

THE HYDROLYTIC DEGRADATION OF TERBUFOS  
IN HOMOGENEOUS AQUEOUS SYSTEMS

by

Craig R. Walker

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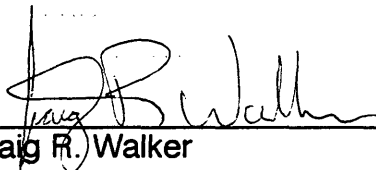
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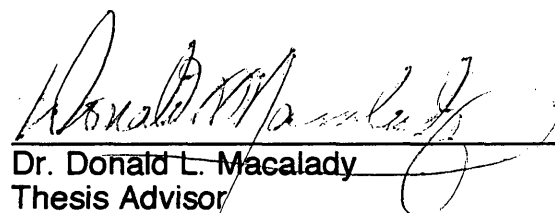
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## ABSTRACT

Terbufos is an organophosphorodithioate insecticide used to control cornroot nematodes in the cultivation of corn and other specific cash crops. Counter<sup>®</sup>, which is the formulation trade name, is 15% (w/w) terbufos sorbed onto granulated clay pellets. The significance of comparing other organophosphorothioate and dithioate esters to terbufos is that the latter exhibits a faster degradation rate than is observed for related compounds. Terbufos hydrolysis is shown to obey pseudo-first-order kinetics over the entire pH range at 25°C. Rate constants yield half-lives from 1.5 days under neutral conditions to 0.4 hours at extreme alkaline conditions. Temperature studies were conducted at pH values 5 and 9 at 15°C, 25°C, 35°C, and 45°C and exhibited pseudo-first-order kinetics except at 45°C. Activation energies calculated from the temperature studies are also higher than would be expected from those for compounds of similar structure. The non-linear behavior observed in the pseudo-first-order plots at 45°C suggests the possibility of a rate-limiting complex that changes the order of the reaction after several half-lives. This could explain the discrepancy that the activation energy calculated at the pH of 9 is larger than that calculated at a pH of 5. However, additional temperature studies are warranted to support such a conclusion. Attempts to identify the hydrolysis products of terbufos gave inconclusive results.

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## INTRODUCTION

Insecticide use in the United States has seen a large change in the past few decades. Organochlorine insecticides, once widely used, have been phased out because of their detrimental effects on the environment. The insecticides of choice have now become carbamate and organophosphorus compounds. Half to 60% of all the corn crops in the United States are treated annually with these types of insecticides (Felsot and Dahm, 1979; Chio and Metcalf, 1979). On the whole, their roles as insecticides seem to be effective and provide short-term persistence in the environment. Concerns have arisen, however, about water run-off systems from agricultural fields and their content of pesticides (Wauchope, 1978, Frank, et al, 1991).

Terbufos is an organophosphorodithioate larvicide used to control corn rootworms in the cultivation of corn and other specific cash crops (Figure 1).

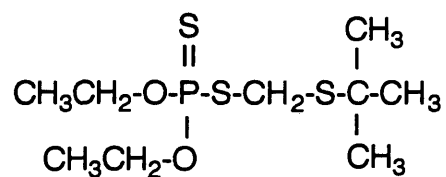


Figure 1. The structure of terbufos.

In Iowa and Illinois alone, more than 3.5 million acres are annually applied with Counter 15G, which is the formulation trade name for terbufos. Counter is applied as a pellet that consists of granulated clay in which 15% (w/w) terbufos is sorbed (Felsot, et al., 1982). Field coverage for the active insecticide is on the average of one kg per acre (Laveglia and Dahm, 1975; Sellers, et al, 1976; Ahmad, et al, 1979).

The literature on terbufos, at this time, mainly focuses on the soil characteristics and how they affect the insecticide's persistence in the environment. The primary degradation pathway in soil is oxidation to terbufos sulfoxide and a second oxidation to terbufos sulfone (Laveglia and Dahm, 1975). Several groups have investigated the degradation behavior of terbufos and its metabolites and their relationship to the organic matter content in the soil (Laveglia and Dahm, 1975; Felsot and Dahm, 1979; Chapman and Harris, 1980; Felsot, Wei, Wilson, 1982; Chapman, Tu, Harris, Dubois, 1982; Bowman and Sans, 1982; Chapman and Cole, 1982). These studies suggest that soils with higher organic matter content decrease the disappearance rate of terbufos. The experimental factors that have been shown to affect the rates of soil degradation of terbufos include volatility, adsorption, temperature, and sterility. Other studies on the degradation of terbufos in the soil include investigations of detoxification mechanisms in rootworms (Chio and Metcalf, 1979), of enhanced microbial degradation (Racke and Coats, 1988), and of the effects of tillage practices (Felsot, et al., 1987).

The literature on the hydrolytic degradation of terbufos is limited and relatively inconsistent (Miller and Jenney, 1973; Chapman and Cole, 1982;

Bowman and Sans, 1982; Frank et al., 1991). Table 1 summarizes the observed rate constants and half-lives reported for these investigations along with the pH and temperature at which the studies were conducted. In only two of these studies were the oxidative and photolytic degradation pathways eliminated via control of the experimental conditions. In the Bowman and Sans 1982 study, terbufos solutions were stored in the dark and the study from Frank et al, 1991 reported no significant differences in the rates of hydrolysis for terbufos in the dark and in the light. No attempts to find the hydrolytic degradation products were reported in any of the studies.

The first objective for this research was to gain a better understanding of the kinetics of the hydrolytic degradation of terbufos. In comparison to other thioate and dithioate insecticides (see Table 2) this study shows that terbufos degrades faster than would be expected. Linear free energy relationships for organophosphorothioates can also be used to estimate the rate constants for environmental fate assessments (Wolfe, 1980). Based on Wolfe's LFER for O,O,-diethyl-O-alkyl and aryl phosphorothioates and assuming the pKa of the leaving group to be ~10, the half-lives predicted for terbufos are 180, 18, and 1.8 days at the pH values of 11, 12, and 13, respectively.

Activation energy values for the hydrolysis of terbufos have yet to be reported. However, there are studies on other organophosphorus insecticides that lead to estimations for the activation energy for the hydrolysis of terbufos. Table 3 lists some activation energies found in the literature for organophosphorates, thioates, and dithioates for neutral and alkaline hydrolysis. The activation energies for alkaline hydrolysis are observed to be

Table 1. Literature Summary of Terbufos Hydrolysis.

Rate Constants (d <sup>-1</sup> )	Half-Life (d)	Temperature (°C)	pH	Source
0.154	4.5	N/A	5	Miller and Jenney 1973
0.126	5.5	N/A	7	Miller and Jenney 1973
0.082	8.5	N/A	9	Miller and Jenney 1973
0.210	3.3	20	5.5	Bowman and Sans 1982
0.217	3.2	20	7.93	Bowman and Sans 1982
0.198	3.5	20	8.7	Bowman and Sans 1982
0.341	2.03	25	4.5	Chapman and Coles 1982
0.354	1.96	25	6	Chapman and Coles 1982
0.354	1.96	25	7	Chapman and Coles 1982
0.309	2.24	25	8	Chapman and Coles 1982
0.020	34	4	8	Frank, Braun, Chapman, and Burchat 1991
0.301	2.3	21	8	Frank, Braun, Chapman, and Burchat 1991
0.315	2.2	21	8	Frank, Braun, Chapman, and Burchat 1991
0.347	2.0	21	8	Frank, Braun, Chapman, and Burchat 1991

N/A indicates that this information was not reported.

Table 2. Thioate and Dithioate Insecticides and Their Half-Lives at pH Values of 7 and 11.

Compound	t <sub>1/2</sub> at pH 7 (d)	t <sub>1/2</sub> at pH 11 (d)
Dichlorfention	138	N/A
Bromophosethyl	295	N/A
Fenthion	N/A	4.7
Chlorpyrifos	77	1.33
Diazinon	183	2.1
Methyl Parathion	89	.8
Dimethoate	56	N/A
Phosmet	13	14 (sec)
Azinophos-Methyl	28	1
Disulfoton	62	4
Thiometon	73	1.2
Phorate	4.7	1.45

N/A indicates that this information was not reported.

(Macalady et al 1992, Ostear et al 1989, Atwood et al 1987)

lower than those for neutral hydrolysis. An estimation for the activation energy for terbufos hydrolysis at pH 8, based on only two temperatures, was calculated to be ~ 25 kcal/mole ( Frank et al, 1991).

The second objective of this study was to identify, if possible, the hydrolysis products of terbufos. No attempts have been made to find the hydrolysis products in any of the literature studies that investigated terbufos hydrolysis. The mechanisms that would be expected for terbufos hydrolysis are based upon the observed hydrolysis of phosphate triesters and phosphorothioates. Phosphate triesters under alkaline conditions hydrolyze by simple nucleophilic displacement at the P-O bond (Barnard et al., 1961). However, it has been observed that phosphorothioates usually undergo hydrolytic fission at the P-S bond (Bruice and Benkovic, 1966). The approach for this study was to look for the possible products by GC-MS and to attempt to identify them via comparison to standards.

## EXPERIMENTAL SECTION

### Materials

#### Chemicals

The pesticides terbufos and chlorpyrifos were used in the study. The first sample of terbufos was obtained from the EPA ERL in Athens, GA as a 3.160 g/L solution in hexane. The rest of the terbufos was purchased from Chem. Service Inc., West Chester, PA (98.1 % +/- 0.5% purity). The chlorpyrifos was from Dow Chemical Company, Midland, Michigan. HPLC grade methanol and isooctane were purchased from Aldrich Chemical Company Inc. and Sigma Chemicals, respectively. The 2-methyl-2-propanethiol and diethyl dithiophosphate were obtained from Aldrich Chemical Company Inc.. All chemicals were used as received from the manufacturer.

#### Buffer and Nonbuffer Aqueous Solutions

The buffer compositions are summarized in Table 4. Solutions on the extreme ends of the pH range were simply made by adjusting the pH with either hydrochloric acid or sodium hydroxide to the desired pH value. All solutions were adjusted with either sodium hydroxide or hydrochloric acid to achieve the desired pH. The nonbuffer solutions were titrated for confirmation of their actual pH.

Table 3. Average Activation Energies for Several Organophosphoro Insecticides under Neutral and Alkaline Conditions.

$E_a$ (kcal/mol)	pH	Compound(s)	Source
16	Alkaline	Trimethyl Phosphates	Barnard et al 1961
22	Neutral and Acidic	Trimethyl Phosphates	Barnard et al 1961
10	Alkaline	Triphenyl Phosphates	Barnard et al 1961
22-24	Alkaline and Neutral	Triesters and Phosphonate Esters	Cox and Ramsay 1964
25	Alkaline	Malathion	Wolfe et al 1977
25	Neutral and Acidic	Malathion	Wolfe et al 1977
13	Alkaline	Chlorpyrifos	Macalady and Wolfe 1983
22	Neutral	Chlorpyrifos	Macalady and Wolfe 1983
23	Neutral	Methyl Parathion	Smith et al 1978

Table 4. Acid, base , and buffer solution composition.

pH	Composition
0	Hydrochloric Acid
1	Hydrochloric Acid
3	Acetic Acid
5	Sodium Acetate and Acetic Acid
7	Potassium Dihydrngen Phosphate
9	Sodium Bicarbonate
10	Sodium Bicarbonate
11a*	Trisodium Phosphate and Sodium Bicarbonate
11b	Sodium Bicarbonate
12	Sodium Hydroxide
13	Sodium Hydroxide

\* a,b are separate experiments.

