the formation of a reactive intermediate and its reaction with a sensitive macromolecule alters the chemical nature of the substance in such a way that a second metabolic activation is either unlikely or impossible.

If the methylamine-liberating substances in swine muscle are capable of forming reactive intermediates that can bind to cellular macromolecules the formation of "carcass" residues would be expected on administration of the swine muscle to rats. The lack of detection of methylamine-liberating residues in the rat carcass indicates that the covalent binding potential of this fraction is lower than that of ronidazole (Wolf et al., 1984).

Administration of ronidazole at a dose of 16 μg gave carcass residues of 0.7% of the dose of methylamine-liberating residues. From these experiments it seems reasonable to conclude that the potential of the bound residues to form reactive intermediates that can bind to cellular macromolecules has been diminished by the primary activation–reaction sequence.

ACKNOWLEDGMENT

We are indebted to Dr. H. Mertel and G. Gatto for the synthesis of radioactive ronidazole, to H. T. Meriwether for purity and specific activity determination, and to Rose Caamano and Terry Rafferty for the preparation of the manuscript.

Registry No. Ronidazole, 7681-76-7.

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Received for review December 27, 1982. Revised manuscript received February 9, 1984. Accepted March 12, 1984.

Hydrolysis of Aldicarb, Aldicarb Sulfoxide, and Aldicarb Sulfone at Parts per Billion Levels in Aqueous Mediums

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Degradation rates of aldicarb, aldicarb sulfoxide, and aldicarb sulfone in aqueous solution were measured as part of a larger study to systematically investigate detoxification methodology for carbamate pesticides in drinking water. Gas chromatographic methods were developed for the study and are described. Pseudo-first-order rate constants for base hydrolysis were determined for 25-ppb solutions of each species at 15 °C. Second-order rate constants were calculated, and the order for rate of hydrolysis was found to be the same as that reported for ppm solutions: aldicarb sulfone > aldicarb sulfoxide > aldicarb. The temperature effect for hydrolysis of aldicarb sulfone was determined, and Arrhenius behavior was observed. An activation energy of 15.6 kcal/mol was calculated. Base hydrolysis rates of aldicarb sulfone in chlorinated water and in actual well water were measured and were found to be slower than those measured in distilled water. Data for rates of hydrolysis were extrapolated to hydroxide ion concentrations equivalent to environmental pH values, and good agreement with experimental data obtained in buffered pH solutions is shown.

Toxic metabolites of the pesticide aldicarb have been found in drinking water wells in several locations throughout the country including New York and Wisconsin (Rothschild et al., 1982). The most severe contamination still appears to be in New York State in eastern Suffolk County on Long Island (Guerrera, 1981; Zaki et al., 1982). Despite discontinued use of the pesticide since the 1979 growing season, it is still being found in groundwater wells at concentrations of total aldicarb greater than the New York State advisory guideline of 7 ppb. A recent study (Hansen and Spiegel, 1983) has predicted that the total aldicarb concentration will not remain above this level in groundwater beyond this decade. Even if these predictions are accurate, there is serious concern in the near future about the contamination of these wells and concern about aldicarb and other carbamate pesticides contaminating groundwater supplies in other areas in the country.

The high water solubility of aldicarb sulfoxide and aldicarb sulfone and their stability under some environmental conditions have made them a serious threat to groundwater. The degradation and leaching of aldicarb in various soil types have been studied by many researchers (Richey et al., 1977; Elgindi et al., 1978; Smelt et al., 1978, 1981; Bromilow et al., 1980; Bromilow and leistra, 1980). Early work by Richey et al. (1977) indicated extensive degradation of the aldicarb molecules in specific soils. Smelt et al. (1978) computed that 91–100% of the aldicarb applied to soil would be oxidized to the sulfoxide. They also showed that aldicarb sulfoxide and sulfone degraded considerably more slowly in deeper layers than in top layers of the soil profile; the degradation also varied with soil type. None of these studies predicted the environmental persistence of the sulfoxide and the sulfone in groundwater.

The work described herein is part of a broader investigation of the chemical degradation of aldicarb and its metabolites in water. The overall goal of this project is to develop detoxification methodology based on acid or base hydrolysis on reactive ion-exchange resin beds. This method has been shown to be effective in detoxifying organophosphate compounds (Janauer et al., 1981) and, if successful, will have an important application in the pro-

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0021-8561/84/1432-0714$01.50/0

tection of the public against the hazards of ingesting drinking water contaminated with enzyme-inhibiting carbamate pesticides.

