+00	INTERCEPT
1.330E+00	9.190E-03	-4.690E+00	-4.396E+00
3.750E+00	6.080E-03	-5.103E+00	
3.750E+00	5.830E-03	-5.145E+00	CORR COEF
8.500E+00	2.270E-03	-6.088E+00	-9.994E-01
8.500E+00	2.340E-03	-6.058E+00	
1.100E+01	1.290E-03	-6.653E+00	STD. OF SLOPE
1.100E+01	1.280E-03	-6.661E+00	1.871E-03
1.350E+01	7.770E-04	-7.160E+00	
1.350E+01	7.810E-04	-7.155E+00	NO. OF POINTS
1.600E+01	4.550E-04	-7.695E+00	1.600E+01
1.600E+01	4.520E-04	-7.702E+00	
1.950E+01	2.090E-04	-8.473E+00	NO. OF 1/2 LIVES
1.950E+01	2.090E-04	-8.473E+00	5.801E+00

HYDROLYSIS OF METHYL PARATHION AT PH 14 RUN B

TIME(MIN)	CONC. (mM)	LN [mM]	
**********	**********	***********	SLOPE = -k(obs)
0.000E+00	1.170E-02	-4.448E+00	-1.968E-01
0.000E+00	1.160E-02	-4.457E+00	
1.500E+00	9.370E-03	-4.670E+00	INTERCEPT
1.500E+00	9.400E-03	-4.667E+00	-4.406E+00
3.000E+00	6.790E-03	-4.992E+00	
3.000E+00	6.810E-03	-4.989E+00	CORR COEF
4.500E+00	5.160E-03	-5.267E+00	-9.996E-01
4.500E+00	5.170E-03	-5.265E+00	
6.000E+00	3.870E-03	-5.555E+00	STD. OF SLOPE
6.000E+00	3.760E-03	-5.583E+00	1.557E-03
7.500E+00	2.810E-03	-5.875E+00	
7.500E+00	2.730E-03	-5.903E+00	NO. OF POINTS
9.000E+00	2.000E-03	-6.215E+00	1.600E+01
9.000E+00	2.020E-03	-6.205E+00	
1.567E+01	5.580E-04	-7.491E+00	NO. OF 1/2 LIVES
1.567E+01	5.640E-04	-7.480E+00	4.375E+00

HYDROLYSIS OF METHYL PARATHION AT PH 13.5 RUN A

TIME(MIN)	CONC. (mM)	LN [mM]	
**********	**********	***********	SLOPE = -k(obs)
0.000E+00	1.050E-02	-4.556E+00	-6.308E-02
0.000E+00	1.090E-02	-4.519E+00	
1.100E+01	5.940E-03	-5.126E+00	INTERCEPT
1.100E+01	6.080E-03	-5.103E+00	-4.460E+00
2.100E+01	3.300E-03	-5.714E+00	
2.100E+01	3.350E-03	-5.699E+00	CORR COEF
3.000E+01	1.800E-03	-6.320E+00	-9.988E-01
3.000E+01	1.830E-03	-6.303E+00	
3.700E+01	1.160E-03	-6.759E+00	STD. OF SLOPE
3.700E+01	1.100E-03	-6.812E+00	8.433E-04
4.233E+01	7.760E-04	-7.161E+00	
4.233E+01	7.320E-04	-7.220E+00	NO. OF POINTS
4.783E+01	5.290E-04	-7.545E+00	1.600E+01
4.783E+01	5.390E-04	-7.526E+00	
5.700E+01	3.290E-04	-8.019E+00	NO. OF 1/2 LIVES
5.700E+01	3.260E-04	-8.029E+00	5.010E+00

HYDROLYSIS OF METHYL PARATHION AT PH 13.5 RUN B

TIME(MIN)	CONC. (mM)	LN [mM]	
**********	**********	***********	SLOPE = -k(obs)
0.000E+00	1.190E-02	-4.431E+00	-6.232E-02
0.000E+00	1.180E-02	-4.440E+00	
1.100E+01	6.540E-03	-5.030E+00	INTERCEPT
1.100E+01	6.600E-03	-5.021E+00	-4.382E+00
2.100E+01	3.510E-03	-5.652E+00	
2.100E+01	3.700E-03	-5.599E+00	CORR COEF
3.000E+01	2.010E-03	-6.210E+00	-9.984E-01
3.000E+01	2.020E-03	-6.205E+00	
3.700E+01	1.240E-03	-6.693E+00	STD. OF SLOPE
3.700E+01	1.190E-03	-6.734E+00	9.532E-04
4.233E+01	8.130E-04	-7.115E+00	
4.233E+01	8.320E-04	-7.092E+00	NO. OF POINTS
4.783E+01	6.020E-04	-7.415E+00	1.600E+01
4.783E+01	5.770E-04	-7.458E+00	
5.700E+01	3.860E-04	-7.860E+00	NO. OF 1/2 LIVES
5.700E+01	3.940E-04	-7.839E+00	4.917E+00