### Standards

Standard solutions were made for terbufos and chlorpyrifos using isooctane as the solvent. Varying volumes of  $2.0 \times 10^{-6}$  M terbufos (in isooctane) were mixed with a fixed volume of  $2.0 \times 10^{-6}$  M chlorpyrifos. The resulting solutions were diluted to the same final volume with isooctane to provide standards with a constant chlorpyrifos concentration of  $1.0 \times 10^{-6}$  M and varying terbufos concentrations. Plotting terbufos concentration versus terbufos divided by chlorpyrifos area and/or height ratio's from the GC integrator gave the calibration curves.

### Instrumentation

#### GC-NPD

Samples in the kinetic studies were analyzed using a Hewlett Packard 5890A gas chromatograph attached to a Hewlett Packard 3392A integrator. The detector was a nitrogen phosphorus detector (NPD). The column used in conjunction with the NPD was a Hewlett Packard 530 $\mu$  series, 5% phenyl methyl siloxane, of length 10m and i.d. 0.53mm, with a film thickness of 2.65mm.

The experimental parameters for the gas chromatograph were the same for all kinetic data measurements. The cylinder pressures for helium, air, and hydrogen were 69.5, 42.2, and 20.0 psi, respectively. The flow rates for optimum conditions were helium at 5.0 ml/min, air and helium at 131 ml/min, hydrogen and helium at 37 ml/min. The injector and detector temperatures were 200°C and 275°C, respectively. The oven temperature was 185°C for one

minute, after which it was raised at 15°C/min to a final value of 250°C, at which it was maintained for five minutes.

### GC-MS

Product analyses were performed with a Perkin-Elmer Autosystem Gas Chromatograph in line with a Perkin-Elmer Q-mass 910 Mass Spectrometer for the purpose of product identification. The SPB-5 capillary column from Supelco was 30m in length with an i.d. of 0.2mm and a film thickness of 0.2mm.

The carrier gas was helium with a split flow ratio of 1/100. The molecular mass range was set at 25 to 300 daltons. Baseline and threshold were 11 and 4, respectively. The starting oven temperature was 35°C for an initial time of 3.0 min followed by a temperature rise of 10°C/min to the final temperature of 250°C which was maintained for 1.0 min. The injector temperature was 250°C while the auxiliary zone between instruments was at 220°C.

### pH Determination

pH measurements were made using an Orion Research Model SA 230 pH meter with an Orion Combination pH electrode. Calibrations were performed daily with buffer solutions at the pH values of 4, 7, and 10.

### Computer and Programs

All the data were analyzed using a Macintosh Performa 6116CD. Microsoft Excel 4.0 was used to calculate the data needed for all plots and

tables. Cricket Graph 1.2.1 and/or 1.3.1 was used to create all plots and regression calculations.

#### Procedure for Kinetics Measurements

Terbufos was added to 200 ml of buffered water to make an initial concentration of  $1.0 \times 10^{-6}$  M. Duplicate experiments were run simultaneously to check for reproducibility of the resulting rate constants. The aqueous solutions were purged with nitrogen then stoppered and covered with parafilm to minimize the entrance of oxygen into the reaction flask. This limits, as much as possible, the oxidative degradation pathway found to occur in soils. The flasks were then placed into a water bath at a specific temperature. Reaction temperature was controlled at 15°C for kinetic measurements in a Honeywell Environmental Growth Chamber model TC-1. Precautions were taken to keep light away from the system to avoid any photolysis. The reaction flasks were only exposed to light when sampled and were immediately covered upon their return to the water bath. Two ml aliquots were taken from the flask and combined in a test tube with 2 ml of a  $1.0 \times 10^{-6}$  M solution of chlorpyrifos, as the internal standard, in isooctane (Figure 2). Chlorpyrifos is known to undergo hydrolysis; however, the time in which it was in contact with any water is assumed to be negligible.

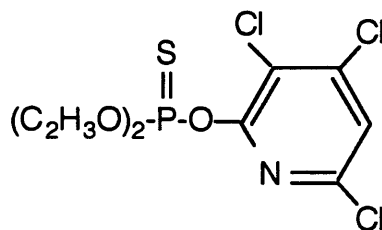


Figure 2. The structure of chlorpyrifos.

The time was recorded for each aliquot taken. The reaction flask was then purged with nitrogen before returning it to the bath. The test tube was capped and then shaken for a minute and vortexed for another minute to extract the terbufos into the isooctane layer. The isooctane layer was then separated using a Mohr pipette and the disappearance of terbufos was followed by gas chromatography.

#### Procedure for Product Analysis

Several procedures were used to attempt to identify the hydrolysis products. Samples consisting of 100  $\mu$ l of terbufos solution and 5 ml pH 9 buffered de-ionized water were allowed to undergo hydrolysis for several half-lives. The samples and buffers were purged with nitrogen and kept away from light by wrapping the reaction flasks in duct tape, as well as, keeping them covered while in the water bath. The water bath was set at approximately 45°C to accelerate the hydrolysis. After the reaction was predicted to have undergone several half-lives and to have produced products at sufficient

concentrations, the samples were extracted three times with 5 ml each of anhydrous ether. The combined ether extracts were then evaporated to near dryness using nitrogen as a blow-down gas. The remaining residue was analyzed by gas chromatograph mass spectrometry (GC/MS).

Terbufos samples were made up with the same concentration and by the method above but stored in serum bottles that were capped so that any volatile products could be trapped. The head space gases of these bottles were directly injected into the GC-MS. The remaining solutions were acidified by injecting a few drops of approximately 0.1 M hydrochloric acid to protonate any anionic species and to improve the extraction of acid products. The solutions were then mixed with 1 ml of anhydrous ether and/or methylene chloride by injecting the organic solvent into the serum bottle. Using a syringe to withdraw the organic layer, it was then analyzed directly by GC-MS. Ethanol, tert-butyl alcohol, 2-methyl-2-propanethiol, and diethyl dithiophosphate were purchased to help identify the retention times and mass spectra of these possible hydrolysis products. Experiments were also conducted to observe whether or not the standards themselves could be extracted from water by both ether and methylene chloride.

#### Calculations and Graphs

The concentrations of terbufos at various times during the reaction were found by calculating the observed ratios after analysis by gas chromatography. The observed ratios were found by dividing the area and/or height of the terbufos peak by the area and/or height of the chlorpyrifos peak. i.e.;

observed ratio = area (height) of terbufos / area (height) of chlorpyrifos

Standard curves of the area and/or height observed ratios vs. concentration of terbufos yield slopes equal to the response factors which are then used to calculate the concentrations of terbufos remaining in a reaction solution.

The calculated initial concentration of terbufos ( $C_0$ ) was assumed at time zero for the reaction. The concentration of terbufos ( $C$ ) at a given time during the reaction was then divided by the initial concentration to produce values of the concentration ratio ( $C/C_0$ ), which describe the disappearance of terbufos.

The next step was to see if the data fit pseudo-first-order kinetics by plotting natural log  $C/C_0$  versus time. The slope of the linear plot was taken as equal to the negative of the pseudo-first-order rate constant at that specific pH and temperature. Half-lives were calculated from the equation:

$$t_{1/2} = \ln 2 / k(\text{obs})$$

where  $k(\text{obs})$  is the observed rate constant at a specific pH and temperature.

The Arrhenius activation energy and pre-exponential factor were calculated by measuring the rate constants at several different temperatures and plotting natural log  $k(\text{obs})$  versus  $1/T$ . The slope equals the negative of the activation energy divided by the universal gas constant  $R$ .

## RESULTS & DISCUSSION

### Kinetic Measurements

Kinetic experiments were performed at several different values of pH and at 25°C to study the hydrolysis of terbufos throughout the pH range. At each selected pH, duplicate reactions were run simultaneously to determine experimental reproducibility. At several values of pH the reactions were repeated with duplicates. After integration the chromatographic data provided the area and heights due to chlorpyrifos and terbufos. Using both sets of data allowed an internal check for reproducibility in the chromatography as well as information pertaining to detector and column performance. At each pH there are four pseudo-first-order rate plots, two for the area data and two for the height data. Typical pseudo-first-order plots for area and height are shown in Figures 3 and 4, respectively.

The results for the observed rate constants and half-lives for the pH range between 0 and 10 were quite similar (Appendix A). The averages of the rate constants and half-lives are given in Table 5 along with the correlation coefficient range for all the plots at that specific pH. The only discrepancy in the data evolves from a three year lapse between kinetics experiments. The differences between the 1992 and 1995 data will be discussed throughout the results.

Plotting the log of all the observed rate constants (area and height values averaged) against pH summarizes nicely the overall hydrolysis kinetics of terbufos at 25°C (Figure 5). The average observed rate constants of the

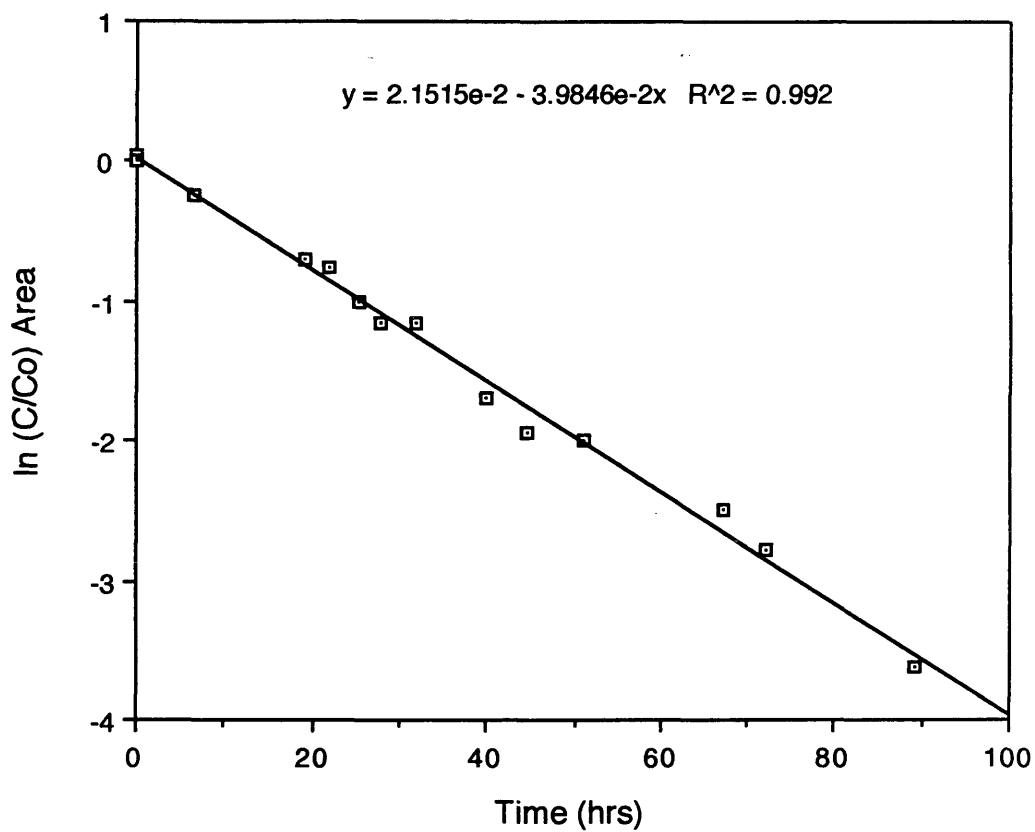


Figure 3. Natural log concentration using area integration vs. time for the disappearance of terbufos in water at pH 5 and 25°C.

