

# Investigation of the Heterogeneously Catalyzed Hydrolysis of Organophosphorus Pesticides

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The hydrolysis of four organophosphorus pesticides (demeton S, diazinon, disulfoton, and thiometon) in the presence or absence of three iron oxides (hematite, goethite, and ferrihydrite) and aluminum hydroxide has been investigated. Metal oxide surfaces can catalyze as well as inhibit the hydrolysis of organophosphorus insecticides and thus significantly affect the fate of these compounds in the environment. Adsorption of the organophosphorus pesticides onto the metal oxides seems to take place at specific binding sites, and the fraction adsorbed can be as high as 0.4. Activation parameter studies show that the rate-determining step of the mechanism of surface catalysis is complex formation between the pesticide and the oxide when the catalysis takes place only at low temperatures. Product studies show that hazardous, persistent compounds can be formed. An example is 1,2-bis(ethylthio)ethane, a previously unreported and persistent product of insecticide hydrolysis. The research also shows that different products can be formed depending on the reaction conditions (e.g., dissolved oxygen and pH), especially when the reactants contain alkyl sulfide moieties as their primary leaving group.

**Keywords:** *Pesticides; organophosphorus; hydrolysis; oxides; products*

## INTRODUCTION

Esters and thioesters of phosphoric acid and thiophosphoric acid are widely applied as insecticides (Khan, 1980; Lores et al., 1985; Wang et al., 1987; Lacorte et al., 1993, 1995; Brown et al., 1993; Lacorte and Barcelo, 1994), having largely replaced organochlorine pesticides such as DDT because of concerns over their persistence and bioaccumulation in the environment (Schimmel et al., 1983). Diazinon, one of the studied insecticides, was estimated to be used at a rate of >2.6 million pounds per year prior to 1983 (Howard, 1991). The insecticides thiometon and disulfoton, also a part of this study, were accidentally released into the Rhine River in 1986 (Wanner et al., 1989). Furthermore, some trialkyl and triaryl phosphates are used in very large quantities in fire-resistant hydraulic fluids and as fire-retarding plasticizers. In addition, in the surface organic microlayer of water bodies, pesticides can cause deleterious effects on fish embryos (Von Westerhagen et al., 1987), and recent research has been carried out to bioassay the pesticides present in the surface organic microlayer (Premdas and Kendrick, 1992). Consequently, these compounds are of great environmental concern.

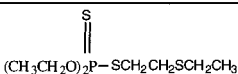
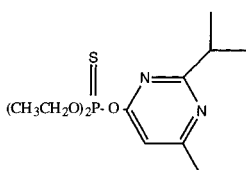

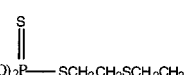
The studied organophosphorus pesticides are relatively persistent in the environment, with hydrolysis half-lives >50 days (at pH 7 and 25 °C) (Mabey and Mill, 1978). Hydrolysis and microbial degradation are two important degradation pathways. Photodegradation is also a transformation pathway. Most homogeneous hydrolysis studies of phosphoric and thiophosphoric acid esters to date have not included analysis for any transformation products with some exceptions (Muhl-

mann and Schrader, 1957; Faust and Gomaa, 1972; Weber, 1976; Wanner et al., 1989; Torrents and Stone, 1994). Therefore, the conclusions regarding hydrolysis mechanisms are still mostly speculative. Additionally, most of the studies were carried out at very high temperatures (e.g., at 70 °C) and/or in mixed solvents (e.g., in water/methanol) to facilitate solubility. These experimental conditions may not reflect hydrolysis behavior in natural water systems.

Oxide surface catalyzed hydrolysis of some carboxylate and phosphorothioate esters was observed recently (Weber, 1976; Torrents and Stone, 1994). Torrents and Stone (1994) carried out hydrolysis studies of some carboxylate and phosphorothioate esters in the presence of 10 g/L of various metal oxides and in the presence of methanol as a cosolvent. Torrents and Stone (1994) concluded that the formation of surface chelate is not necessary for surface-catalyzed hydrolysis to take place. Heterogeneous hydrolysis of organophosphorus pesticides with a smaller oxide loading of 1 g/L and without a cosolvent was investigated in more detail in this study. A variety of iron oxides were investigated, since many of them exist in natural water systems (Schwertmann and Cornell, 1991) and exhibit differences in catalytic activity (Sulzberger and Laubscher, 1992; Pehkonen et al., 1993). The role of dissolved metals in the transformation and fate of organic esters has been known for a while (Ketelaar et al., 1956). Enhanced hydrolysis of phosphate, phosphorothioate, and other acid esters by dissolved metal ions such as Cu(II), Zn(II), Co(III), and Mg(II) has also been previously documented (Tetas and Lowenstein, 1963; Jones et al., 1984; Hendry and Sargeson, 1986, 1990). Hendry and Sargeson (1990) discuss the possible mode of action of metals in the catalyzed reactions of phosphate derivatives. They suggest that metal ion coordination to a phosphate

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**Table 1. Structures and Selected Physical Characteristics of the Studied Pesticides**

Pesticide	Structure	Water Solubility	Half Life <sup>1</sup>
Disulfoton		$9 \times 10^{-5}$ M	57 d
Diazinon		$1.3 \times 10^{-4}$ M	178 d
Demeton S		$7.8 \times 10^{-3}$ M	53 d <sup>2</sup>
Thiometon		$8.1 \times 10^{-4}$ M	73 d

<sup>1</sup> At pH 7 and 20 °C, half-life data from Faust and Gomaa (1972), Mabey and Mill (1978), and Wanner et al. (1989), except for demeton S calculated from our data. <sup>2</sup> At pH 5.7 and 27 °C.

derivative will enhance the reactivity in two ways: to increase the positive charge on the phosphorus and to make the phosphorus center more electrophilic (Hendry and Sargeson, 1990). They also report on the difficulties of using labile metal ion complexes when investigating mechanisms of enhanced reactivity with phosphorus derivatives (Hendry and Sargeson, 1990). Hendry and Sargeson (1990) also conclude that one of the more effective ways for a metal ion to enhance reactivity of phosphate derivatives is to provide an intramolecular nucleophile.

The adsorption of the pesticides on the studied metal oxide surfaces was also quantified since there are no reported data available. Selected hydrolysis rates were determined at several different temperatures to obtain more detailed information about the activation enthalpy and entropy. This information can be useful in distinguishing between possible alternative mechanisms since the different mechanisms vary in the rate-determining step and therefore have different activation enthalpies and entropies. The approach of studying both homogeneous and heterogeneous hydrolysis with detailed measurement of the kinetic parameters as well as the identification of stable intermediates and products is unique in this field and provides a better understanding of the hydrolysis chemistry than has been obtained to date.

## MATERIALS AND METHODS

Solutions and suspensions were prepared from 18 MΩ cm water (deionized and distilled). The insecticides demeton S, diazinon, and disulfoton were obtained from Supelco (Bellefonte, PA) at 95%, 98.2%, and 99% purity, respectively. Thiometon of 98.5% purity was obtained from Sandoz Ltd. (Basel, Switzerland). Table 1 shows the structures and selected physical characteristics of the studied pesticides. Hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), two-line ferrihydrite (Fe<sub>5</sub>HO<sub>8</sub>·4H<sub>2</sub>O), and goethite ( $\alpha$ -FeOOH) were prepared according to previously reported methods (Schwertmann and Cornell, 1991). Aluminum hydroxide was obtained from Allied Chemical (New York, NY). Selected oxide characteristics are listed in Table 2. Heterogeneous experiments at elevated temperatures were conducted mostly only with the more stable metal oxides due to the possibility of conversion from one form to another (e.g., ferrihydrite to goethite).