HYDROLYSIS OF METHYL PARATHION AT PH 13 RUN A

TIME(MIN)	CONC. (mM)	LN [mM]	
**********	**********	***********	SLOPE = -k(obs)
0.000E+00	1.250E-02	-4.382E+00	-1.966E-02
0.000E+00	1.250E-02	-4.382E+00	
1.500E+01	9.480E-03	-4.659E+00	INTERCEPT
1.500E+01	9.470E-03	-4.660E+00	-4.365E+00
3.000E+01	7.110E-03	-4.946E+00	
3.000E+01	6.980E-03	-4.965E+00	CORR COEF
4.500E+01	5.390E-03	-5.223E+00	-9.997E-01
4.500E+01	5.360E-03	-5.229E+00	
6.000E+01	3.950E-03	-5.534E+00	STD. OF SLOPE
6.000E+01	3.900E-03	-5.547E+00	1.384E-04
7.500E+01	3.030E-03	-5.799E+00	
7.500E+01	2.920E-03	-5.836E+00	NO. OF POINTS
9.000E+01	2.120E-03	-6.156E+00	1.600E+01
9.000E+01	2.110E-03	-6.161E+00	
1.050E+02	1.590E-03	-6.444E+00	NO. OF 1/2 LIVES
1.050E+02	1.620E-03	-6.425E+00	2.948E+00

HYDROLYSIS OF METHYL PARATHION AT PH 13 RUN B

TIME(MIN)	CONC. (mM)	LN [mM]	
**********	**********	***********	SLOPE = -k(obs)
0.000E+00	1.260E-02	-4.374E+00	-1.953E-02
0.000E+00	1.290E-02	-4.351E+00	
1.500E+01	9.810E-03	-4.624E+00	INTERCEPT
1.500E+01	9.840E-03	-4.621E+00	-4.348E+00
3.000E+01	7.320E-03	-4.917E+00	
3.000E+01	7.310E-03	-4.919E+00	CORR COEF
4.500E+01	5.340E-03	-5.233E+00	-9.990E-01
4.500E+01	5.430E-03	-5.216E+00	
6.000E+01	3.900E-03	-5.547E+00	STD. OF SLOPE
6.000E+01	4.020E-03	-5.516E+00	2.350E-04
7.500E+01	2.850E-03	-5.860E+00	
7.500E+01	2.780E-03	-5.885E+00	NO. OF POINTS
9.000E+01	2.350E-03	-6.053E+00	1.600E+01
9.000E+01	2.320E-03	-6.066E+00	
1.050E+02	1.670E-03	-6.395E+00	NO. OF 1/2 LIVES
1.050E+02	1.660E-03	-6.401E+00	2.924E+00

HYDROLYSIS OF METHYL PARATHION AT PH 12 RUN A

TIME(MIN)	CONC. (mM)	LN [mM]	
**********	**********	***********	SLOPE = -k obs.
0.000E+00	1.330E-02	-4.320E+00	-2.043E-03
0.000E+00	1.260E-02	-4.374E+00	
2.700E+02	8.080E-03	-4.818E+00	INTERCEPT
2.700E+02	8.170E-03	-4.807E+00	-4.282E+00
4.850E+02	5.520E-03	-5.199E+00	
4.850E+02	5.510E-03	-5.201E+00	CORR. COEFF.
6.600E+02	3.540E-03	-5.644E+00	-9.993E-01
6.600E+02	3.480E-03	-5.661E+00	
1.290E+03	1.050E-03	-6.859E+00	STD. OF SLOPE
1.290E+03	1.060E-03	-6.849E+00	2.035E-05
1.440E+03	7.110E-04	-7.249E+00	
1.440E+03	7.300E-04	-7.222E+00	NO. OF POINTS
1.635E+03	4.550E-04	-7.695E+00	1.600E+01
1.635E+03	4.640E-04	-7.676E+00	
1.935E+03	2.620E-04	-8.247E+00	NO. OF 1/2 LIVES
1.935E+03	2.720E-04	-8.210E+00	5.612E+00