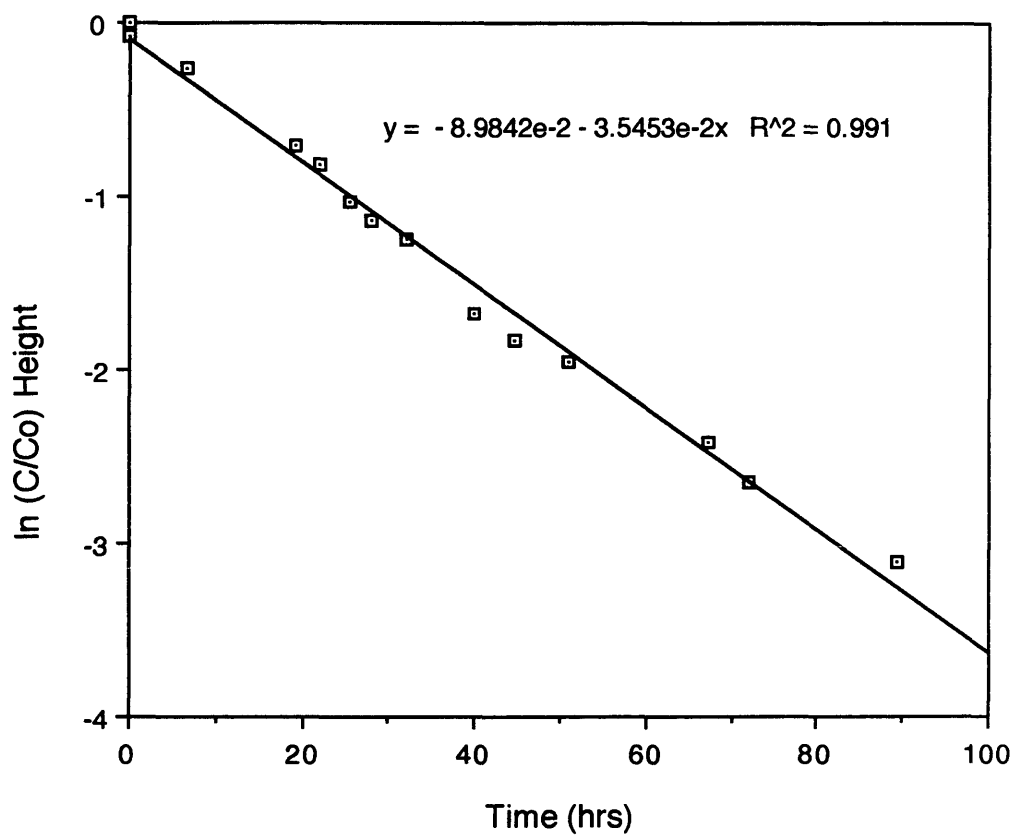


Figure 4. Natural log concentration using height integration vs. time for the disappearance of terbufos in water at pH 5 and 25°C.

Table 5. Rate constants, half-lives, and correlation coefficients at the pH values investigated at 25°C.

pH	K(obs) Average	Approximate Half- Life Average (hrs)	Linear Regression Correlation Coefficients (R <sup>2</sup> )
0	0.046	15	0.971-0.994
0.8	0.022	32	0.965-0.999
3	0.016	42	0.984-0.997
5	0.018	38	0.970-0.983
5 (95)†	0.049	15	0.979-0.992
5 o‡ (95)	0.032	21	0.991-0.995
5 n (95)	0.043	16	0.988-0.992
7	0.017	41	0.967-1.000
9 (95)	0.045	15	0.963-0.988
10	0.019	37	0.976-0.999
11a*	0.042	16	0.971-0.999
11b	0.062	11	0.971-0.999
12a	0.153	5	0.791-0.934
12b	0.016	4	0.962-0.999
13a	1.694	0.4	0.914-0.991
13b	2.112	0.3	0.942-0.994

† represents the experiments that were conducted in 1995. All others were conducted in 1992.

‡ o and n represent terbufos from EPA and Chem Service, respectively.

\* a and b represent replicate experiments.

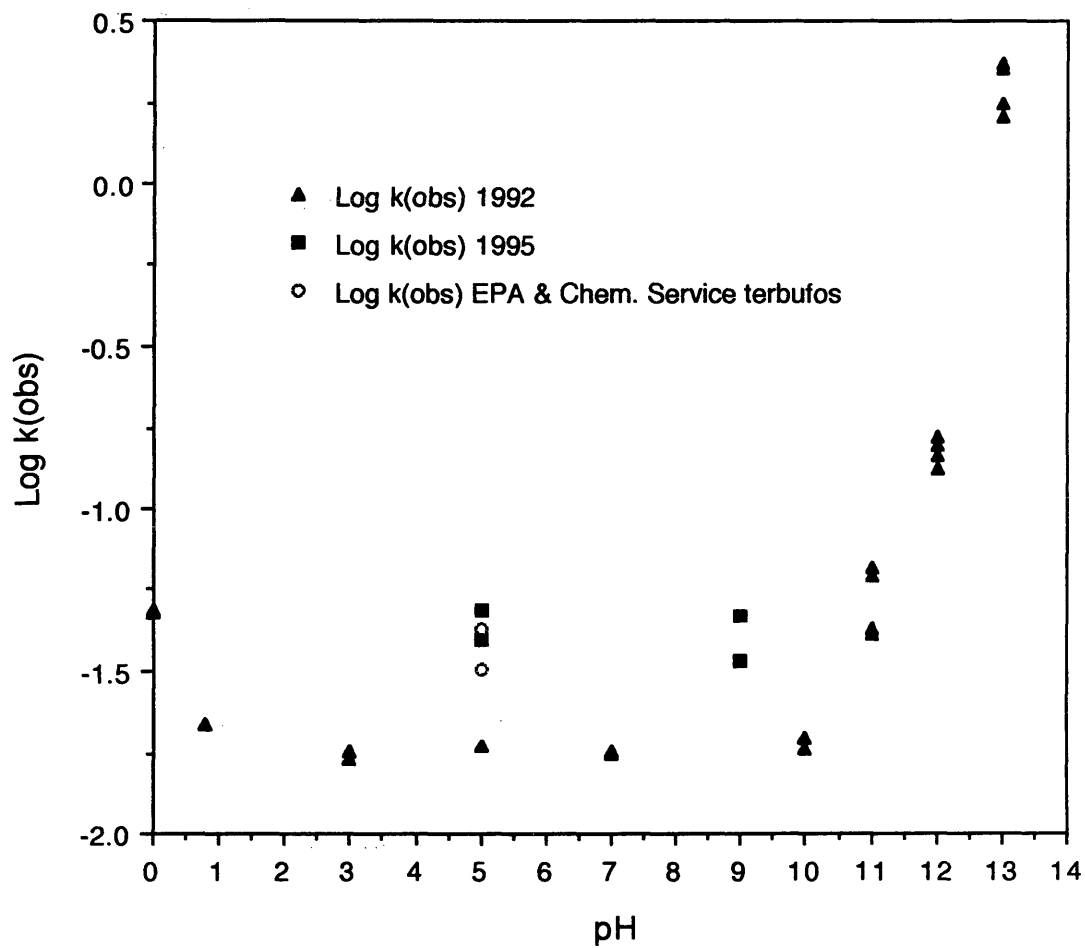


Figure 5. Log of the observed rate constants versus pH using the area integration values at 25°C for the 1992, and 1995 studies, including the values found for the different sources of terbufos.

replicate values yield  $0.052 \text{ hr}^{-1}$ ,  $0.158 \text{ hr}^{-1}$ , and  $1.90 \text{ hr}^{-1}$ , at pH 11, 12, and 13, respectively. The resulting half-lives are 13, 4 and 0.4 hours, respectively.

Alkaline hydrolysis is shown to be an important component in the overall reaction kinetics as the rate of reaction appears to increase almost exponentially at higher pH (see Figure 5). Alkaline hydrolysis for organophosphoro esters is usually first-order in both hydroxide activity and concentration of the ester. A plot of log observed rate constant versus pH should yield a linear slope equal to one. The observed rate constants and pH values at 11, 12, and 13 give a slope of 0.788 ( $R^2 = 0.935$ ) for this study (Figure 6). Because the slope is not unity, this suggests, but does not verify, that the hydrolysis reaction under alkaline conditions is not first-order with respect to the hydroxide concentration.

Plots of 1992 data give average observed rate constants that range from  $0.022$  to  $0.016 \text{ hr}^{-1}$  for the values of pH from 0.8 to 10. Corresponding half-lives for these results range from approximately 32 to 42 hours. The observation that this range of rate constants came between the pH values of 0.8 and 3, respectively, led to the hydrolysis experiment at pH of 0. The resulting average rate constant of  $0.046 \text{ hr}^{-1}$  and half-life of about 15 hours suggested an acid-catalyzed component for the overall hydrolysis reaction. However, 1995 results at pH 5 and pH 9 present a different story. The average observed rate constants were  $0.041 \text{ hr}^{-1}$  for both values of pH corresponding to average half-lives of about 15 hours. Figure 5 then suggests, comparing the 1992 rate constants at pH 0 and the 1995 rate constants at the pH values of 5 and 9, that there is no acid-catalyzed hydrolysis for terbufos. Therefore, the observed rates

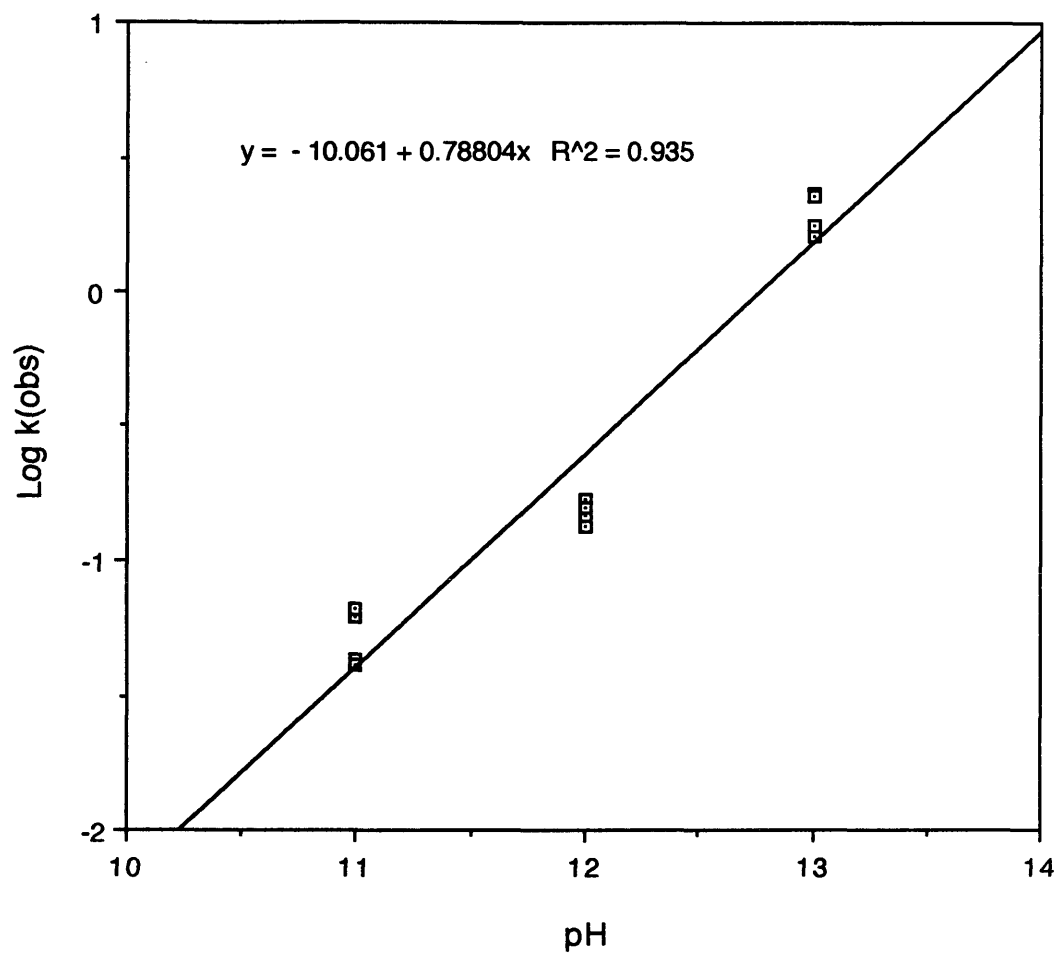


Figure 6. Log of the observed rate constants versus pH at ambient temperatures for the pH values of 11, 12, and 13.