**Table 2. Selected Characteristics of Studied Metal (Hydr)Oxides**

oxide	surface area (m <sup>2</sup> /g of oxide)	zpc pH <sup>a</sup>
ferrihydrite	170 <sup>b</sup>	8.0
goethite	41 <sup>b</sup>	7.5
hematite	80–90 <sup>c</sup>	8.3
Al(OH) <sub>3</sub>	low <sup>b</sup>	9.3

<sup>a</sup> Data from James and Parks (1982). zpc, zero point of charge. <sup>b</sup> Measured, EGME method (Carter et al., 1986). <sup>c</sup> Data from Schwertmann and Cornell (1991).

Experiments were carried out in 250-mL Pyrex or Teflon flasks using Teflon-coated magnetic stir bars. Prior to use, the flasks were cleaned with 1.4% nitric acid and rinsed several times with water. The flasks were closed to the atmosphere with rubber or glass stoppers. The pesticides were added to the reactor at or below their reported water solubility (demeton S,  $1.9 \times 10^{-4}$  M; diazinon,  $1.3 \times 10^{-4}$  M; thiometon,  $7.3 \times 10^{-5}$  M; disulfoton,  $6.2 \times 10^{-5}$  M). To prevent bacterial growth, 0.2 mL of carbon tetrachloride was added ( $7.9 \times 10^{-3}$  M). Experiments were carried out at pH 5.7 (0.01 M acetate buffer) and 8.5 (0.01 M borate buffer). These values were selected because they cover the pH range expected in natural waters and because the (hydr)oxide surface charge is pH dependent. The pH was monitored throughout the experiment and adjusted with 0.1 M HNO<sub>3</sub> or NaOH. No other ionic strength adjusting salt was added. Homogeneous experiments without metal oxides were carried out as baseline control experiments. Heterogeneous experiments were carried out as described above with the addition of oxide to yield a concentration of 1 g/L. Oxide agglomerates were broken up initially by sonicating the reaction mixture for 2 min. Many experiments were performed in triplicate to provide a basis to calculate the relative standard deviation (RSD) of the experiment.

Pesticide hydrolysis was monitored by extracting an aliquot of the stirred reaction mixture (10 mL) with benzene (1.5 mL). Extractions to monitor the effectiveness of removing adsorbed pesticides from the oxide surface with benzene were carried out. In these control experiments, the slurry containing the pesticide and the oxide was allowed to equilibrate at 10 °C for 5 days prior to the extraction. The recovery of the pesticide from the oxide surface by benzene extraction varied from 93% to 99%. The benzene contained  $3.5 \times 10^{-4}$  M 4-chloro-3-methylphenol as an internal GC standard. Sample extracts were analyzed by GC/MS and GC under the following conditions. GC/MS: HP GC 5890, MS Engine 5970; 30 m by 0.25 mm i.d. DB-5 fused silica capillary column (J&W Scientific, Folsom, CA), 0.25 μm film thickness; carrier gas helium (50 psi). GC: HP 5890 Series II equipped with an FID detector; 30 m by 0.32 mm i.d. DB-5 fused silica capillary column (J&W Scientific), 0.25 μm film thickness; carrier gas nitrogen (80 psi).

Whether oxide surfaces enhanced or inhibited the rate of hydrolysis was determined by using Student's *t* distribution with 2 degrees of freedom and a 95% confidence interval. Standard deviation values of 15% (of the average of three rate constants) for demeton S, 24% for diazinon, 5% for thiometon, and 27% for disulfoton were used to determine the confidence interval.

As previously reported (Muhlmann and Schrader, 1957), the homogeneous hydrolysis of organophosphorus pesticides can be described by a first-order rate law:  $r = k_{\text{obs}}[\text{pesticide}]$ , where  $k_{\text{obs}}$  is the observed pseudo-first-order rate constant. The  $k_{\text{obs}}$  can be considered to be a sum of three terms:  $k_A[\text{H}^+] + k_N + k_B[\text{OH}^-]$ . Some experiments that yielded an  $R^2$  value of <0.95 for the curve fit in the natural log of pesticide concentration vs time plot were discarded. These cases constituted ≈10% of all hydrolysis experiments. The main reasons for getting scattered data plots were mixing problems of water and the neat pesticide, the formation of emulsions, and the use of aged pesticide. Improvements were made by dissolving the pesticide in 1 mL of methanol before addition to the reactor, followed by 10 min of sonication. Rapid aging of the pesticides

**Table 3. Summary of Rate Constants for Disulfoton Hydrolysis at pH 5.7 and 8.5 and Comparison with Those of Mabey and Mill (1978)**

exptl conditions	obsd rate constant (s <sup>-1</sup> ) (RSD) <sup>a</sup>	
At pH 5.7		
no oxides (25 °C)	3.1 × 10 <sup>-7</sup>	(22%)
ferrihydrite (25 °C)	3.1 × 10 <sup>-7</sup>	
goethite (25 °C)	2.9 × 10 <sup>-7</sup>	
aluminum hydroxide (25 °C)	1.7 × 10 <sup>-7</sup>	
no oxides (34.1 °C)	5.1 × 10 <sup>-7</sup>	
goethite (34.1 °C)	5.6 × 10 <sup>-7</sup>	
no oxides (45.1 °C)	1.7 × 10 <sup>-6</sup>	
goethite (45.1 °C)	1.7 × 10 <sup>-6</sup>	(9%)
At pH 8.5		
no oxides (23 °C)	2.1 × 10 <sup>-7</sup>	(20%)
ferrihydrite <sup>b</sup> (27 °C)	1.6 × 10 <sup>-7</sup>	
goethite (23 °C)	2.2 × 10 <sup>-7</sup>	
aluminum hydroxide <sup>c</sup> (23 °C)	4.6 × 10 <sup>-8</sup>	
aluminum hydroxide (23 °C)	1.9 × 10 <sup>-7</sup>	
no oxides (34.1 °C)	5.4 × 10 <sup>-7</sup>	
no oxides (45.6 °C)	3.4 × 10 <sup>-6</sup>	
goethite (45.6 °C)	1.9 × 10 <sup>-6</sup>	
hematite (45.6 °C)	2.0 × 10 <sup>-6</sup>	
aluminum hydroxide (45.6 °C)	1.5 × 10 <sup>-6</sup>	
exptl condition	this study	Mabey and Mill (1978)
pH 5.7	3.1 × 10 <sup>-7</sup>	1.6 × 10 <sup>-7</sup>
pH 8.5	2.1 × 10 <sup>-7</sup>	1.5 × 10 <sup>-7</sup>

<sup>a</sup> RSD = 100% × SD/av. <sup>b</sup> R<sup>2</sup> = 0.93. <sup>c</sup> Aged at pH 8.5 for 20 days.

was minimized by storing them neat at 4 °C instead of preparing solutions in methanol.

For the adsorption studies, the pesticide/oxide/water mixtures were prepared as described above except with slightly different pesticide concentrations: diazinon, 6.1 × 10<sup>-5</sup> M; thiometon, 6.3 × 10<sup>-5</sup> M; and disulfoton, 6.3 × 10<sup>-5</sup> M. The pH values used for the adsorption studies were 5.7 and 8.5. The mixtures were allowed to equilibrate for 16 h. This short time minimized the hydrolysis of the pesticides (<5% in all cases) and simplified data treatment. The amount of pesticide in solution was determined by centrifuging (Eppendorf centrifuge Model 5415) the mixture for 15 min at 13 000 rpm, extracting the supernatant with benzene, and analyzing by GC as described above.

