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Effect of pH on the Rate of Aldicarb Hydrolysis

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Aldicarb [2-methyl-2-(methylthio)propionaldehyde O-(methylcarbamoyl)oxime] is a systemic carbamate pesticide applied to the soil in granular form. Degradation products include aldicarb sulfoxide and aldicarb sulfone, both of which are as toxic to insects and mammals as the parent compound; collectively the three toxic compounds make up the total toxic residue (TTR). Hydrolysis of these toxic compounds results in relatively nontoxic oximes and nitriles.

In plants and soil aldicarb is rapidly oxidized to the aldicarb sulfoxide (Maitlen et al. 1968; Smelt et al. 1978c; Bromilow et al. 1980), which can then hydrolyze to aldicarb sulfoxide oxime and/or oxidize to aldicarb sulfone (Union Carbide 1983; Smelt et al. 1978a,b,c). Since most of the TTR in groundwaters have been associated with the sulfur-oxidized derivatives of aldicarb (i.e., aldicarb sulfoxide and aldicarb sulfone) (Hansen and Spiegel 1983; Porter et al. 1984), most short-and long-term studies designed to determine the pH and temperature effects on hydrolysis rates have used aldicarb sulfoxide and aldicarb sulfone as the primary substrates (Lemley and Zhong 1983; Porter et al. 1984). This paper reports on the hydrolysis rates of aldicarb at pH values bracketing those found in natural waters.

MATERIALS AND METHODS

Buffered reaction solutions for the aldicarb hydrolysis experiment were prepared by adding 3 mL of a 10 mg/L aldicarb solution in water to 297 mL of 1.67 x 10^{-2}M pH buffer solution (4.1 x 10^{-3}M buffer for pH 8.85) in duplicate BOD bottles to give a 0.10 mg/L aldicarb concentration. The sterile buffer systems and their final pH values (after incubating 15-89 days) were potassium hydrogen phosphate-sodium hydroxide (pH 6.02, 7.06, and 7.96), sodium tetraborate-hydrochloric acid (pH 8.85), and sodium bicarbonate-sodium hydroxide (pH 9.85). Buffer solutions and glassware were autoclaved before use. The BOD bottles were plugged with sterilized foam plugs and placed in an incubator in the dark at 20° ± °2C. Controls without aldicarb were included, and were

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always below the limit of detection of 3 ppb. To determine whether sterility was maintained throughout the incubations, thioglycollate broth media was employed on the first and last day of incubation to test for contamination and was always negative.

TTR was determined according to the methodology developed by Union Carbide (1980). At appropriate intervals, fifty mL aliquots were removed from each duplicate incubation container of pH-buffered distilled water solution and placed into a 125-mL separatory funnel. Two mL of peracetic acid was added to oxidize aldicarb and aldicarb sulfoxide to aldicarb sulfone. Conversion of aldicarb and aldicarb sulfoxide to aldicarb sulfone is necessary since chromatographic peaks of aldicarb and aldicarb sulfoxide are indistinguishable from the solvent peak using gas chromatography (Galoux et al. 1979). The contents in the separatory funnel were mixed and allowed to stand for 30 minutes with occasional mixing. After 30 minutes, 15 mL of 10% $NaHCO_3$ were added, mixed, and allowed to stand with occasional mixing for 15 minutes. Fifty mL of methylene chloride were added with frequent venting to release evolved CO_2. After the layers separated, the lower methylene chloride layer was drained through approximately 80 g of prewet sodium sulfate in a 4-inch funnel with a glass wool plug. The extraction was repeated with another 50 mL of methylene chloride and the extracts combined. After rinsing the sodium sulfate bed with an additional 20 mL of methylene chloride, the combined extracts and rinse were collected and concentrated in a 45°C water bath by evaporating just to dryness with a stream of dry N_2 gas. The residue was then dissolved in acetone to 1-2 mL and stored in 3 mL septum-capped vials at -5°C until analyzed by gas chromatography.

Gas chromatography was performed on a Perkin-Elmer Sigma 300 GC equipped with a flame photometric detector with a 394 nm filter to quantify the sulfone. A coiled glass column, 1m x 2mm (ID), packed with 5% SP-1000 on Supelcoport (100/120 mesh) was used for separation. Normal operating conditions were 260°C injector temperature, 175°C column temperature, 250°C detector temperature, and helium, hydrogen, and air flow rates of 35, 20, and 26 mL/min, respectively. The minimum detectable concentration was 1.8 ng absolute or 300 ng/mL in a 6 µL injection. Chromatograms were recorded on a Hewlett-Packard 3390A Integrator in the linearized mode and a Varian 9176 recorder in the non-linearized mode.

Inter-laboratory comparisons of four samples with two independent labs (two samples to each lab) were within ± 29% of the concentration values measured in our lab. Spiked recoveries ranged from 93 to 109%, averaging 103%.