are constant in the pH range of 0 to 9, meaning there are no significant acid or base catalysis components for the hydrolysis of terbufos in that range.

The overall observed rate constant for the hydrolysis of terbufos can be expressed by the following equation (Schwarzenbach, et al. 1993.):

$$k(\text{obs}) = k_{\text{H}^+}[\text{H}^+] + k_{\text{n}} + k_{\text{OH}^-}[\text{OH}^-]$$

where:

$k(\text{obs})$  = observed rate constant

$k_{\text{H}^+}$  = acid-catalyzed rate constant

$k_{\text{n}}$  = pH-independent rate constant

$k_{\text{OH}^-}$  = alkaline-catalyzed rate constant

$[\text{H}^+]$  = hydrogen ion concentration

$[\text{OH}^-]$  = hydroxide ion concentration

The calculated values for the acid-catalyzed, pH-independent, and alkaline-catalysis rate constants for terbufos from the 1992 data are  $0.028 \text{ M}^{-1} \text{ hr}^{-1}$ ,  $0.017 \text{ hr}^{-1}$ , and  $18.7 \text{ M}^{-1} \text{ hr}^{-1}$ , respectively. The values of pH used to calculate these rate constants were 0.8, 7, and 13, respectively. Values for the acid-catalyzed, pH-independent, and alkaline-catalysis rate constants for terbufos from the 1995 data are  $20 \text{ M}^{-1} \text{ hr}^{-1}$ ,  $0.039 \text{ hr}^{-1}$ , and  $20.0 \text{ M}^{-1} \text{ hr}^{-1}$ , respectively. These calculations used the 1995 rate constants at the pH values of 5 and 9 and the 1992 values at pH 13.

It is unclear whether or not acid catalyzed hydrolysis occurs. Acid catalyzed hydrolysis has not been reported for other phosphorodithioates (Bruice and Benkovic, 1966, Cox and Ramsay, 1964, Barnard, et al., 1961). Experiments were not repeated at the lower and higher pH values, so it is questionable as to whether or not higher rates would have been observed at these pH values.

Differences between the rate constants and half-lives for these experiments completed three years apart could have resulted from several experimental factors. The first was that the terbufos used for the two sets of experiments came from different sources. A separate experiment was conducted in 1995 using both terbufos samples at pH 5 and a temperature at 25°C (see Appendix A). The resulting average rate constants were 0.032 hr<sup>-1</sup> and 0.043 hr<sup>-1</sup> for the EPA terbufos and Chem. Service terbufos, respectively. The fact that these rate constants are similar to those found for the 1995 pH 5 experiments suggests that the different sources of terbufos do not account for the discrepancy.

Photolysis and oxidation could also affect the rate constants observed for acidic and neutral hydrolysis. Extreme care was taken to ensure that oxygen was not present during the reaction. If, however, oxygen was present and oxidation of terbufos occurred an apparent increase in the rates would be observed. The same could be said for photolysis which would also give the appearance of an increased rate of reaction; however, Frank et al., 1991, observed that photolysis does not significantly affect the rate of hydrolysis of terbufos.

The correlation coefficients,  $R^2$ , for the pseudo-first-order plots at all values of pH at 25°C are given in Table 5. The correlations indicate that pseudo-first-order kinetics, at each pH, best describe the hydrolysis reaction. At pH 12 and 13 the first experiments resulted in the poorest correlations. Repeating these experiments improved the correlations yet only slightly changed the observed rate constants. The level of precision throughout the experimentation at 25°C leads to the assumption that the method of experimentation is accurate. In Figure 5 we see that even though there is a change in the rate of reaction between the 1992 results and those of 1995, the difference is only about 0.4 log units at pH of 5. Comparing this to values found in the literature between the pH values of 4.5 and 9 gives a range of about 1.2 log units (Figure 7). Figure 7 shows that the degradation rates found in this study are faster than all the literature values for hydrolysis of terbufos. The rates found in the 1992 studies are similar to those found by Chapman and Cole, 1982, and Frank et al., 1991. The reasons for the increased reaction rates for this study are unknown. Photolysis and oxidation could not account for this difference because of the precautions taken to limit these degradation pathways.

#### Arrhenius Activation Energy Measurements

Kinetic studies at varying temperatures were conducted to determine the Arrhenius activation energies for the observed rate constants at neutral and alkaline pH values. In 1992 studies were conducted at a pH of 5 at 15°C and 35°C. Results at 15°C were inadequate because sampling was terminated

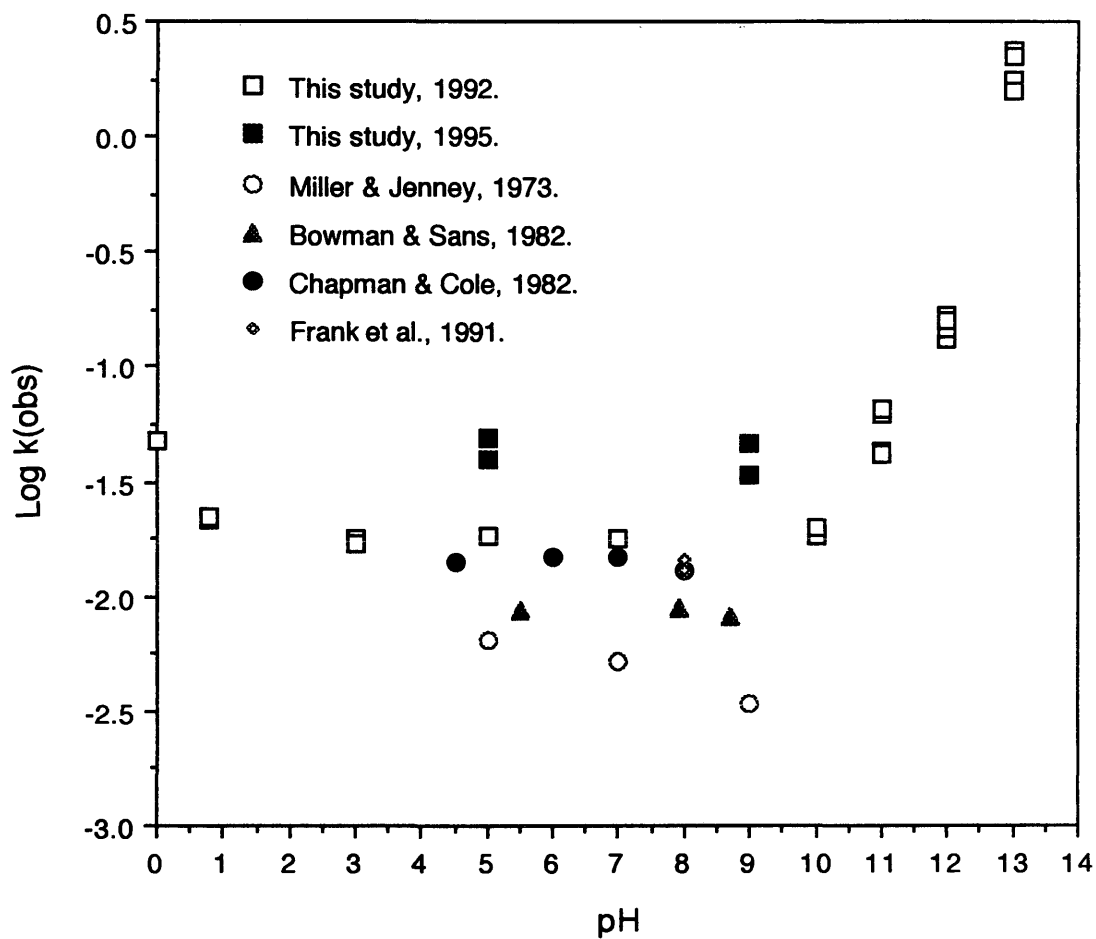


Figure 7. Log of the observed rate constants versus pH at ambient temperatures comparing the literature values given in Table 1 to the values obtained in both the 1992 and 1995 studies.

before the reaction could achieve one half-life. Studies in 1995 included experiments at pH 5 and pH 9 for 15°C, 35°C, and 45°C. All the observed rate constants and half-lives are given in Appendix A. Table 6 lists the average rate constants and half-lives along with the range of correlation coefficients for the pseudo-first-order plots at each temperature for the pH values of 5 and 9.

The observation of nonlinear behavior for the 45°C kinetic data at both pH 5 and 9 obviates the data from being used for calculating the Arrhenius activation energy. The experiments at the remaining temperatures of 15°C, 25°C, and 35°C have nearly the same precision as the pseudo-first-order plots in previous studies. This gives a high confidence that first order kinetics is indeed occurring at both pH 5 and 9.

Activation energies of 28 kcal/mol and 41 kcal/mol for pH 5 and 9, respectively, were determined using the average rate constants at both pH values and at 15°C, 25°C, and 35°C. Figure 8 is the Arrhenius plot for the area data at a pH of 9. The correlation for this plot is very good but it yields a higher activation energy than would be expected based on the literature values for neutral or alkaline hydrolysis listed in Table 3.

The opposite was found at pH of 5 (Figure 9). The correlation coefficient for the plot was 0.798 which appears to result from the difference in the observed rate constants for the 1992 and 1995 studies at 25°C and 35°C. (Note that the 35°C data show the same discrepancy as the 25°C data between the years 1992 and 1995. ) Omitting the data from 1992, results in a correlation of .987 for the Arrhenius plot at a pH of 5 (Figure 10). The calculated activation energy is 36 kcal/mol. Using only the 1995 rate constants gives a better

Table 6. Rate constants, half-lives, and correlation coefficients at the pH values of 5 and 9 for the temperature investigations.

pH	Temperature (°C)	K(obs) Average	Approximate Half-Life Average (hrs)	Range of R <sup>2</sup> for Plots
5	15	0.0062	112	0.903-0.987
5 (92)†	25	0.018	38	0.970-0.983
5	25	0.049	14	0.979-0.992
5 (92)†	35	0.062	11	0.991-0.995
5	35	0.351	2	0.971-0.980
5	45 *	0.941	0.7	0.797-0.833
9	15	0.0050	139	0.971-0.987
9	25	0.045	15	0.963-0.988
9	35	0.554	1	0.917-0.971
9	45 *	1.59	0.4	0.699-0.823

\* Based on best linear fit.