Product studies in this research were performed mostly qualitatively due to the lack of LC/MS. A mass balance comparing reactant and product concentrations was not achieved. Only in the hydrolysis experiments in which unusual, previously unreported products were identified were the concentrations of products quantified. All products were identified by GC/MS. Benzene was used to extract the less polar hydrolysis products. For polar hydrolysis products, solid phase extraction disks (3M Empore Extraction Disks SDB-XC from Fisher Scientific, Pittsburgh, PA) were used. The presence of thiols, possible products of disulfoton, demeton S, and thiometon hydrolysis, was examined using a spectrophotometric method (Grassetti and Murray, 1967; Humphrey et al., 1970) with a Shimadzu UV-1201S spectrophotometer and a 1-cm quartz cell.

Homogeneous and some heterogeneous reactions were carried out at several different temperatures (e.g., at 24, 34, and 45 °C) to obtain values of the activation parameters and to measure the hydrolysis rates of the pesticides at different temperatures. The elevated temperature experiments were conducted in a water bath controlled by a Contraves Rheotherm 15. The experiments at ~25 °C were conducted under ambient conditions and therefore resulted in some variation in the temperature (≈1–1.5 °C). With the ambient temperature experiments, the temperature was recorded every other day and a time-averaged value was used in the tables. The activation enthalpy, Δ*H*<sup>‡</sup>, and the activation entropy, Δ*S*<sup>‡</sup>, were calculated using the standard procedure (Carey and Sundberg, 1984). For activation parameters with metal oxides, the

**Table 4. Summary of Rate Constants for Diazinon Hydrolysis at pH 5.7 and 8.5 and Comparison with Those of Mabey and Mill (1978)**

exptl conditions	obsd rate constant (s <sup>-1</sup> ) (RSD) <sup>a</sup>	
At pH 5.7		
no oxides (25 °C)	2.0 × 10 <sup>-7</sup>	(19%)
goethite (25 °C)	3.1 × 10 <sup>-7</sup>	
hematite (25 °C)	2.3 × 10 <sup>-7</sup>	(7%)
aluminum hydroxide (25 °C)	2.2 × 10 <sup>-7</sup>	
no oxides (34.3 °C)	3.2 × 10 <sup>-7</sup>	
goethite (34.2 °C)	3.6 × 10 <sup>-7</sup>	
no oxides (45.2 °C)	1.7 × 10 <sup>-6</sup>	
ferrihydrite (45.2 °C)	1.6 × 10 <sup>-6</sup>	
goethite (45.2 °C)	1.5 × 10 <sup>-6</sup>	
hematite (45.2 °C)	2.0 × 10 <sup>-6</sup>	
aluminum hydroxide (45.2 °C)	1.4 × 10 <sup>-6</sup>	
At pH 8.5		
no oxides <sup>b</sup> (24.1 °C)	5.4 × 10 <sup>-8</sup>	
no oxides (34.0 °C)	3.2 × 10 <sup>-7</sup>	
goethite (34.0 °C)	3.5 × 10 <sup>-7</sup>	
hematite (34.0 °C)	3.5 × 10 <sup>-7</sup>	
aluminum hydroxide (34.0 °C)	3.4 × 10 <sup>-7</sup>	
no oxides (45.4 °C)	1.6 × 10 <sup>-6</sup>	
ferrihydrite (45.4 °C)	1.5 × 10 <sup>-6</sup>	
goethite (45.4 °C)	1.6 × 10 <sup>-6</sup>	
hematite (45.4 °C)	1.4 × 10 <sup>-6</sup>	
aluminum hydroxide (45.4 °C)	1.7 × 10 <sup>-6</sup>	
exptl condition	this study	Mabey and Mill (1978)
pH 5.7	2.0 × 10 <sup>-7</sup>	8.4 × 10 <sup>-8</sup>
pH 8.5	5.4 × 10 <sup>-8</sup>	5.6 × 10 <sup>-8</sup>

<sup>a</sup> RSD = 100% × SD/av. <sup>b</sup> R<sup>2</sup> = 0.94.

**Table 5. Summary of Rate Constants for Demeton S Hydrolysis at pH 5.7 and 8.5**

exptl conditions	obsd rate constant (s <sup>-1</sup> ) (RSD) <sup>a</sup>
At pH 5.7	
no oxides (25 °C)	1.3 × 10 <sup>-7</sup> (19%)
no oxides (34.0 °C)	2.8 × 10 <sup>-7</sup>
ferrihydrite <sup>b</sup> (34.0 °C)	2.8 × 10 <sup>-7</sup>
goethite (34.0 °C)	2.8 × 10 <sup>-7</sup>
hematite (34.0 °C)	2.5 × 10 <sup>-7</sup>
aluminum hydroxide (34.0 °C)	3.8 × 10 <sup>-7</sup>
no oxides (44.5 °C)	9.6 × 10 <sup>-7</sup>
At pH 8.5	
no oxides (27 °C)	2.3 × 10 <sup>-7</sup>
goethite (24 °C)	1.3 × 10 <sup>-7</sup>
hematite (27 °C)	1.7 × 10 <sup>-7</sup>
no oxides (34.0 °C)	7.3 × 10 <sup>-7</sup> (7%)
no oxides (39.0 °C)	1.6 × 10 <sup>-6</sup>
ferrihydrite (39.0 °C)	7.1 × 10 <sup>-7</sup>
goethite (39.0 °C)	1.4 × 10 <sup>-6</sup>
aluminum hydroxide (39.0 °C)	1.5 × 10 <sup>-6</sup> (11%)
no oxides (44.6 °C)	2.4 × 10 <sup>-6</sup> (10%)

<sup>a</sup> RSD = 100% × SD/av. <sup>b</sup> R<sup>2</sup> = 0.93.

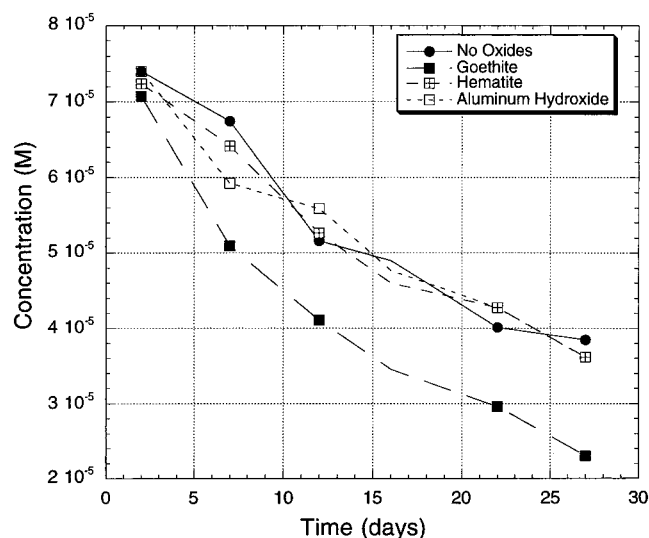
concentration of the surficial hydroxy groups can only be estimated from the surface area of the oxides. However, since the surficial hydroxy concentration is part of the denominator of each data point, each data point will be divided by the same number. Thus, the observed rate constant instead of the true rate constant was used to calculate the heterogeneous case activation parameters. The only assumption here is that the surficial hydroxy concentration of the metal oxides does not vary with temperature.