Pseudo-first-order rate constants, k, were obtained from the slope of the line (-2.30 X regression coefficient) by a linear least-squares analysis of the data. The second-order reaction rate constant, k_{OH}, was determined from the slope between pH 8 and pH 10 in a plot of log k vs. pH according to the relationship

$$k_{OH} = \frac{k}{[OH^-]} \qquad (1)$$

RESULTS AND DISCUSSION

At pH = 6, 7, and 8 aldicarb hydrolyzes slowly, but increases at higher and lower pH levels (Fig. 1). Plotting log k v. pH in Fig. 2 demonstrates that there are only slight changes in the pseudo-first-order rate constant in the pH 6 to 8 range. The data obtained at pH = 7 showed a slight increase in aldicarb and its oxidation products over time, resulting in a low coefficient of determination and a positive slope (Fig. 1). The rates and resulting half-life values for pH 6-8 (Table 1) are only estimates since the slopes of the log percent remaining vs. time regression lines in Fig. 1 were probably not significantly different from zero. To accurately estimate the half-life for these pH conditions, experiments lasting longer than 89 days would have to be performed. Above pH 8 the pseudo-first-order rate constant increases with increasing pH and the slope of the line is approximately +1 (Fig. 2), indicating aldicarb hydrolysis is first-order with respect to hydroxide ion concentration. The second-order reaction rate constant for base hydrolysis, k_{OH}, calculated from Equation 1 using the data obtained at pH 7.96, 8.85, and 9.85,was $1.94 \times 10^3 \pm 3.54 \times 10^2$ L mole^{-1} day^{-1}. At pH < 6, the rate of hydrolysis appears to be acid catalyzed, but not to the extent as for base catalysis since the slope is less than 1.

Table 1. Pseudo-first-order Rate Constants (d), Half-life Values ($t_{1/2}$), and Coefficient of Determination of the Regression Line (r^2) For Aldicarb Hydrolysis at 20°C in pH-buffered Distilled Water.

pH	Period(days)	k(day^{-1})	$t_{1/2}$(days)	r^2
3.95	89	5.3×10^{-3}	131	0.86
6.02	89	1.2×10^{-3}	559	0.90
7.96	89	2.1×10^{-3}	324	0.62
8.85	89	1.3×10^{-2}	55	0.98
9.85	15	1.2×10^{-1}	6	1.00

The acid hydrolysis constant, k_H, which was not first-order with respect to hydrogen, had a computed value (based only on the data acquired at pH 3.95) of 4.72×10^1 L mole^{-1} day^{-1}.

Laboratory hydrolysis studies of any xenobiotic using sterile pH-buffered distilled water can only be interpreted as representing a "worst case" situation since all the environmental

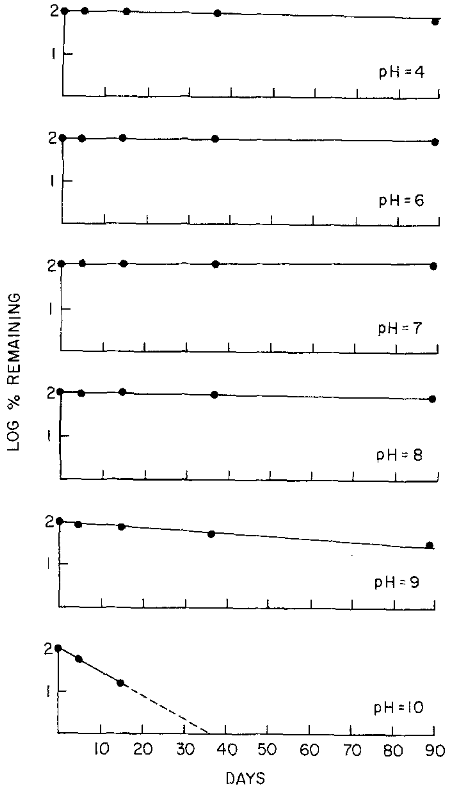

Figure 1. Hydrolysis of Aldicarb in Sterile pH-buffered Distilled Water at 20°C. Each Data Point is the Mean of Duplicate Samples.