† represents the experiments that were conducted in 1992. All others were conducted in 1995.

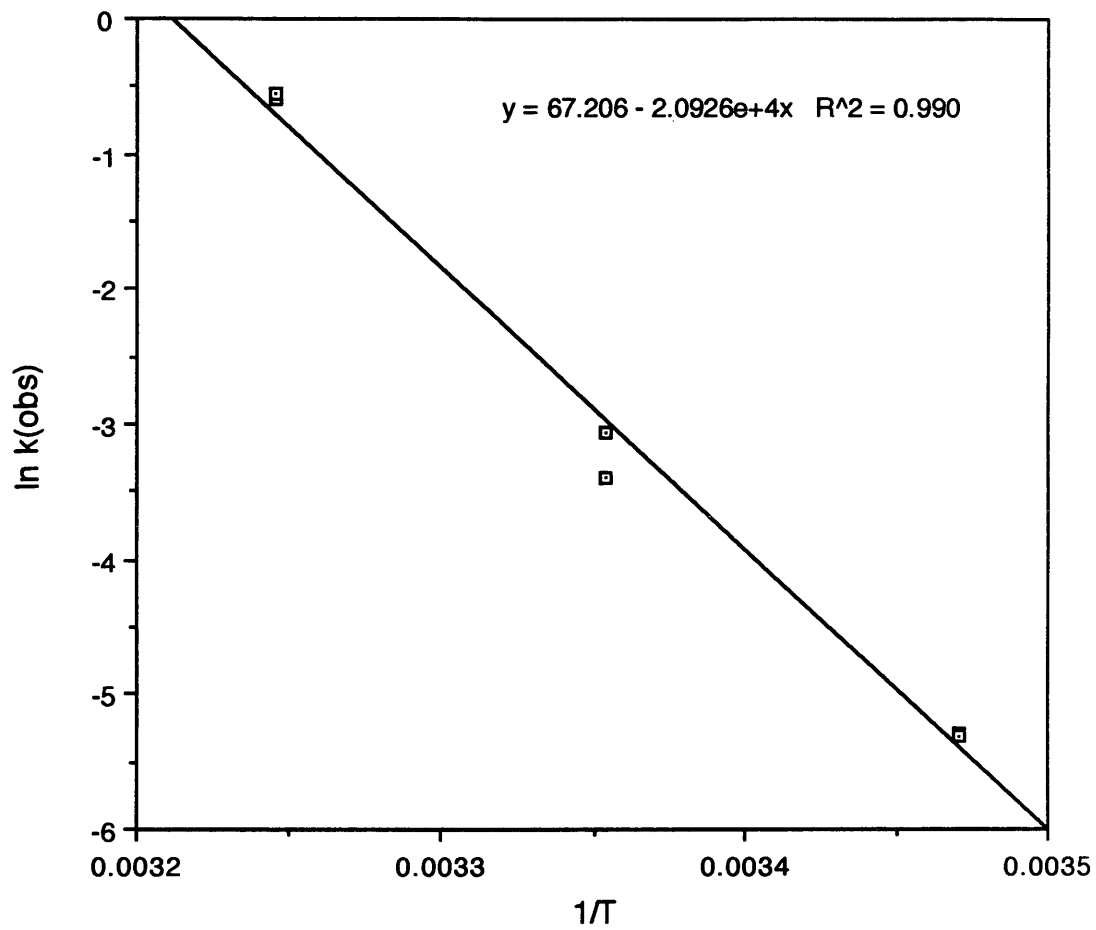


Figure 8. Natural log of the observed rate constant versus the inverse temperature using the area integration at the pH of 9.

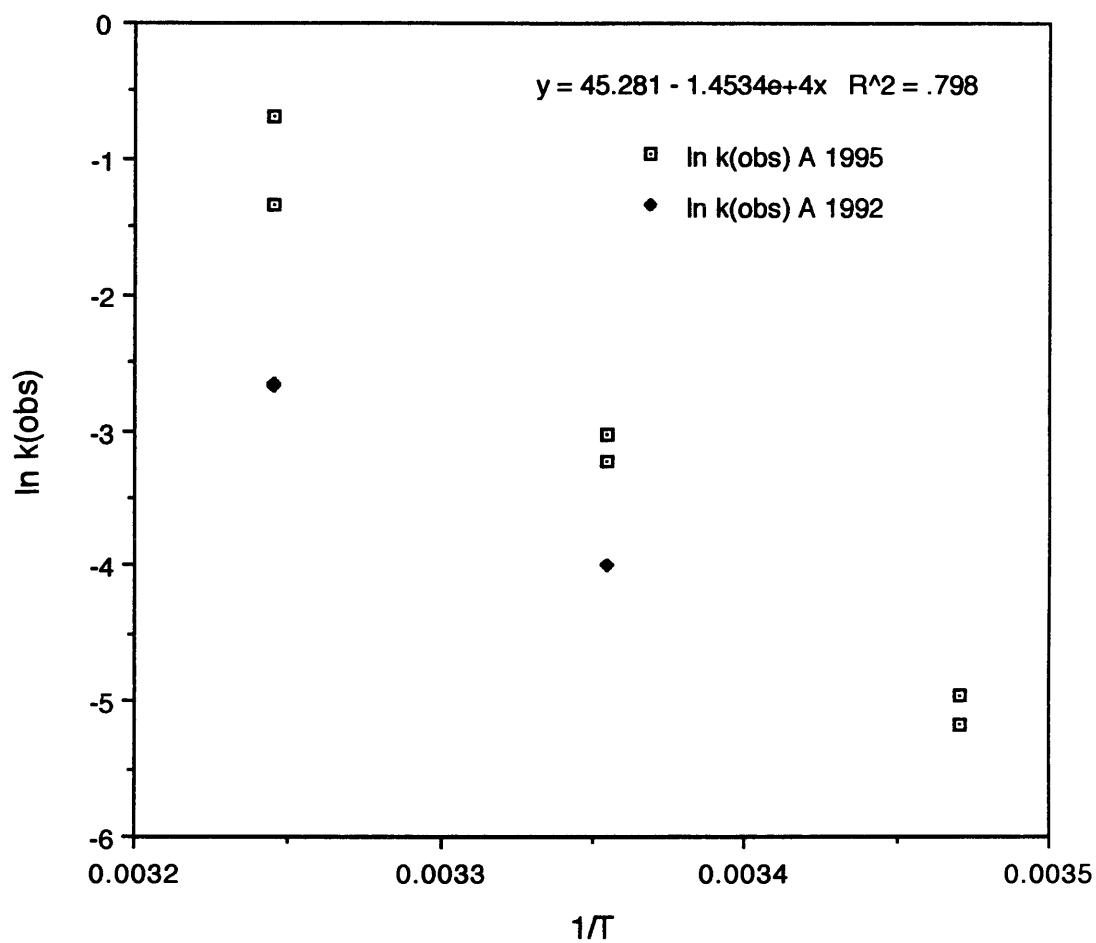


Figure 9. Natural log of the observed rate constants versus the inverse temperature using the area integration at the pH of 5 for both the 1992 and 1995 studies.

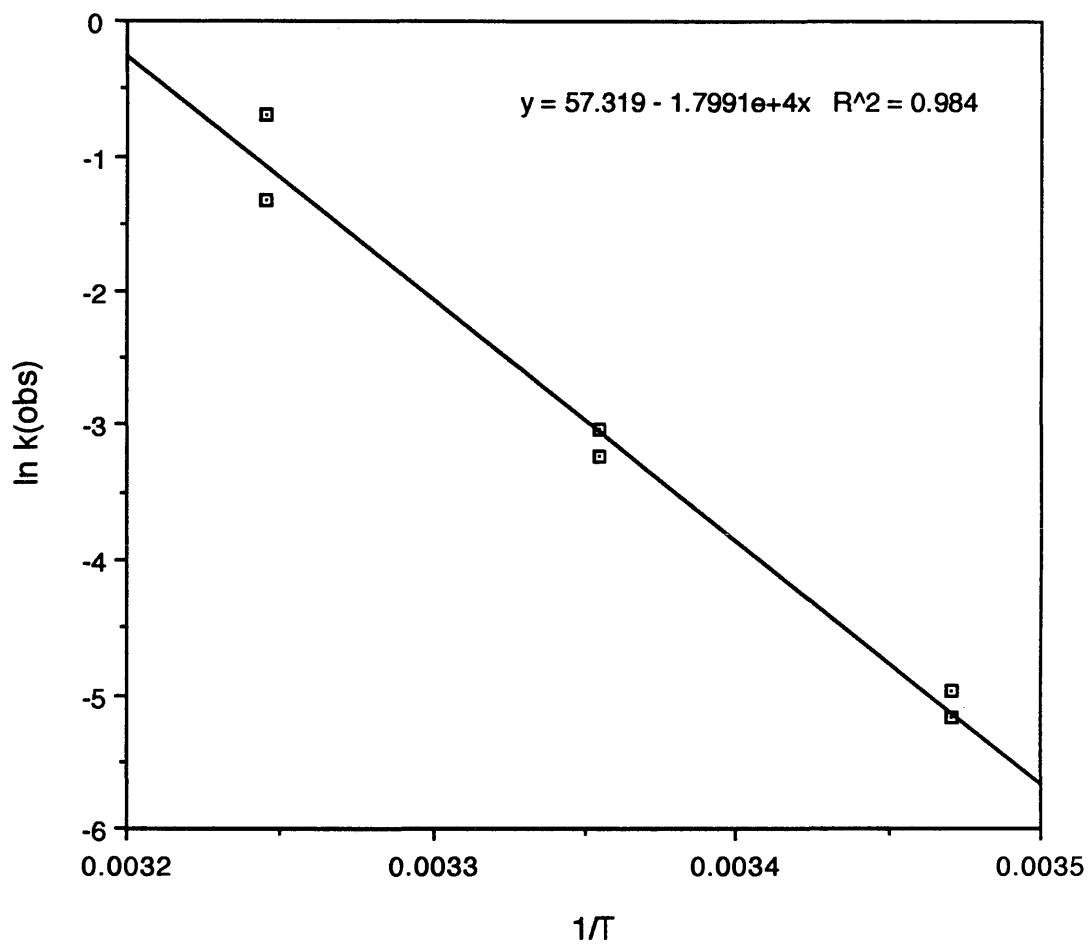


Figure 10. Natural log of the observed rate constants versus the inverse temperature using the area integration at the pH of 5 for the 1995 studies.

comparison for the activation energies at the pH values of 5 and 9. The observation that the activation energy at the pH of 9 is larger than that for the pH of 5 is a mystery. There are two possible explanations for this observation.