## RESULTS

**Homogeneous and Heterogeneous Hydrolysis.** Tables 3–6 provide a listing of the homogeneous and heterogeneous hydrolysis rate constants. Homogeneous experiments were carried out to provide baseline data

**Table 6. Summary of Rate Constants for Thiometon Hydrolysis at pH 5.7 and 8.5 and Comparison with Those of Mabey and Mill (1978)**

exptl conditions	obsd rate constant (s <sup>-1</sup> ) (RSD) <sup>a</sup>	
At pH 5.7		
no oxides (25 °C)		$1.4 \times 10^{-7}$
ferrihydrite (25 °C)		$2.1 \times 10^{-7}$
goethite (25 °C)		$7.2 \times 10^{-8}$ (7%)
hematite (25 °C)		$2.9 \times 10^{-7}$
hematite <sup>b</sup> (25 °C)		$1.1 \times 10^{-6}$
aluminum hydroxide (25 °C)		$1.4 \times 10^{-7}$
no oxides (34 °C)		$3.8 \times 10^{-7}$
goethite (34 °C)		$6.1 \times 10^{-7}$
no oxides (44.5 °C)		$1.2 \times 10^{-6}$
goethite (44.5 °C)		$3.8 \times 10^{-6}$
At pH 8.5		
no oxides (25 °C)		$1.7 \times 10^{-7}$ (9%)
ferrihydrite (25 °C)		$2.1 \times 10^{-7}$
goethite (25 °C)		$1.6 \times 10^{-7}$ (5%)
hematite (25 °C)		$2.4 \times 10^{-7}$
aluminum hydroxide (25 °C)		$4.7 \times 10^{-7}$ (5%)
aluminum hydroxide <sup>c</sup> (25 °C)		$2.5 \times 10^{-7}$
no oxides (34.4 °C)		$5.3 \times 10^{-7}$
aluminum hydroxide (34.3 °C)		$7.5 \times 10^{-7}$
no oxides (44.6 °C)		$2.0 \times 10^{-6}$
aluminum hydroxide (44.6 °C)		$1.9 \times 10^{-6}$
exptl conditions	this study	Mabey and Mill (1978)
pH 5.7	$1.4 \times 10^{-7}$	$1.1 \times 10^{-7}$
pH 8.5	$1.7 \times 10^{-7}$	$1.3 \times 10^{-7}$

<sup>a</sup> RSD = 100% × SD/av. <sup>b</sup> Half the usual pesticide concentration.<sup>c</sup> Oxide loading of 0.1 g/L instead of the usual 1.0 g/L.**Figure 1.** Diazinon hydrolysis at pH 5.7 and at room temperature.

to evaluate the heterogeneous studies. Good agreement was obtained with earlier homogeneous research (Mabey and Mill, 1978) with rate constants differing by no more than a factor of 2.4 from previously reported values (Tables 3, 4, and 6). Figure 1 shows a typical degradation plot of diazinon at pH 5.7 and room temperature. Catalysis of diazinon hydrolysis is observed in the presence of goethite (Table 4). Table 7 shows that metal oxides can catalyze, have no effect, or hinder the hydrolysis of the studied pesticides. At 25 °C, catalysis by oxides was observed for diazinon at pH 5.7 with goethite and for thiometon at pH 5.7 and 8.5 (e.g., the thiometon half-life decreased from 58 to 28 days at pH 5.7 and 24 °C with hematite). In only two cases (demeton S and especially thiometon at pH 5.7), catalysis was observed also at the higher temperatures

**Table 7. Summary of Heterogeneous Catalysis/Inhibition Determined at Room Temperature unless Otherwise Noted**

insecticide, pH	catalytic (or inhibitory) surfaces
demeton S, pH 5.7	Al(OH) <sub>3</sub> <sup>a</sup>
demeton S, pH 8.5	ferrihydrite
diazinon, pH 5.7	goethite
diazinon, pH 8.5	
disulfoton, pH 5.7	
disulfoton, pH 8.5	(aged Al(OH) <sub>3</sub> ) <sup>b</sup>
thiometon, pH 5.7	hematite, goethite, <sup>c</sup> ferrihydrite (goethite)
thiometon, pH 8.5	Al(OH) <sub>3</sub> , hematite

<sup>a</sup> At 34 °C. <sup>b</sup> Preparation of Al(OH)<sub>3</sub> slurry in water and stirring (aging) for 30 days prior to use in hydrolysis experiments. <sup>c</sup> At 34 and 45 °C.

of 34 and 45 °C with some oxides (Tables 5 and 6). Additionally, dependence of the magnitude of catalysis on the pesticide/oxide ratio was observed. Experiments with half the thiometon concentration ( $3.7 \times 10^{-5}$  M) at hematite loading of 1 g/L resulted in a rate constant increase by a factor of 4 compared to the typical thiometon concentration ( $7.3 \times 10^{-5}$  M) (Table 6). Another example of this effect was observed with thiometon and aluminum hydroxide at 0.1 g/L instead of the normal 1 g/L (Table 6). Baldwin et al. (1995) also showed that the change in the hydrolysis rate constant of *p*-nitrophenyl phosphate varies linearly with the amount of amorphous iron hydroxide present. Inhibition of the hydrolysis relative to the homogeneous cases was also observed; for demeton S/ferrihydrite at pH 8.5, disulfoton/aged Al(OH)<sub>3</sub> at pH 8.5 and for thiometon/goethite at pH 5.7. In the presence of aged aluminum hydroxide, under basic conditions and at 23 °C, disulfoton has a hydrolysis half-life of 173 days compared to 40 days without oxides!

**Adsorption Studies.** Adsorption study results for the studied pesticides are presented in Table 8. The standard error is 21% of the reported adsorption values for diazinon, 25% for disulfoton, and 30% for thiometon. The amount of pesticide adsorbed was also normalized to the oxide surface area, using surface areas of 173 m<sup>2</sup>/g for ferrihydrite, 41 m<sup>2</sup>/g for goethite, and 85 m<sup>2</sup>/g for hematite (Table 8). Reasons for the relatively high standard error are mixing problems, the formation of emulsions of the pesticide, and adsorption of pesticides onto Eppendorf centrifuge tube walls in some adsorption experiments.

The fraction of pesticide adsorbed to the oxide surface generally ranges from 0.20 to 0.40 except for demeton S (results not shown). The fraction of demeton S adsorbed ranged from 0 to 0.05, which may be due to the much higher aqueous solubility of demeton S compared to the other pesticides (see Table 1). Even though thiometon is more soluble in water than diazinon and disulfoton by 1 order of magnitude, the magnitude of adsorption did not differ significantly. This finding implies that the adsorption of these pesticides is taking place at specific oxide surface sites forming metal–ligand surface complexes. Very little dependence of adsorption on the solution pH and the zero point of charge pH of the oxide has been observed. Thiometon is the exception; lower adsorption is consistently observed at pH 5.7 compared to pH 8.5, with an average fraction adsorbed of 0.17 and 0.38, respectively.

Among the oxides, goethite shows the greatest ability to adsorb organophosphorus pesticides. This still holds true when adsorption is normalized to moles of pesticide

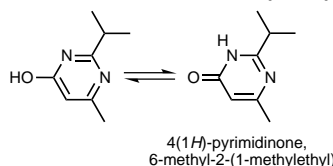
**Table 8. Adsorption Study Results**

exptl conditions	disulfoton		diazinon		thiometon	
	fraction adsorbed	mol of pesticide <sup>a/</sup> m <sup>2</sup> of surface area	fraction adsorbed	mol of pesticide <sup>b/</sup> m <sup>2</sup> of surface area	fraction adsorbed	mol of pesticide <sup>c/</sup> m <sup>2</sup> surface area
ferrihydrite, pH 5.7	0.17	$2.4 \times 10^{-8}$	0.44	$1.3 \times 10^{-7}$	0.21	$6.8 \times 10^{-8}$
ferrihydrite, pH 8.5	0.29	$5.3 \times 10^{-8}$	0.24	$7.0 \times 10^{-8}$	0.34	$1.1 \times 10^{-7}$
goethite, pH 5.7	0.40	$1.7 \times 10^{-7}$	0.39	$3.4 \times 10^{-7}$	0.33	$3.2 \times 10^{-7}$
goethite, pH 8.5	0.34	$1.9 \times 10^{-7}$	0.30	$2.6 \times 10^{-7}$	0.43	$4.5 \times 10^{-7}$
hematite, pH 5.7	0.25	$7.2 \times 10^{-8}$	0.33	$9.3 \times 10^{-8}$	0.01	$6.6 \times 10^{-9}$
hematite, pH 8.5	0.24	$8.9 \times 10^{-8}$	0.34	$2.0 \times 10^{-7}$	0.33	$2.3 \times 10^{-7}$
aluminum hydroxide, pH 5.7	0.20	na <sup>d</sup>	0.16	na	0.14	na
aluminum hydroxide, pH 8.5	0.24	na	0.34	na	0.42	na