HYDROLYSIS OF METHYL PARATHION AT PH 12 RUN B

TIME(MIN)	CONC. (mM)	LN [mM]	
**********	**********	***********	SLOPE = -k obs.
0.000E+00	1.320E-02	-4.328E+00	-2.037E-03
0.000E+00	1.320E-02	-4.328E+00	
2.700E+02	7.960E-03	-4.833E+00	INTERCEPT
2.700E+02	7.760E-03	-4.859E+00	-4.294E+00
4.850E+02	5.280E-03	-5.244E+00	
4.850E+02	5.360E-03	-5.229E+00	CORR. COEFF.
6.600E+02	3.610E-03	-5.624E+00	-9.994E-01
6.600E+02	3.470E-03	-5.664E+00	
1.290E+03	1.060E-03	-6.849E+00	STD. OF SLOPE
1.290E+03	1.030E-03	-6.878E+00	1.869E-05
1.440E+03	7.200E-04	-7.236E+00	
1.440E+03	7.400E-04	-7.209E+00	NO. OF POINTS
1.635E+03	4.420E-04	-7.724E+00	1.600E+01
1.635E+03	4.510E-04	-7.704E+00	
1.935E+03	2.780E-04	-8.188E+00	NO. OF 1/2 LIVES
1.935E+03	2.670E-04	-8.228E+00	5.628E+00

HYDROLYSIS OF METHYL PARATHION AT PH 11.5 RUN A

TIME(MIN)	CONC. (mM)	LN [mM]	
**********	**********	***********	SLOPE = -k obs.
0.000E+00	2.884E-02	-3.546E+00	-1.183E-03
0.000E+00	2.570E-02	-3.661E+00	
8.500E+02	6.761E-03	-4.997E+00	INTERCEPT
8.500E+02	7.762E-03	-4.858E+00	-3.977E+00
1.300E+03	2.692E-03	-5.918E+00	
1.300E+03	2.884E-03	-5.849E+00	CORR. COEFF.
2.400E+03	1.047E-03	-6.862E+00	-9.939E-01
2.400E+03	1.000E-03	-6.908E+00	
3.000E+03	4.266E-04	-7.760E+00	STD. OF SLOPE
3.000E+03	5.012E-04	-7.599E+00	3.519E-05
3.880E+03	1.820E-04	-8.612E+00	
3.880E+03	1.698E-04	-8.681E+00	NO. OF POINTS
4.570E+03	8.318E-05	-9.395E+00	1.600E+01
4.570E+03	7.586E-05	-9.487E+00	
5.470E+03	4.467E-05	-1.002E+01	NO. OF 1/2 LIVES
5.470E+03	3.388E-05	-1.029E+01	9.734E+00

HYDROLYSIS OF METHYL PARATHION AT PH 11.5 RUN B

TIME(MIN)	CONC. (mM)	LN [mM]	
**********	**********	***********	SLOPE = -k obs.
0.000E+00	2.630E-02	-3.638E+00	-1.162E-03
0.000E+00	2.188E-02	-3.822E+00	
8.500E+02	7.762E-03	-4.858E+00	INTERCEPT
8.500E+02	7.762E-03	-4.858E+00	-4.023E+00
1.300E+03	2.570E-03	-5.964E+00	
1.300E+03	2.884E-03	-5.849E+00	CORR. COEFF.
2.400E+03	1.023E-03	-6.885E+00	-9.931E-01
2.400E+03	1.096E-03	-6.816E+00	
3.000E+03	5.129E-04	-7.576E+00	STD. OF SLOPE
3.000E+03	5.012E-04	-7.599E+00	3.670E-05
3.880E+03	1.479E-04	-8.819E+00	
3.880E+03	1.445E-04	-8.842E+00	NO. OF POINTS
4.570E+03	8.511E-05	-9.372E+00	1.600E+01
4.570E+03	9.772E-05	-9.233E+00	
5.470E+03	4.898E-05	-9.924E+00	NO. OF 1/2 LIVES
5.470E+03	3.631E-05	-1.022E+01	9.502E+00

HYDROLYSIS OF METHYL PARATHION AT PH 11 RUN A

TIME(MIN)	CONC. (mM)	LN [mM]
**********	**********	***********
0.000E+00	2.512E-02	-3.684E+00
0.000E+00	2.692E-02	-3.615E+00
8.500E+02	1.778E-02	-4.030E+00
8.500E+02	1.738E-02	-4.052E+00
2.370E+03	9.550E-03	-4.651E+00
2.370E+03	1.072E-02	-4.536E+00
3.730E+03	6.457E-03	-5.043E+00
3.730E+03	6.761E-03	-4.997E+00