Assuming the reaction follows the expression;

$$k(\text{obs}) = k_n + k_{\text{OH}^-}[\text{OH}^-]$$

then the activation energy data can not be correct. If the activation energies are correct the observed rate constant at pH of 9 would become smaller than the observed rate constant at the pH of 5 at lower temperatures. This is not possible due to the fact that  $k_n$  represents the minimum rate that can be observed. The second explanation would assume that the activation energies are correct. The reason is that the effective activation energy is a composite of activation energies for several competing hydrolysis pathways producing different products. As the temperature changes, the importance of the pathways may change, thus changing the effective activation energies. Therefore, the observed activation energy is not really a constant, and the Arrhenius equation may not apply.

The addition of the 45°C studies at both pH 5 and 9 is questionable but some observations are to be made from their inclusion. Typical pseudo-first-order plots are shown in Figures 11 and 12 for pH 5 and 9, respectively. They are not linear as were those in all the other studies that were conducted. However, there are two possible linear segments that could be used to possibly define the rate constant for 45°C in each pseudo-first-order plot, i.e., the line that

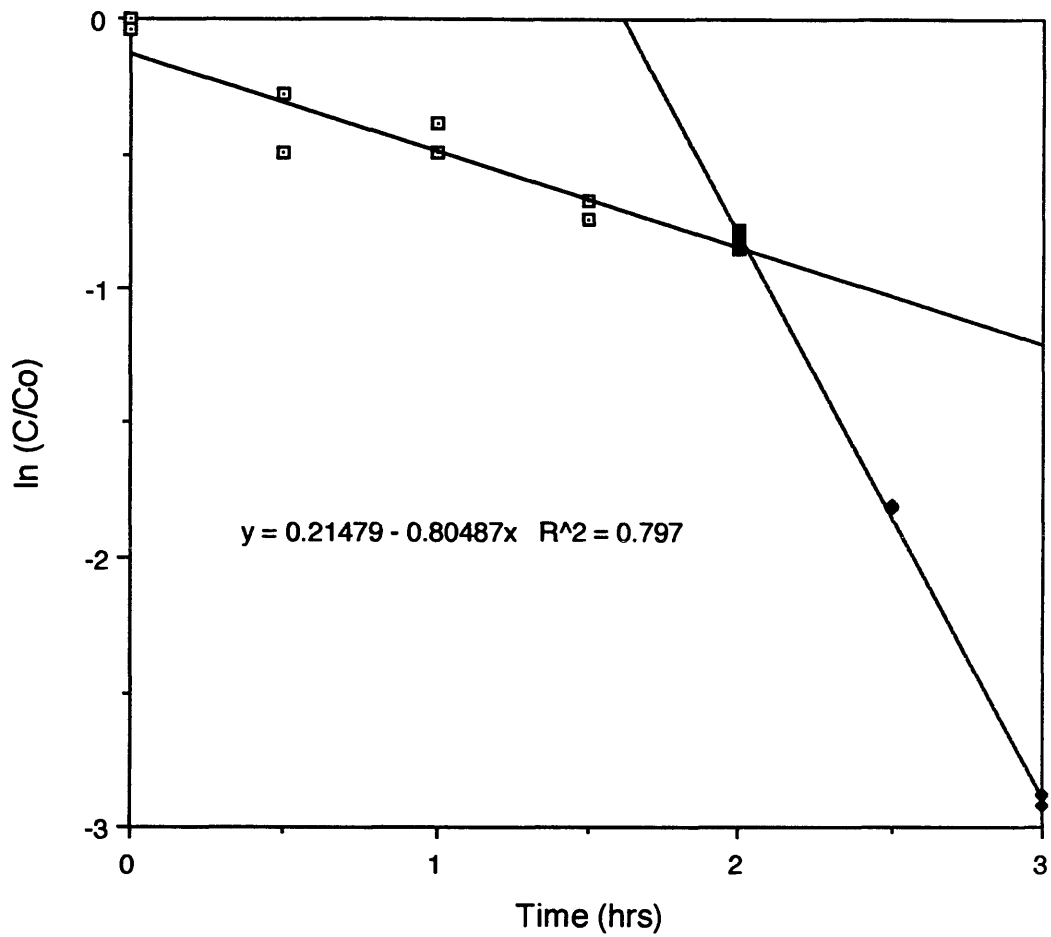


Figure 11. Natural log concentration using area integration vs. time for the disappearance of terbufos in water at pH 5 and 45°C. Equation of the line represents the regression for all the points.

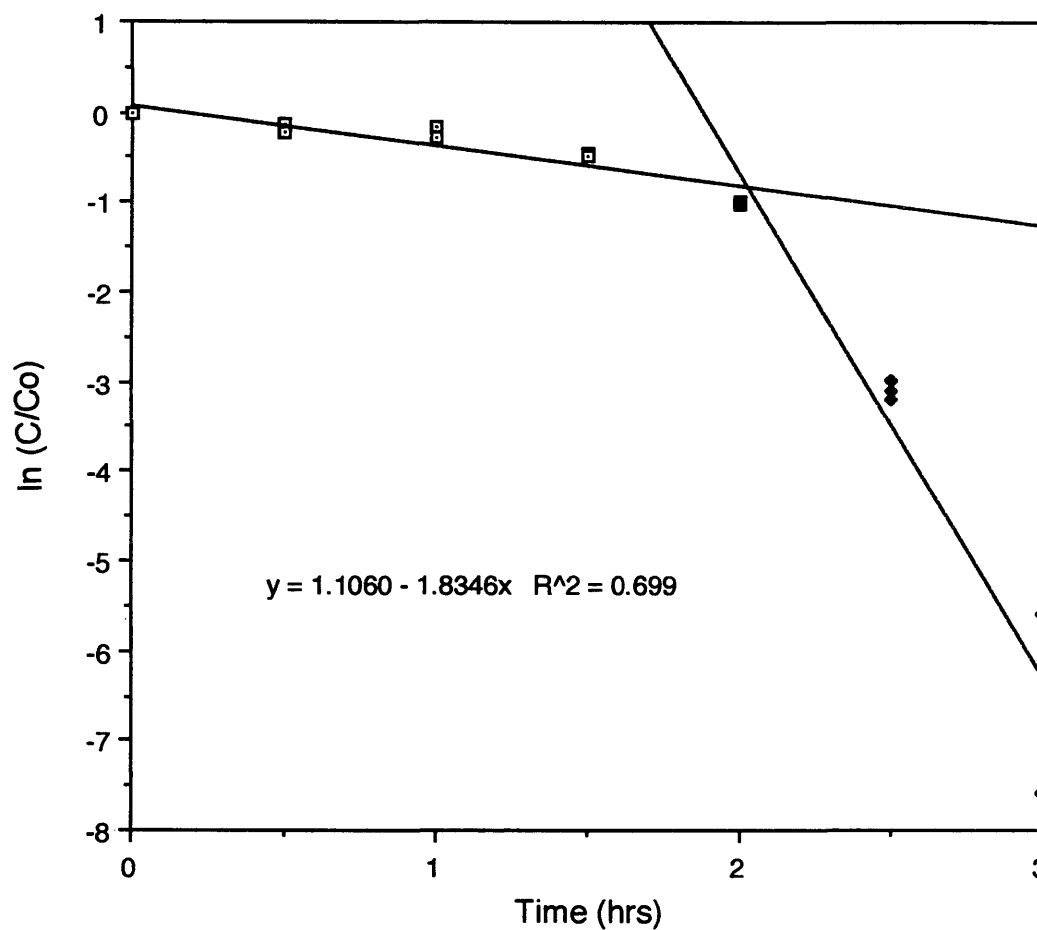


Figure 12. Natural log concentration using area integration vs. time for the disappearance of terbufos in water at pH 9 and 45°C. Equation of the line represents the regression for all the points.

results from the first five points of the plot and the line from the last three points of the plot.

Based on the Arrhenius plots from the 15°C, 25°C, and 35°C studies at both pH values, the observed rate constants at 45°C can be predicted. Figures 13 and 14 show that the observed rate constants, calculated from the last three points of the pseudo-first-order plots, are close to what would be predicted. The resulting average activation energies would be 35 and 42 Kcal/mol at pH 5 and 9, respectively.

Figures 15 and 16 are the results using the slope of the first five points from the 45°C pseudo-first-order plots. The calculated values for the average activation energies using this assumption are 26 and 30 kcal/mol at pH's 5 and 9, respectively. The correlations, however, are not good. The possibility arises that the data at 35°C may be in question. As another exercise, omitting the data at 35°C and using the rate constants from the first five points in the pseudo-first-order plots for 45°C at the pH of 5 and 9 give 24 and 27 kcal/mol, respectively, for the activation energies. A correlation range of 0.956 to 0.984 is obtained using this assumption.

The possibility exists that a thermally labile complex could be involved in the reaction which influences the reaction rates at the higher temperatures. The rate that results from the last points in the 45°C first-order plot at the pH of 9 is found to be much faster than that found for the pH of 5. This suggests that the initial rates observed for both values of pH (first five points) is pH independent; however, as the reaction proceeds alkaline-catalysis may become rate-limiting as the intermediate becomes more concentrated. Felsot et al. 1982 observed a

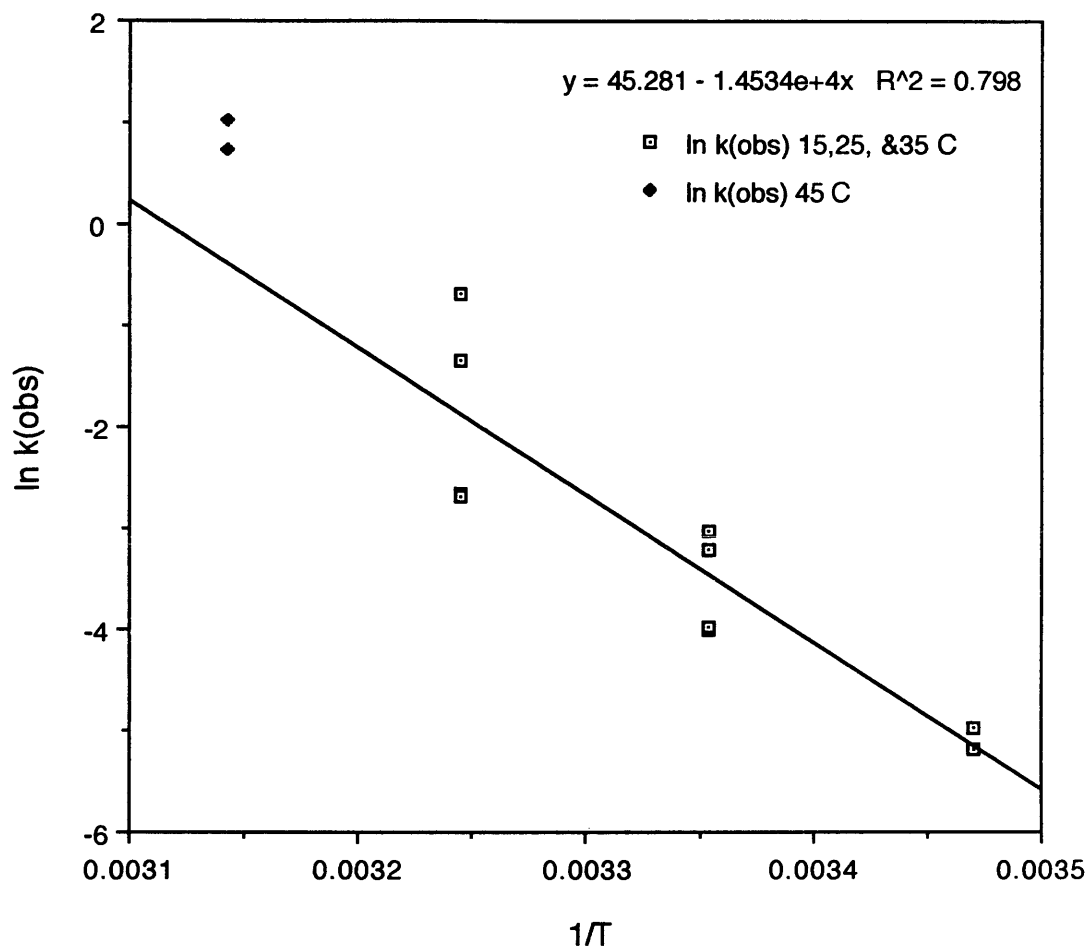


Figure 13. Natural log of the observed rate constants versus the inverse temperature using the area integrations showing the predicted fit of the last three points from the first-order plot at 45°C and a pH of 5. Equation of the line does not include the points predicted at 45°C.