<sup>a</sup> Using disulfoton concentrations of  $2.5 \times 10^{-5}$  M for pH 5.7 and  $3.2 \times 10^{-5}$  M for pH 8.5 as total recoverable pesticide. <sup>b</sup> Using diazinon concentrations of  $4.9 \times 10^{-5}$  M for pH 5.7 and  $5.0 \times 10^{-5}$  M for pH 8.5 as total recoverable pesticide. <sup>c</sup> Using thiometon concentrations of  $5.6 \times 10^{-5}$  M for pH 5.7 and  $6.0 \times 10^{-5}$  M for pH 8.5 as total recoverable pesticide. <sup>d</sup> Surface area was not determined.

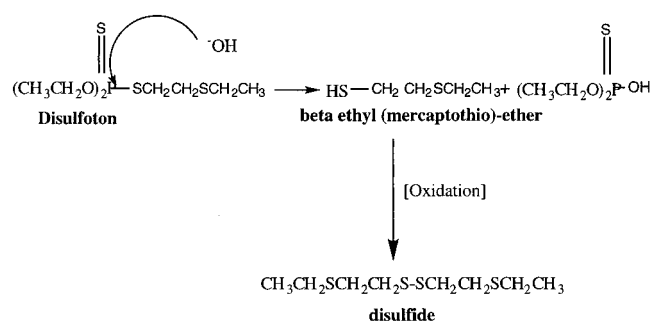
**Table 9. Pesticide Hydrolysis Products Identified in This Study**

exptl conditions	product obsd
demeton S, disulfoton, thiometon, pH 8.5	CH <sub>3</sub> CH <sub>2</sub> SCH <sub>2</sub> CH <sub>2</sub> S-SCH <sub>2</sub> CH <sub>2</sub> SCH <sub>2</sub> CH <sub>3</sub> [dimer of $\beta$ -ethyl (mercaptothio) ether]
disulfoton, under nitrogen, pH 8.5	CH <sub>3</sub> CH <sub>2</sub> SCH <sub>2</sub> CH <sub>2</sub> SCH <sub>2</sub> CH <sub>3</sub> [1,2-bis(ethylthio)ethane]
demeton S, pH 5.7	CH <sub>3</sub> CH <sub>2</sub> SCH <sub>2</sub> CH <sub>2</sub> OH [ethyl 2-hydroxyethyl sulfide]
diazinon, pH 5.7 and 8.5	



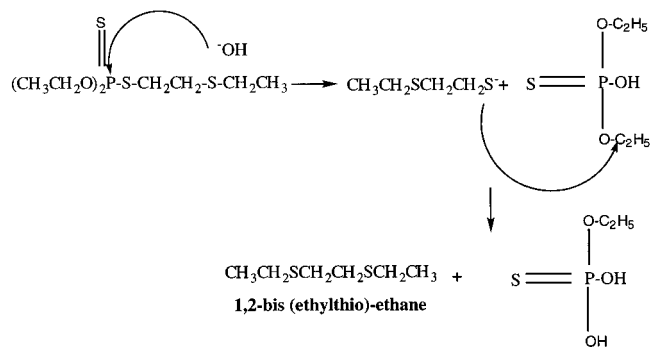
per square meter of surface area. Ferrihydrite and hematite have the largest surface areas, but normalization shows that these oxide surfaces do not adsorb proportionally more pesticide (Table 8). Therefore, one can conclude again that specific oxide surface binding sites are required for the chemical adsorption of these organophosphorus pesticides and that surface area alone cannot be used to estimate the partitioning of these pesticides between water and the oxide.

**Products and Mechanisms.** The hydrolysis products that were identified are shown in Table 9. For disulfoton and thiometon, hydrolysis products could not be identified at pH 5.7. 4(1H)-6-Methyl-2-(1-methylethyl)pyrimidinone was identified as the product of diazinon hydrolysis at pH 5.7. Ethyl 2-hydroxyethyl sulfide was identified as the product of demeton S hydrolysis at pH 5.7 and 45 °C. The product identity could be confirmed by comparison of MS spectrum and GC retention time with an authentic compound obtained from Aldrich Chemical Co. The proposed mechanism is an S<sub>N</sub>2 reaction with a nucleophilic attack at the carbon atom of the leaving group. Failure to identify more hydrolysis products at the low pH is probably due to inadequate extraction techniques for the expected polar products (even with Empore disks) and the unavailability of analytical instrumentation such as LC/MS.

**Figure 2.** Proposed mechanism for disulfoton hydrolysis at pH 8.5.

At pH 8.5, a disulfide could be identified in homogeneous as well as heterogeneous disulfoton, demeton S, and thiometon hydrolysis reactions. The yield of this product varied from 30% to 50% on a mole basis depending on the pesticide/oxide combination. The proposed mechanism shown in Figure 2 involves an S<sub>N</sub>2 type reaction with a nucleophilic attack of the hydroxide ion at the central P atom, followed by P-S cleavage. The resulting thiol is subsequently oxidized by dissolved oxygen in the reactor, yielding the dimerized disulfide.

Selected disulfoton hydrolysis experiments at pH 8.5 were carried out under nitrogen to purge the dissolved oxygen and prevent dimerization of the thiol. Under these conditions, the identified product was 1,2-bis-(ethylthio)ethane. The yield of this product varied from 20% to 40% on a mole basis (three replicates). The proposed mechanism involves P-S cleavage as described above, followed by the leaving group acting as the nucleophile and attacking the diester (Figure 3). The product was confirmed by comparing the MS spectrum and GC retention time to an authentic compound obtained from Aldrich Chemical Co. Even though a complete mass balance comparing reactant and product

**Figure 3.** Proposed mechanism for the formation of 1,2-bis-(ethylthio)ethane.

**Table 10. Activation Parameters for Homogeneous Hydrolysis Experiments Obtained at Three Temperatures**

pesticide and pH	$\Delta H^\ddagger$ <sup>a</sup> (kJ/mol)	$\Delta S^\ddagger$ <sup>b</sup> (J/mol·K)	$\Delta G^\ddagger$ <sup>c</sup> (kJ/mol)	$E_a$ <sup>d</sup> (kJ/mol)	$k_1/k_2$ <sup>e</sup>
diazinon, pH 5.7	77	-4.4	79	80	3.1
diazinon, pH 8.5	120	140	83	130	5.4
disulfoton, pH 5.7	65	-42	78	68	2.6
disulfoton, pH 8.5	95	52	80	98	3.9
demeton S, pH 5.7	92	40	81	95	3.7
demeton S, pH 8.5 <sup>f</sup>	110	95	80	110	4.7
demeton S, pH 8.5	130	170	81	140	6.3
thiometon, pH 5.7	77	-8.1	80	80	3.1
thiometon, pH 8.5	89	29	80	91	3.5

<sup>a</sup> Activation enthalpy. <sup>b</sup> Activation entropy. <sup>c</sup> Gibbs free energy of activation. <sup>d</sup> Energy of activation. <sup>e</sup> Average rate constant increase factor per 10 °C increase in temperature. <sup>f</sup> Four temperatures were used,  $R^2 = 0.97$  instead of  $R^2 = 0.99$  with three temperatures.