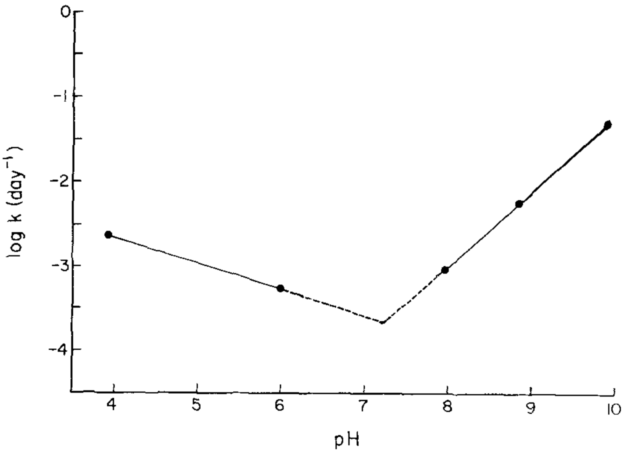

Figure 2. Log k vs. pH for Aldicarb Hydrolysis in Sterile pH-buffered Distilled Water at 20°C.

factors such as volatilization, adsorption, plant uptake, leaching, and microbial degradation present under field conditions have been omitted. As such, hydrolysis rates obtained from laboratory studies can only be used to establish upper bounds for the half-lives of aldicarb in natural waters. The extent of error in not considering the environmental conditions in the field nor using actual well waters and aquifer material when interpreting hydrolysis data has been presented elsewhere (Dierberg and Given 1984).

Carbamates such as aldicarb typically are quite resistant to hydrolysis at neutral pH values, but are relatively unstable under alkaline conditions of pH (Faust and Gomaa 1972), yielding non-toxic aldicarb oxime (which is stable in basic medium), methylamine, and carbonate from the cleavage at the carbonyl carbon (Lemley and Zhong 1983). Trehy et al. (1984) also found from GC/MS analysis that the degradation product for aldicarb in sterile anaerobic water was aldicarb oxime. Oximes can undergo a dehydration to become another non-toxic aldicarb residue: nitrile.

It has been shown that oximes do not interfere under the analytical procedures outlined above, but nitriles are detected and included as part of the TTR (Dierberg and Given 1984; Trehy et al. 1984). Hansen and Spiegel (1983) and Dierberg and Given (1984) indicated interferences from nitriles in causing an overestimation of TTR become quantitatively important only when > 90% of the TTR has disappeared. Moreover, the extra time and effort involved in Florisil removal of nitriles may not be warranted since the relative error (based on the initial TTR) associated with the recoveries from Florisil separation is more than the error introduced by not removing nitriles. Neglecting to remove nitriles from our samples apparently was not a significant source of error in analyzing TTR.

Comparisons of hydrolytic half-life values reported by other investigators for aldicarb in sterile, pH-buffered distilled water are presented in Table 2.

Table 2. A Comparison of Hydrolytic Half-lives for the Disappearance of TTR in Sterile pH-buffered Distilled Water Amended with Aldicarb.

pH	Temp(°C)	Half-life(days)	Reference
3.95	20	131	This study
6.02	20	559	This study
7.96	20	324	This study
8.85	20	55	This study
9.85	20	6	This study
12.90	15	4.0 min	Lemley and Zhong 1983
13.39	15	1.3 min	Lemley and Zhong 1983
8.5	20	69	Hansen and Spiegel 1983
8.2	None given	43	Trehy et al. 1984

Not only is there a scarcity of published literature on aldicarb hydrolysis, but only a few of the published studies included the range of pH values which bracket the pH of natural waters. For those cases when the raw data were available, the rate constants derived for temperatures other than 20°C were adjusted to a temperature of 20°C by constructing Arrhenius plots.

The Hansen and Spiegel (1983) work is the closest data set comparable to the conditions of our experiment. Their data (adjusted to 20°C)for pH 8.5 yielded a half-life of 69 days, which is almost twice as fast as the pseudo-first-order rate constant extrapolated from Fig. 4 at pH 8.5 ($k = 5.8 \times 10^{-3}$ day^{-1}), corresponding to a half-life of 120 days.

To the authors' knowledge, the only published values for second-order rate constants of aldicarb hydrolysis is from Lemley and Zhong (1983). Based on using high hydroxide and aldicarb concentrations, and a different method (i.e. titrimetric) to measure the progress of hydrolysis, they found k_{OH} for aldicarb to be $1.35 \times 10^3 \pm 0.03 \times 10^3$ L mole^{-1} day^{-1} at 15°C. After adjusting to a temperature of 20°C (assuming the activation energy of the aldicarb is the same as the activation energy measured by Lemley and Zhong for aldicarb sulfoxide (= 15.2 ± 0.1 kcal/mol)), their k_{OH} becomes 2.12×10^3 L mole^{-1} day^{-1}, which compares favorably to the 1.94×10^3 L mole^{-1} day^{-1} rate measured by us.

Compared to the hydrolyses of aldicarb sulfoxide and aldicarb sulfone, aldicarb hydrolyzes at much slower rates under the same pH and temperature (Hansen and Spiegel 1983; Porter et al. 1984). If it was not for the apparent rapid oxidation of aldicarb to its faster hydrolyzing oxidation products, aldicarb would be more persistent in the environment.

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