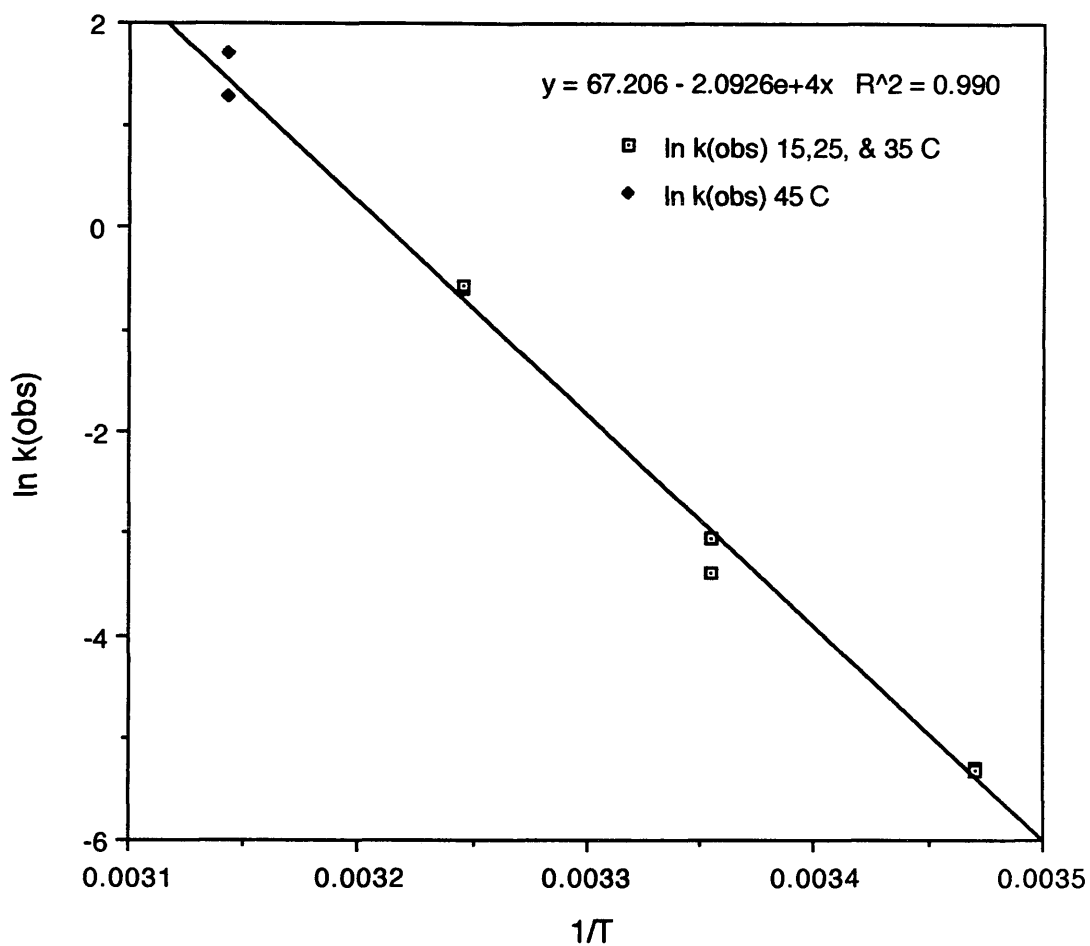


Figure 14. Natural log of the observed rate constants versus the inverse temperature using the area integrations showing the predicted fit of the last three points from the first-order plot at 45°C and a pH of 9. Equation of the line does not include the points predicted at 45°C.

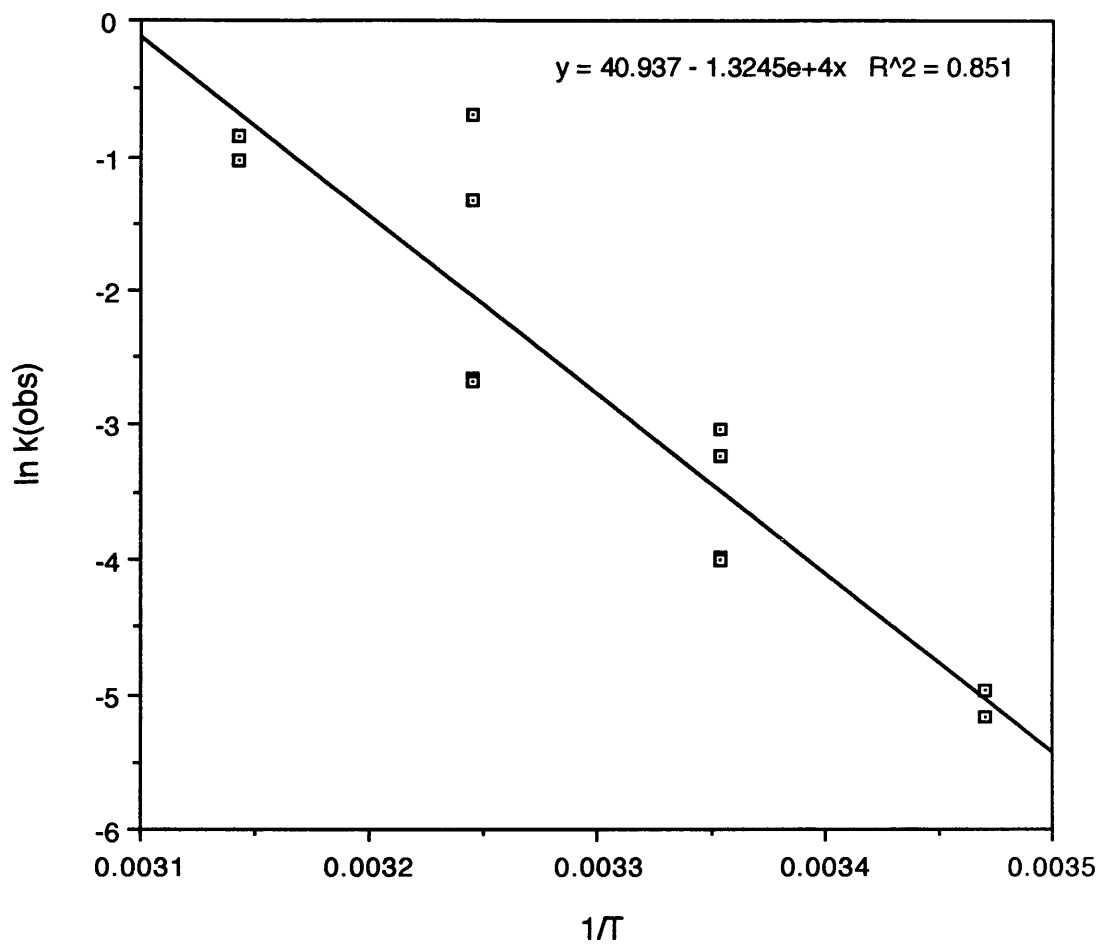


Figure 15. Natural log of the observed rate constants versus the inverse temperature using the area integrations showing the predicted fit of the first five points from the first-order plot at 45°C and a pH of 5. Equation of the line does not include the points predicted at 45°C.

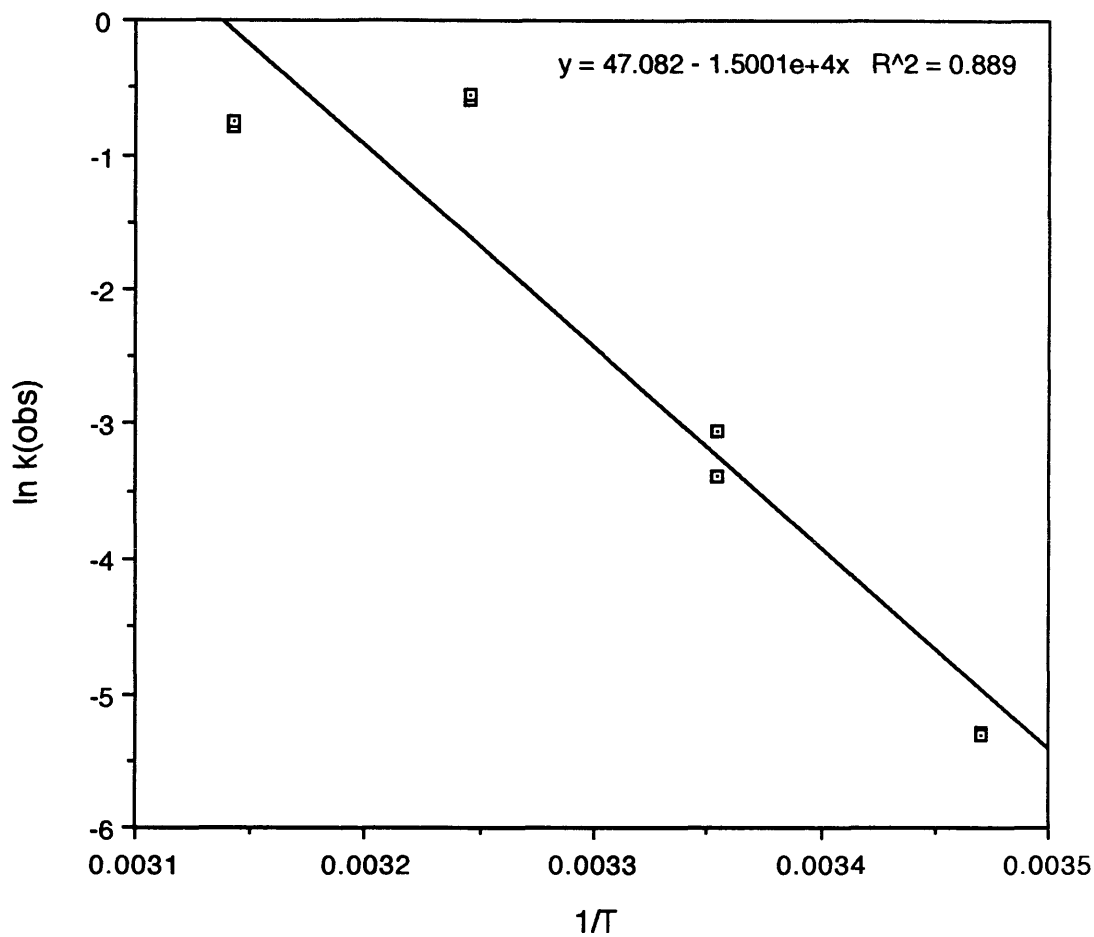


Figure 16. Natural log of the observed rate constants versus the inverse temperature using the area integrations showing the predicted fit of the first five points from the first-order plot at 45°C and a pH of 9. Equation of the line does not include the points predicted at 45°C.

temperature dependence for the disappearance of terbufos in soil. The study reported that as the temperature increased so did the disappearance of terbufos; however, they observed a break in their disappearance curves at 25°C and 35°C. Their results show initially a faster rate of disappearance for terbufos followed by a decrease in the rate after ~ 35 days. This dependence is opposite that found in the hydrolysis of terbufos at 45°C but can not be directly compared due to the obvious differences in the studies. The observation is that the reaction order of terbufos degradation in soil as well as in aqueous systems may be influenced by some chemical or physical property that is temperature dependent.