**Table 11. Activation Parameters for Heterogeneous Hydrolysis Experiments Obtained at Three Temperatures**

pesticide and pH	$\Delta H^\ddagger$ (kJ/mol)	$\Delta S^\ddagger$ (J/mol·K)	$\Delta G^\ddagger$ (kJ/mol)	$E_a$ (kJ/mol)	$k_1/k_2$
diazinon, pH 5.7; goethite	45	-110	77	47	2.0
disulfoton, pH 5.7; goethite	65	-43	78	68	2.5
thiometon, pH 5.7; goethite	140	200	81	140	7.0
thiometon, pH 8.5; aluminum hydroxide	56	-74	78	58	2.3

concentrations was not achieved, the reported compounds are significant products under the reaction conditions.

4(1*H*)-6-Methyl-2-(1-methylethyl)pyrimidinone was identified as the product of diazinon hydrolysis, at pH 5.7 and 8.5, with and without oxides. The yield of this product varied from 30% to 45% on a mole basis depending on the reaction conditions. The proposed mechanism at pH 5.7 involves protonation of the oxygen connecting the phosphorus atom to the pyrimidine ring and a subsequent cleavage of the alcohol moiety either via P–O or C–O cleavage. Both pathways lead to the same product. At pH 8.5, the expected reaction mechanism of diazinon hydrolysis is an  $S_N2$  mechanism (Faust and Gomaa, 1972; Mabey and Mill, 1978) with a nucleophilic attack at the phosphorus or carbon atom.

**Activation Parameters.** The activation entropy and enthalpy are used to gain information about the activated complex leading from reactants to products. Activation entropy and enthalpy can further be related to the Gibbs free energy of activation,  $\Delta G^\ddagger$ , and to evaluate the temperature dependence of the pesticide hydrolysis reactions (Tables 10 and 11). Most of these plots were linear, with  $R^2$  values  $\geq 0.97$  for the three applied temperatures. The  $\Delta G^\ddagger$  is fairly similar for the studied insecticides, ranging from 77 to 83 kJ/mol, reflecting the overall similarity of these organophosphorus compounds and the similarity in the mechanism of hydrolysis (Tables 10 and 11).

Comparison of the activation parameters of homogeneous and heterogeneous hydrolysis shows three distinct cases. The first case is disulfoton hydrolysis at pH 5.7. No change in the activation parameters in the presence of oxides could be observed; for example, the activation enthalpy values are 65 kJ/mol in both cases,

the free energy of activation values are 78 kJ/mol in both cases, and the temperature dependence factors are 2.6 and 2.5. Activation parameter studies clearly show that the oxides have no effect on the hydrolysis of disulfoton at pH 5.7. Diazinon hydrolysis at pH 5.7 with goethite and thiometon hydrolysis at pH 8.5 with aluminum hydroxide demonstrate the second case. The effect of the oxides is a decrease in all activation parameters (e.g., from 77 to 45 kJ/mol for the activation enthalpy of diazinon hydrolysis and from 89 to 56 kJ/mol for the activation enthalpy of thiometon hydrolysis). Finally, in the case of thiometon hydrolysis at pH 5.7 with goethite, all activation parameters increase (e.g., the activation enthalpy increases from 77 to 140 kJ/mol).

## DISCUSSION

**Product Studies.** This study shows that the hydrolysis behavior of demeton S, thiometon, and disulfoton is quite complex; different products were identified depending on the reaction conditions such as pH and dissolved oxygen. Unfortunately, several of the earlier reported studies on the hydrolysis of these compounds did not clearly report the reaction conditions under which the products were found, making it difficult to compare the results. Identification of the reaction conditions (i.e., pH, dissolved oxygen, and temperature) is necessary to make inferences from laboratory results to behavior in the natural environment. The product of diazinon hydrolysis at pH 5.7 and 8.5, 4(1*H*)-pyrimidinone, has also been identified in earlier studies (Muhlmann and Schrader, 1957; Faust and Gomaa, 1972). Thiols, even though a reported product in several earlier studies of demeton S, disulfoton, and thiometon hydrolysis (Muhlmann and Schrader, 1957; Faust and Gomaa, 1972; Wanner et al., 1989), were not identified in this study as a stable product of hydrolysis despite a variety of measurement techniques attempted. However, they are clearly formed as intermediates on the basis of the mechanisms proposed in Figures 2 and 3 [e.g., the disulfide dimer originating from the thiol (Figure 2) has been identified in this study]. Several sensitive assays for thiols were performed in this study on disulfoton hydrolysis using aerated conditions at pH 5.7 and 8.5 and deaerated conditions at pH 8.5 using the spectrophotometric DTNB method (Grassetti and Murray, 1967; Humphrey et al., 1970). The failure to detect thiols with the DTNB method (a detection limit of 0.2  $\mu$ M with a 5-cm cell) suggests that the importance of thiols as the hydrolysis product of these pesticides has been overestimated. Additionally, the results of this study are more relevant under ambient conditions than those obtained in previous studies, because pH values of 5.7 and 8.5 are more representative of pH values in natural waters in contrast to studies using pH of 12, and temperatures of 25, 34, and 45 °C are closer to ambient temperatures than is 70 °C (Weber, 1976). It is also interesting to note that the  $S_{Ni}$  mechanism (i.e., an internal nucleophilic attack) proposed for demeton S hydrolysis (Muhlmann and Schrader, 1957) would result in the formation of ethyl 2-hydroxyethyl sulfide. We have observed this product only at pH 5.7, not at pH 8.5. Therefore, the importance of the  $S_{Ni}$  mechanism seems to be limited to the lower pH of 5.7, not a wide range of pH values as suggested by Muhlmann and Schrader (1957).

Finally, the identification of 1,2-bis(ethylthio)ethane as the degradation product of demeton S, disulfoton, and

thiometon at pH 8.5 and under deaerated conditions emphasizes the importance of the study of the products of hydrolysis. 1,2-Bis(ethylthio)ethane belongs to a group of compounds called disulfides. Disulfides can also be formed from  $S_N2$  reactions of halogenated alkanes with hydrogen sulfide and alkyl mercaptans under anaerobic conditions (Schwarzenbach et al., 1985). Schwarzenbach et al. (1985) described disulfides as hazardous and persistent in the subsurface. The half-life of these degradation products in the environment should be investigated especially because of their perceived persistence (Schwarzenbach et al., 1985).

**Activation Parameters.** Comparison of the activation parameters with the values obtained in earlier studies shows some significant differences. However, somewhat different reaction conditions (e.g., pH, use of laboratory water vs natural water) allow only approximate comparison. Studies by Muhlmann and Schrader (1957) at pH 1–5 show energies of activation of 111 kJ/mol for demeton S and 55.8 kJ/mol for diazinon. Lartiges and Garrigues (1995) found an activation energy of 13 kJ/mol for diazinon hydrolysis at pH 6.1. The values obtained here are similar to those of Muhlmann and Schrader (1957) with activation energies of 80 kJ/mol for diazinon and 95 kJ/mol for demeton S at pH 5.7. Wanner et al. (1989), in a study of pesticide degradation in the Rhine River, determined activation energies of 76 kJ/mol for disulfoton and 89 kJ/mol for thiometon at pH 6 and of 61 kJ/mol for both compounds at pH 12. In the present study, higher activation energies were found at pH 8.5 than at pH 5.7. Activation energies were 68 and 80 kJ/mol at pH 5.7 and 98 and 91 kJ/mol at pH 8.5 for disulfoton and thiometon, respectively. Overall, fairly good agreement exists with data from earlier studies except for the low values obtained by Lartiges and Garrigues (1995). The reasons for the disagreement between the results of the current study and those of Lartiges and Garrigues (1995) might arise from the presence of some catalytic species in their system, since they used ambient water to carry out the hydrolysis studies. Either the presence of microorganisms or the presence of some unknown chemical catalysts might have lowered their activation energy values compared to those of Muhlmann and Schrader (1957) and the results herein.