SLOPE = -k obs.
-3.644E-04

INTERCEPT
-3.693E+00

CORR. COEFF.
-9.950E-01

STD. OF SLOPE
1.496E-05

NO. OF POINTS
8.000E+00

NO. OF 1/2 LIVES
1.894E+00

HYDROLYSIS OF METHYL PARATHION AT PH 11 RUN B

TIME(MIN)	CONC. (mM)	LN [mM]
**********	**********	***********
0.000E+00	2.042E-02	-3.891E+00
0.000E+00	2.692E-02	-3.615E+00
8.500E+02	1.820E-02	-4.006E+00
8.500E+02	1.820E-02	-4.006E+00
2.370E+03	1.230E-02	-4.398E+00
2.370E+03	1.096E-02	-4.514E+00
3.730E+03	6.457E-03	-5.043E+00
3.730E+03	6.320E-03	-5.064E+00

SLOPE = -k obs.
-3.437E-04

INTERCEPT
-3.720E+00

CORR. COEFF.
-9.836E-01

STD. OF SLOPE
2.574E-05

NO. OF POINTS
8.000E+00

NO. OF 1/2 LIVES
1.692E+00

Appendix B

Summary of Kinetic Data

HYDROLYSIS OF CHLORPYRIFOS

PH	1/OH Act.	k obs. (min)E-1	LOG k obs.	1/k obs.	NO. OF POINTS	1/2 LIVES
13.56	3.03E+00	2.095E-01	-6.788E-01	4.773E+00	16	2.2
13.57	2.97E+00	2.152E-01	-6.672E-01	4.647E+00	16	2.3
13.33	4.93E+00	1.200E-01	-9.208E-01	8.333E+00	16	3.7
13.33	4.86E+00	1.239E-01	-9.069E-01	8.071E+00	16	3.8
12.87	1.35E+01	3.714E-02	-1.430E+00	2.693E+01	16	3.2
12.87	1.35E+01	3.677E-02	-1.435E+00	2.720E+01	16	3.2
12.40	4.01E+01	1.015E-02	-1.994E+00	9.852E+01	16	2.7
12.40	3.95E+01	9.949E-03	-2.002E+00	1.005E+02	16	2.6
11.88	1.33E+02	3.145E-03	-2.502E+00	3.180E+02	16	3.1
11.89	1.30E+02	3.090E-03	-2.510E+00	3.236E+02	16	3.2
11.43	3.75E+02	1.051E-03	-2.978E+00	9.515E+02	16	2.7
11.44	3.66E+02	8.547E-04	-3.068E+00	1.170E+03	16	2.6
10.77	1.70E+03	1.880E-04	-3.726E+00	5.319E+03	14	2.8
10.77	1.71E+03	1.830E-04	-3.738E+00	5.464E+03	14	2.8
10.29	5.19E+03	9.939E-05	-4.003E+00	1.006E+04	12	2.1
10.44	3.62E+03	1.192E-04	-3.924E+00	8.389E+03	12	2.4

2nd ORDER RESULTS; LOG(k obs.) = m(pH) + b

Slope	=	1.058E+00
Intercept	=	-1.506E+01
Corr. Coef	=	9.983E-01
Stdev. of slope	=	1.645E-02

INTERMEDIATE RESULTS; 1/k obs. = m(1/aOH) + b

Slope	=	2.141E+00
Intercept	=	2.326E+02
Corr. Coef	=	9.792E-01
Stdev. of slope	=	1.185E-01

HYDROLYSIS OF DIAZINON

PH	1/OH Act.	k obs. (min)E-1	LOG k obs.	1/k obs.	NO. OF POINTS	1/2 LIVES
13.83	1.73E+00	1.441E-01	-8.413E-01	6.940E+00	10	7.3
13.80	1.84E+00	1.566E-01	-8.052E-01	6.386E+00	16	4.8
13.33	4.94E+00	5.009E-02	-1.300E+00	1.996E+01	16	4.4
13.33	4.93E+00	5.043E-02	-1.297E+00	1.983E+01	16	4.5
12.87	1.35E+01	1.745E-02	-1.758E+00	5.731E+01	16	3.2
12.87	1.35E+01	1.805E-02	-1.744E+00	5.540E+01	16	3.1
12.37	4.31E+01	5.330E-03	-2.273E+00	1.876E+02	16	4.1
12.40	3.97E+01	5.262E-03	-2.279E+00	1.900E+02	16	4.1
11.44	3.66E+02	1.089E-03	-2.963E+00	9.183E+02	14	7.3
11.44	3.66E+02	1.152E-03	-2.939E+00	8.681E+02	16	9.0
10.95	1.12E+03	3.568E-04	-3.448E+00	2.803E+03	16	4.4
10.95	1.12E+03	2.618E-04	-3.582E+00	3.820E+03	16	3.1