The reasons for using the rate constants from the first five points of the pseudo-first-order rate plots at 45°C are twofold. The first reason is that it's the start of the hydrolysis reaction and assumed to be less affected by experimental factors such as reversibility, competing reactions, etc. The second is that the activation energies calculated using the first five points from the 45°C experiments are closer to what is expected for the hydrolysis of a phosphorodithioate (see Table 2).

### Product studies

The experiments conducted to identify the hydrolysis products of terbufos concluded with no results. Terbufos was readily identified by GC-MS after extraction from water with both ether and methylene chloride. No peaks that correspond to possible degradation products were observed other than that for terbufos in any of the gas chromatograms (Figure 17). Head space analysis

gave no indication of volatile products. Several of the possible products such as ethanol, tert-butyl alcohol, and 2-methyl-2-propanethiol were readily identified by GC-MS after extraction of standards from water with either ether or methylene chloride. Diethyl dithiophosphate, however, was not extractable from water with either of the solvents. I believe that further research should focus on using a GC column that allows for the direct injection of the terbufos/water solution. This method would better analyze water soluble as well as organic products that may not be extractable with organic solvents.

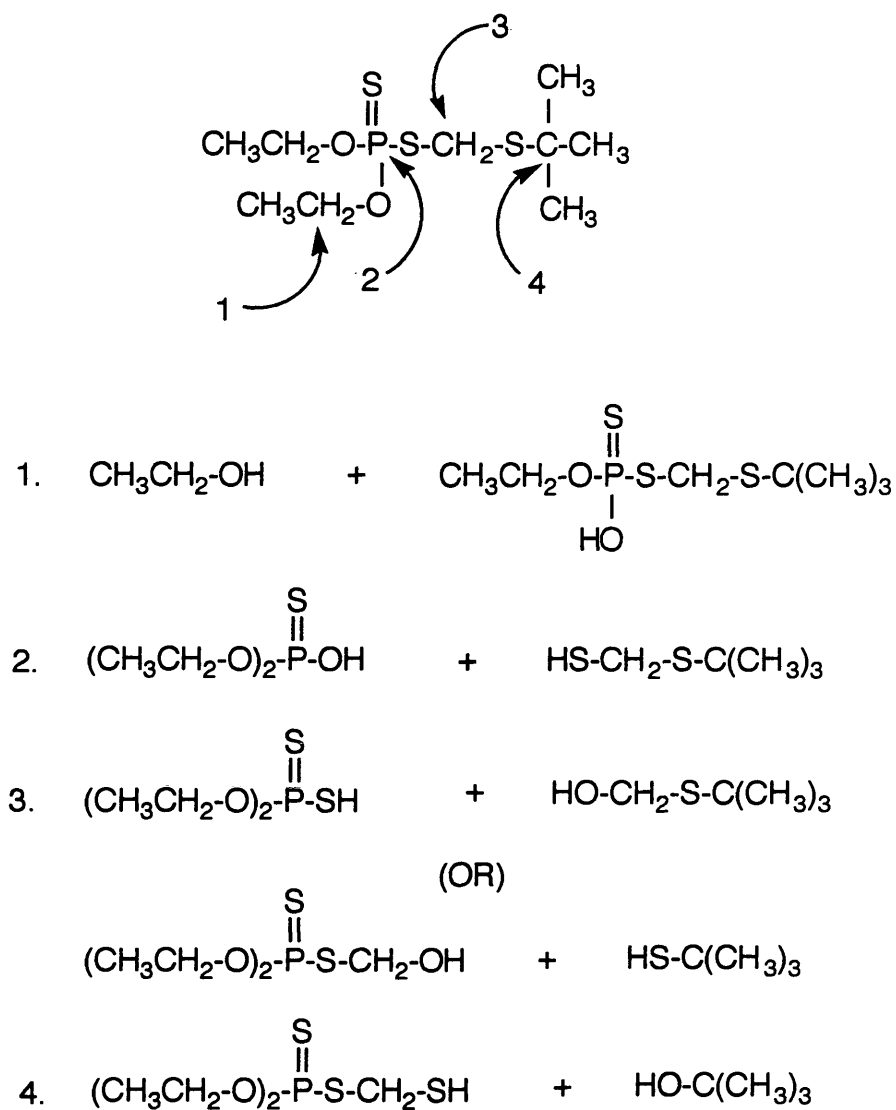


Figure 17. The four possible sites for nucleophilic attack of terbufos and resulting products from each mechanism.

## CONCLUSION

The degradation of terbufos by hydrolysis was found to obey pseudo-first-order kinetics over the entire pH range at 15°C, 25°C, and 35°C. The rates observed for pH independent and alkaline catalyzed hydrolysis of terbufos are reported to be faster than for any phosphorodithioate reported in the literature. It is unclear why terbufos exhibits such a fast rate of hydrolysis compared to other organophosphorodithioate insecticides. The high activation energies calculated at the pH values of 5 and 9 are perplexing as low activation energies would be expected for such rates of reaction. Studies conducted at 45°C indicate that increasing temperatures may influence the order of the rate of hydrolysis for terbufos and could possibly explain the calculated activation energies. Further evidence is required, however, to support such a conclusion. Hydrolysis products were not identified by the experimental methods used. Several standards of the possible products for hydrolysis were observed by GC-MS after extraction from water indicating that the method used for extracting the possible products was not entirely inadequate.

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pH	Temp	Year	k(obs) Area	k(obs) Height	Log k(obs) A	Log k(obs) H	Half-life A	Half-life H	Correlation A	Correlation H
0.00	25	92	0.0485	0.0415	-1.3146	-1.3822	14.30	16.71	0.994	0.992
0.00	25	92	0.0476	0.0442	-1.3226	-1.3549	14.57	15.69	0.971	0.993
0.80	25	92	0.0217	0.0214	-1.6642	-1.6699	31.99	32.41	0.980	0.999
0.80	25	92	0.0219	0.0213	-1.6602	-1.6716	31.70	32.54	0.965	0.997
3.00	25	92	0.0180	0.0162	-1.7440	-1.7904	38.44	42.78	0.986	0.984
3.00	25	92	0.0170	0.0150	-1.7692	-1.8248	40.74	46.31	0.987	0.997
5.00	15	95	0.0070	0.0067	-2.1557	-2.1720	99.20	103.01	0.903	0.922
5.00	15	95	0.0056	0.0053	-2.2484	-2.2743	122.82	130.35	0.983	0.987
5.00	25	92	0.0186	0.0179	-1.7314	-1.7483	37.35	38.83	0.978	0.983
5.00	25	92	0.0185	0.0175	-1.7333	-1.7570	37.51	39.61	0.970	0.971
5.00	25	95	0.0487	0.0394	-1.3124	-1.4050	14.23	17.61	0.979	0.979
5.00	25	95	0.0398	0.0355	-1.3996	-1.4503	17.40	19.55	0.992	0.991
5.00	25	95 O	0.0324	0.0322	-1.4895	-1.4921	21.39	21.53	0.986	0.992
5.00	25	95 N	0.0430	0.0434	-1.3665	-1.3625	16.12	15.97	0.982	0.993
5.00	35	92	0.0691	0.0534	-1.1604	-1.2726	10.03	12.99	0.995	0.991
5.00	35	92	0.0708	0.0537	-1.1499	-1.2704	9.79	12.92	0.992	0.991
5.00	35	95	0.2638	0.2445	-0.5788	-0.6118	2.63	2.84	0.977	0.980
5.00	35	95	0.4981	0.3958	-0.3027	-0.4025	1.39	1.75	0.980	0.971
5.00	45	95	0.8049	0.7936	-0.0943	-0.1004	0.86	0.87	0.797	0.809
5.00	45	95	1.0752	1.0908	0.0315	0.0377	0.64	0.64	0.826	0.833
7.00	25	92	0.0176	0.0160	-1.7538	-1.7966	39.32	43.39	0.967	1.000
7.00	25	92	0.0179	0.0167	-1.7480	-1.7769	38.80	41.47	0.973	0.999
9.00	15	95	0.0051	0.0051	-2.2951	-2.2928	136.73	136.02	0.987	0.981
9.00	15	95	0.0049	0.0047	-2.3083	-2.3263	140.96	146.94	0.971	0.979
9.00	25	95	0.0338	0.0340	-1.4712	-1.4690	20.51	20.41	0.984	0.988
9.00	25	95	0.0472	0.0471	-1.3265	-1.3273	14.70	14.73	0.963	0.969
9.00	35	95	0.5517	0.5323	-0.2583	-0.2738	1.26	1.30	0.917	0.941
9.00	35	95	0.5702	0.5628	-0.2440	-0.2496	1.22	1.23	0.960	0.971
9.00	45	95	1.8346	1.6602	0.2635	0.2202	0.38	0.42	0.699	0.763
9.00	45	95	1.4217	1.4279	0.1528	0.1547	0.49	0.49	0.806	0.823
10.00	25	92	0.0184	0.0172	-1.7358	-1.7632	37.73	40.18	0.976	0.995
10.00	25	92	0.0196	0.0195	-1.7076	-1.7111	35.35	35.64	0.991	0.999
11.00	25	92	0.0429	0.0425	-1.3678	-1.3716	16.17	16.31	0.981	0.971
11.00	25	92	0.0414	0.0419	-1.3830	-1.3776	16.74	16.54	0.983	0.999
11.00	25	92	0.0621	0.0583	-1.2069	-1.2344	11.16	11.89	0.987	0.998
11.00	25	92	0.0666	0.0610	-1.1766	-1.2148	10.41	11.37	0.997	0.999
12.00	25	92	0.1330	0.1821	-0.8762	-0.7396	5.21	3.81	0.820	0.791
12.00	25	92	0.1678	0.1287	-0.7752	-0.8903	4.13	5.38	0.912	0.934
12.00	25	92	0.1463	0.1727	-0.8347	-0.7628	4.74	4.01	0.962	0.997
12.00	25	92	0.1582	0.1726	-0.8008	-0.7629	4.38	4.01	0.990	0.999
13.00	25	92	1.7521	1.7506	0.2436	0.2432	0.40	0.40	0.914	0.989
13.00	25	92	1.5990	1.6753	0.2038	0.2241	0.43	0.41	0.924	0.991
13.00	25	92	2.3321	1.8558	0.3677	0.2685	0.30	0.37	0.942	0.958
13.00	25	92	2.2641	1.9960	0.3549	0.3002	0.31	0.35	0.922	0.994

All other data are provided on disk at the end of the thesis.