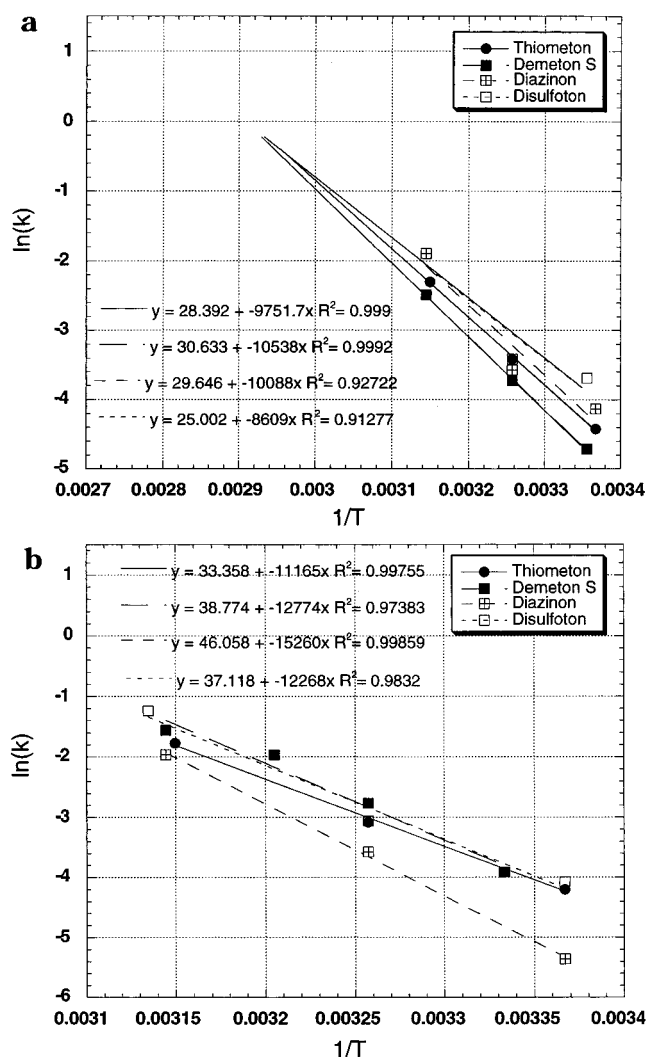
**Effect of Structural Moieties on the Activated Complex.** Even though  $\Delta G^\ddagger$  is fairly similar for all of the studied compounds, there is a large range in activation enthalpy, entropy, the energy of activation, and the temperature sensitivity of the hydrolysis. Values for the activation entropy, for example, range from  $-42$  J/mol·K for disulfoton hydrolysis at pH 5.7 to  $+170$  J/mol·K for demeton S hydrolysis at pH 8.5. Demeton S at pH 8.5 and diazinon at pH 8.5 exhibit the largest entropy values, indicating a large increase in the degrees of translational, vibrational, and rotational degrees of freedom in the activated complex as compared to the pesticide in the free molecular state. For diazinon, the weakened bonds to the large, bulky pyrimidine leaving group could be the reason for the large entropy value. Demeton S is the only compound with an oxygen atom doubly bonded to the central phosphorus atom. Due to the greater electronegativity of oxygen, the phosphorus–oxygen bond is more rigid and shorter than the phosphorus–sulfur bond. A

weakening of the P=O bond in the transition state might thus have a greater relative effect of increasing disorder.

Further structural evaluation is possible by comparing disulfoton and demeton S, which differ only in the atom doubly bonded to the phosphorus atom. Oxygen is the doubly bonded atom in demeton S, sulfur the counterpart in disulfoton. Similarly to the previous case, there is no difference in the overall free energy of activation: 80 kJ/mol for both disulfoton and demeton S at pH of 8.5. The activated complex for demeton S also requires a somewhat larger enthalpy and exhibits a significantly larger entropy of activation. As discussed above, the greater entropy term could be due to the more electronegative and smaller oxygen atom and the shorter bond it forms with the central phosphorus atom. The entropy in the pesticide molecule would thus be smaller for demeton S than for disulfoton, but the weakening of the phosphorus double bond in the activated complex would yield a larger gain in entropy for the former. The larger enthalpy term for demeton S is likely due to the greater stability of demeton S in the solvent due to hydrogen bonding with water (see water solubilities in Table 1). The more stable the pesticide molecule is in the solvent, the greater the enthalpy needed to transform it to the activated complex.

**Temperature Sensitivity of Hydrolysis.** Muhlmann and Schrader (1957) reported an average rate constant increase of 3.75 to 3.8 per 10 °C temperature increase. The current study shows a larger range of temperature dependence for some cases. Disulfoton, diazinon, and thiometon at pH 5.7 have average rate constant factor increases of 2.6, 3.1, and 3.1, respectively. These are similar to the values reported by Muhlmann and Schrader (1957). However, diazinon and demeton S at pH 8.5 have the greatest temperature dependence with factors of 5.4 and 5.5. This larger temperature dependence has important implications for the compound transformation by hydrolysis under ambient conditions. At lower temperatures, these compounds may be very persistent in the environment under slightly basic conditions with half-lives of 347 days for demeton S and 704 days for diazinon at 15 °C. These long half-lives result in prolonged exposure of organisms to these compounds and allow significant migration of these pesticides in the environment. This study shows that the range of temperature dependence for the hydrolysis of organophosphorus pesticides is sometimes larger than previously reported.

Isokinetic relationships have been widely used in the physical organic chemistry field to probe the mechanistic details of related reactions (Leffler and Grunwald, 1963; Exner, 1964; Good et al., 1975). Specifically, a linear relationship often exists between the enthalpies and entropies of activation of a series of related reactions. In cases for which an isokinetic relationship is observed, a temperature exists at which rates of all members of the series are equal, the isokinetic temperature [i.e.,  $1/T$  of 0.00293 (or  $T$  of 68 °C) in Figure 4a and  $1/T$  of 0.00337 (or  $T$  of 24 °C) in Figure 4b]. The existence of an isokinetic relationship is usually interpreted to mean that the reaction parameter being varied (e.g., pesticide structure in this study) is operating on only one type of interaction in the system, while the absence of such an effect can point to a complex interplay of effects or to the presence of more than one reaction mechanism. The profiles in Figure 4 for



**Figure 4.** Determination of isokinetic relationship of pesticide hydrolysis at pH 5.7 (a) and at pH 8.5 (b).

disulfoton, demeton S, and thiometon illustrate that due to their structural similarities and the observed existence of an isokinetic temperature at both pH 5.7 and pH 8.5, their mechanisms of hydrolysis are the same. The figure also lends confidence to the experimental data obtained in the current study as far as the hydrolysis rates are concerned. It would be highly unlikely that with unreliable data two isokinetic temperatures would be found. However, it is interesting to note that diazinon does not behave isokinetically with the other three pesticides at either pH value (Figure 4). This is surprising, especially at pH 8.5, at which the neutral hydrolysis should dominate the hydrolysis of all pesticides (due to the high concentration of  $\text{H}_2\text{O}$ ) and therefore an isokinetic relationship should be observed. It is therefore likely that the base-catalyzed pathway for diazinon plays an important role at pH of 8.5. Finally, the proposed  $\text{S}_{\text{Ni}}$  pathway for demeton S hydrolysis may not be as important as previously reported (Muhlmann and Schrader, 1957), since demeton S should not behave isokinetically with disulfoton and thiometon if its hydrolysis pathway was by  $\text{S}_{\text{Ni}}$  (i.e., an internal nucleophilic attack) instead of  $\text{S}_{\text{N}}2$  mechanism. Furthermore, as previously discussed, product studies and specifically the scarcity of ethyl 2-hydroxy-

**Table 12.** Ratios of Observed Heterogeneous and Homogeneous Rate Constants with Respect to Temperature

exptl conditions	$k_{\text{het}}/k_{\text{hom}}$		
	25 °C	34 °C	45 °C
disulfoton, goethite, pH 5.7	1.0	1.1	1.0
diazinon, goethite, pH 5.7	1.6	1.1	0.9
thiometon, goethite, pH 5.7	0.5	1.6	3.3
thiometon, $\text{Al}(\text{OH})_3$ , pH 8.5	2.8	2.6	0.9

ethyl sulfide formation indicate that the  $\text{S}_{\text{Ni}}$  pathway cannot be the only dominant pathway for demeton S hydrolysis.