2nd ORDER RESULTS; LOG(k obs.) = m(pH) + b

Slope = 9.178E-01
Intercept = -1.354E+01
Corr. Coef = 9.974E-01
Stdev. of slope = 2.113E-02

INTERMEDIATE RESULTS; 1/k obs. = m(1/aOH) + b

Slope = 2.921E+00
Intercept = -6.316E+00
Corr. Coef = 9.828E-01
Stdev. of slope = 1.734E-01

HYDROLYSIS OF FENTHION

PH	1/OH Act.	k obs. (min)E-1	LOG k obs.	1/k obs.	NO. OF POINTS	1/2 LIVES
13.84	1.70E+00	1.497E-02	-1.825E+00	6.680E+01	14	3.4
13.83	1.70E+00	1.460E-02	-1.836E+00	6.849E+01	14	3.3
13.30	5.30E+00	5.073E-03	-2.295E+00	1.971E+02	14	3.0
13.33	4.90E+00	5.028E-03	-2.299E+00	1.989E+02	14	3.0
12.82	1.50E+01	1.361E-03	-2.866E+00	7.348E+02	16	4.4
12.83	1.50E+01	1.453E-03	-2.838E+00	6.882E+02	14	2.8
12.44	3.60E+01	6.777E-04	-3.169E+00	1.476E+03	14	4.3
12.45	3.50E+01	5.821E-04	-3.235E+00	1.718E+03	14	3.7
11.91	1.23E+02	2.167E-04	-3.664E+00	4.615E+03	14	3.0
11.91	1.23E+02	2.015E-04	-3.696E+00	4.963E+03	14	2.9
11.41	3.85E+02	6.289E-05	-4.201E+00	1.590E+04	12	1.9
11.41	3.85E+02	5.943E-05	-4.226E+00	1.683E+04	12	1.8

2nd ORDER RESULTS; LOG(k obs.) = m(pH) + b

Slope = 9.817E-01
Intercept = -1.541E+01
Corr. Coef = 9.992E-01
Stdev. of slope = 1.265E-02

INTERMEDIATE RESULTS; 1/k obs. = m(1/aOH) + b

Slope = 4.231E+01
Intercept = -3.185E+01
Corr. Coef = 9.989E-01
Stdev. of slope = 6.368E-01

HYDROLYSIS OF ISAZOPHOS

PH	1/OH Act.	kobs. (min)E-1	LOG k obs.	1/k obs.	NO. OF POINTS	1/2 LIVES
13.83	1.70E+00	7.095E-01	-1.490E-01	1.409E+00	16	3.5
13.83	1.70E+00	6.642E-01	-1.777E-01	1.506E+00	16	3.6
13.30	5.20E+00	1.981E-01	-7.031E-01	5.048E+00	14	3.9
13.31	5.10E+00	2.173E-01	-6.629E-01	4.602E+00	14	5.1
12.86	1.40E+01	6.897E-02	-1.161E+00	1.450E+01	16	3.9
12.85	1.40E+01	6.696E-02	-1.174E+00	1.493E+01	15	3.6
12.39	4.10E+01	2.158E-02	-1.666E+00	4.634E+01	16	3.6
12.38	4.20E+01	2.022E-02	-1.694E+00	4.946E+01	16	3.3
11.90	1.25E+02	6.531E-03	-2.185E+00	1.531E+02	15	4.0
11.90	1.26E+02	6.303E-03	-2.200E+00	1.587E+02	13	3.4
11.44	3.66E+02	2.106E-03	-2.677E+00	4.748E+02	16	5.6
11.44	3.66E+02	2.234E-03	-2.651E+00	4.476E+02	16	5.6
10.96	1.09E+03	4.677E-04	-3.330E+00	2.138E+03	10	1.4
10.96	1.09E+03	5.647E-04	-3.248E+00	1.771E+03	12	2.5

2nd ORDER RESULTS; LOG(k obs.) = m(pH) + b

Slope	1.081E+00
Intercept	-1.508E+01
Corr. Coef.	9.993E-01
Std. of slope	1.188E-02