**Activation Parameters and Mechanisms of Catalysis by Metal Oxides.** Comparison of the activation parameters of homogeneous and heterogeneous hydrolysis can provide information about the mechanisms of catalysis by metal oxides. When catalysis was not observed by the metal oxides, as is the case for the reaction of disulfoton with goethite at pH 5.7, all activation parameters were practically identical for homogeneous and heterogeneous hydrolysis (Tables 10 and 11).

For thiometon hydrolysis at pH 8.5 with aluminum hydroxide, the results show an increase in the rate constant in the presence of oxides. Activation parameter studies show a very similar behavior. The activation enthalpy decreases significantly in the presence of the oxide, for thiometon from 89 to 56 kJ/mol. This shows that the oxides catalyze the pesticide hydrolysis by lowering the activation enthalpy. This enthalpy decrease also results in a significant decrease in the activation energy and thus in a lowering of the temperature dependence of the hydrolysis. The factor of the rate constant increase per 10 °C increase in temperature in the presence of the oxide is lowered from 3.1 to 2.0 for diazinon and from 3.5 to 2.3 for thiometon (Tables 10 and 11). Furthermore, the activation entropy greatly decreases in the presence of the oxide for both compounds, indicating a loss in the degrees of freedom in the activated complex (Tables 10 and 11). This behavior is consistent with complex formation between pesticide and oxides as the mechanism of catalysis, since a complex is a much more ordered structure than the pesticide and oxide by themselves. Finally, a computation of the ratio of the homogeneous to the heterogeneous rate constant at each temperature shows that the relative contribution of  $k_{\text{het}}$  to the overall rate decreases with temperature for the cases of disulfoton with goethite, diazinon with goethite, and thiometon with aluminum hydroxide (Table 12). This is to be expected since complex formation is typically an exothermic process and thus favored at lower temperatures. Table 12 also shows that catalysis of thiometon by aluminum hydroxide is still significant at 34 °C, while diazinon hydrolysis is catalyzed only at room temperature.

Analogous to complexation between diazinon and copper(II) (Mortland and Raman, 1967), complex formation is likely to account for goethite-catalyzed hydrolysis of diazinon at room temperature and pH 5.7 (see Table 4). Complex formation is a preferred rate-determining step of the mechanism for diazinon due to its ability to provide two binding sites, allowing the formation of a stable, six-membered ring. Electron density at the molecule's central phosphorus atom is reduced, thus enhancing nucleophilic attack. Monodentate chelation of the metal oxide with either the leaving group or the doubly bonded sulfur atom is another possibility; how-



ever, the large decrease in entropy between homogeneous and heterogeneous hydrolysis points toward bidentate chelation. However, it can be noted that the magnitude of catalysis here is much smaller than that found by Mortland and Raman (1967) with dissolved copper(II). This finding may be partly due to steric factors influencing the formation of a surface complex between the bulky diazinon molecule and the mineral oxide surface. In the dissolved copper(II) case, steric hindrance would not be a factor.

The final case of oxide and pesticide interaction is thiometon hydrolysis in the presence of goethite at pH 5.7. Our studies show that hydrolysis is hindered at 25 °C but catalyzed at higher temperatures. Activation parameter studies show that in the presence of the oxide, enthalpy increases from 77 to 140 kJ/mol. Clearly, enhanced hydrolysis is not a result of providing a lower energy pathway. On the contrary, more energy is needed to achieve the activated complex. However, once enough thermal energy is added to the system, the pathway leads to faster degradation. This behavior is opposite from what has been observed in the previous cases, for which the presence of the oxide resulted in a decrease of enthalpy. Interestingly, the activation entropy for thiometon hydrolysis in the presence of goethite is increased from  $-8.1$  to  $200$  J/mol·K. These data show that complex formation is not the mechanism of catalysis in this case. Complex formation is more ordered and should result in an entropy decrease. Table 12 shows that with increasing temperature, the relative contribution of  $k_{\text{het}}$  increases in the case of thiometon and goethite at pH 5.7. The resulting increase in temperature dependence in the presence of goethite at pH 5.7 has negative consequences for the degradation of thiometon in natural waters where high temperatures are not often encountered. Its hydrolysis half-life of 58 days at 25 °C, pH 5.7, and without oxides can increase to over 5 years in the presence of goethite at pH 5.7 and 15 °C!

Our results indicate that complex formation between the pesticide and the oxide surface is the rate-determining step of the mechanism of catalysis when enhanced hydrolysis rate constants are mainly observed at lower temperatures (i.e., 25 °C). Previous studies have proposed this as one of the possible mechanisms (Torrens and Stone, 1994). Since the temperatures of most natural waters are  $<25$  °C, enhancement of hydrolysis in the presence of oxides is expected to be even greater than under the conditions in this study. Oxides can thus play an important role in organophosphorus pesticide degradation in natural environments. Further studies are needed to evaluate the requirements of surface catalysis and why some pesticides are susceptible to catalysis and others are not.

**Inhibition of Hydrolysis by Metal Oxides.** In cases for which inhibition of hydrolysis was observed (Table 7), it may be due to several reasons. Some possible reasons may include blocking of the attack of the nucleophile (e.g., dissolved hydroxide ion or water molecule) by the metal oxide surface or a reduction of the pesticide concentration in the water, thus reducing the encounter frequency of the pesticide molecule and a dissolved hydroxide ion or a water molecule.

## CONCLUSIONS

Metal oxides can increase or decrease the hydrolysis rates of organophosphorus pesticides. Complex forma-

tion between oxide surface and pesticide is the rate-determining step of the mechanism of catalysis when enhanced hydrolysis rate constants are mainly observed at lower temperatures. Of the studied pesticides, thiometon and diazinon are most susceptible to catalysis, with thiometon hydrolysis catalyzed the most. Goethite and aluminum hydroxide are the most effective catalysts for thiometon and diazinon. Oxide/pesticide ratio is a factor in determining the magnitude of catalysis. Adsorption of all studied pesticides except demeton S onto the oxide surfaces is significant, a fraction adsorbed ranging from 0.2 to 0.4. Pesticides whose primary leaving group consists of alkyl sulfides are very sensitive to experimental conditions in their hydrolysis pathways. Different products were observed depending on pH and the amount of dissolved oxygen present. Thiols, products previously reported for demeton S, thiometon, and disulfoton hydrolysis, were not stable products under the experimental conditions in this study and reacted further to form disulfides. The discovery of 1,2-bis-(ethylthio)ethane as a hazardous, persistent hydrolysis product of disulfoton at pH 8.5 and under deaerated conditions underscores the importance of identifying the pesticide degradation products.

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