INTERMEDIATE RESULTS; 1/k obs. = m(1/aOH) + b

Slope	1.785E+00
Intercept	-4.171E+01
Corr. Coef.	9.896E-01
Std. of slope	7.496E-02

HYDROLYSIS OF METHYL PARATHION

PH	1/OH Act.	k obs. (min)E-1	LOG k obs.	1/k obs.	NO. OF POINTS	1/2 LIVES
13.83	1.73E+00	2.062E-01	-6.857E-01	4.850E+00	16	5.8
13.83	1.73E+00	1.968E-01	-7.060E-01	5.081E+00	16	4.4
13.33	5.09E+00	6.308E-02	-1.200E+00	1.585E+01	16	5.0
13.33	5.09E+00	6.232E-02	-1.205E+00	1.605E+01	16	4.9
12.87	1.36E+01	1.966E-02	-1.706E+00	5.086E+01	16	2.9
12.87	1.36E+01	1.953E-02	-1.709E+00	5.120E+01	16	2.9
11.90	1.25E+02	2.043E-03	-2.690E+00	4.895E+02	16	5.6
11.90	1.25E+02	2.037E-03	-2.691E+00	4.909E+02	16	5.7
11.44	3.66E+02	1.183E-03	-2.927E+00	8.453E+02	16	9.7
11.44	3.66E+02	1.162E-03	-2.935E+00	8.606E+02	16	9.5
10.95	1.12E+03	3.644E-04	-3.438E+00	2.744E+03	8	1.9
10.95	1.12E+03	3.437E-04	-3.464E+00	2.910E+03	8	1.7

2nd ORDER RESULTS; LOG(k obs.) = m(pH) + b

- Slope = 9.491E-01
- Intercept = -1.387E+01
- Corr. Coef = 9.977E-01
- Stdev. of slope = 2.019E-02

INTERMEDIATE RESULTS; 1/k obs. = m(1/aOH) + b

- Slope = 2.489E+00
- Intercept = 3.101E+01
- Corr. Coef = 9.967E-01
- Stdev. of slope = 6.366E-02

APPENDIX C

pH Study Results

THIOPHOSPHATE TRIESTER=[R] AND INITIAL CONC.	INIT. PH	INITIAL [OH]	FINAL PH	FINAL [OH]	CHANGE IN [OH]	FINAL [R]	EQLBRM CNSTNT
TRIMETHYL	10.45	2.82E-04	10.35	2.24E-04	5.80E-05	1.24E-03	208.4688
THIOPHOSPHATE	8.99	9.77E-06	7.5	3.16E-07	9.46E-06	1.29E-03	23170.81
ACCUPHAST PROB	7.5	3.16E-07	6.2	1.58E-08	3.00E-07	1.30E-03	14582.31
1.3E-03 M	6.5	3.16E-08	5.5	3.16E-09	2.85E-08	1.30E-03	6923.228
REPEAT OF TMTP	9.86	7.24E-05	9.77	5.89E-05	1.36E-05	2.45E-04	938.1846
2.6E-04 M	7.86	7.24E-07	6.6	3.98E-08	6.85E-07	2.58E-04	66573.69
	7.28	1.91E-07	6.7	5.01E-08	1.40E-07	2.59E-04	10823.99
	6.93	8.51E-08	4.1	1.26E-10	8.50E-08	2.59E-04	2607353.
DIAZINON	10.3	2.00E-04	9.4	2.51E-05	3.02E-04	-2.37E-04	-50710.5
6.5E-05 M	9.3	2.00E-05	5.6	3.98E-09	3.05E-05	3.45E-05	2.2E+08
	8.4	2.51E-06	5.2	1.58E-09	3.74E-06	6.13E-05	38524034
ISAZOPHOS	10.4	2.51E-04	9.2	1.58E-05	3.63E-04	-3.41E-04	-67132.8
2.2E-05 M	9.3	2.00E-05	6.2	1.58E-08	3.05E-05	-8.69E-06	-2.2E+08
	8.45	2.82E-06	6	1.00E-08	4.04E-06	1.78E-05	22672747
FENTHION	10.25	1.78E-04	9.8	6.31E-05	2.43E-04	-2.28E-04	-16892.8
1.5E-05 M	8.6	3.98E-06	8	1.00E-06	4.21E-06	1.08E-05	390314.1
	8.7	5.01E-06	7.75	5.62E-07	5.68E-06	9.32E-06	1083614.