Previous work by Lemley and Zhong (1983) on the degradation of aldicarb and its environmental metabolites reported on the base and acid hydrolysis of aldicarb (A), aldicarb sulfoxide (A-SO), and aldicarb sulfone (A-SO_2) in aqueous solution (37 ppm). This study was the first report of the kinetics of hydrolysis of aldicarb and its metaboites at high pHs in water, although hydrolysis of aldicarb at pH ≤8.0 has recently been reported by Chapman and Cole (1982) and hydrolysis of other carbamates in aqueous medium has reported by Ventor et al. (1972), Aly and El-Dib (1972), and Faust and Gomaa (1972). Pseudo-first-order rate constants were determined at different hydroxide concentrations with acid–base titration. Second-order rate constants were calculated and temperature effects were determined. As expected, acid-catalyzed rates were much slower (10^5) than base hydrolysis rates. The work described in this paper extends the base hydrolysis study of A, A-SO, and A-SO_2 to ppb concentrations. Rate studies in chlorinated water and in actual well water are also reported. Gas chromatographic methods have been developed for detection at these levels and are also described.

EXPERIMENTAL SECTION

Materials. Crystalling samples of A-SO (98% pure), A-SO_2 (99% pure), aldicarb sulfone oxime, and aldicarb sulfone nitrile were supplied by Union Carbide Corp. A reference standard of aldicarb (100% pure) was obtained from the U.S. Environmental Protection Agency, Quality Assurance Section. Diethyl-*p*-phenylenediamine oxalate and the sodium hypochlorite solution (4–6%) were purchased from Fisher Scientific Co. Analytical reagent grade chemicals and solvents were used in all experiments. Methylene chloride used for bulk extractions of aldicarb/aldicarb metabolites was recovered, distilled, and used again. Distilled, deionized, and then glass distilled water (DDD water) was used throughout except for the experiment with actual groundwater from Oakdale, NY, and the experiment with chlorinated water.

Kinetics. A solution (79 mL) of known concentration of NaOH in DDD water was added to a 200-mL flask and brought to the desired thermal equilibrium in a Cannon Instrument Co. thermostated water bath (±0.5 °C). The pH range of these solutions was from 11 to 13. To this was added 1 mL of a 2 μg/mL solution of A, A-SO, or A-SO_2 (freshly prepared); the final concentration was 25 ppb. The mixture was shaken immediately, and a slight excess amount of HCl was added at zero time and periodically thereafter (at 2-min intervals measured by stopwatch) to neutralize the base and stop the hydrolysis reaction. The solution was immediately transferred to a separatory funnel for extraction and analysis.

Five data points were obtained for each concentration of NaOH. Each data point was determined with two or three analyses. Initial experiments were done at 15 °C, but the temperature effect on hydrolysis was also studied by setting the water bath to equilibrium temperatures from 5 to 35 °C at 5 °C intervals.

Two types of experiments were performed in chlorinated water. In one experiment, the kinetics of base hydrolysis of A-SO and A-SO_2 were measured as described above in a water solution containing 0.5 ppm of free chlorine. The solutions were made with a sodium hypochlorite solution, and the free chlorine residual was measured by using the *N,N*-diethyl-*p*-phenylenediamine (DPD) method (Palin, 1957). In another experiment the degradation of A-SO_2 in chlorinated water was measured. Sodium hypochlorite solution was added to the temperature-equilibrated A-SO_2 solution so that the final concentration of A-SO_2 was 25 ppb and the free chlorine residual was either 0.5 or 1 ppm. A blank sample containing no chlorine accompanied each run. Periodically, 100-mL samples were extracted and analyzed.

Experiments conducted in Long Island well water were performed identically with those in DDD water.

Table I. Recovery of Residues from DDD Water with Methylene Chloride

name of compound	initial mass, g	initial concn, ppb	recovered mass, g	% recovered
aldicarb sulfone	2.00	25	2.02	101
	2.00	25	1.97	99
	2.00	25	2.00	100
aldicarb sulfoxide	2.06	26	2.02	98
	2.06	26	2.01	98
	2.06	26	1.97	96
aldicarb	1.90	24	1.88	99
	1.90	24	1.82	96
	1.90	24	1.85	97

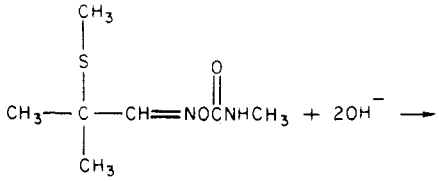
Extraction. The extraction procedure used was based on the method supplied by Union Carbide Corp. (1980). The reaction solution was extracted 3 times with 50 mL of methylene chloride. The extracts were dried by passing through sodium sulfate. They were combined into a 250-mL Kuderna-Danish flask connected to a 10-mL concentrator tube and then evaporated under vacuum at 45 °C with a rotary evaporator just until dryness was attained. Aldicarb sulfone residues were immediately dissolved in 1 mL of 1:9 chloroform–carbon disulfide and stored in the refrigerator for analysis. Recoveries attained by this method ranged from 99 to 101% and are listed in Table I.

A and A-SO residues were analyzed after oxidation to A-SO_2. After evaporation the residue was redissolved in 50 mL of water. One-half milliliter of 40% peracetic acid was added, and the solution was allowed to stand for 15 min. Excess acid was neutralized by adding a proportionate amount of 10% aqueous $NaHCO_3$. The extraction procedure was repeated, and residues were dissolved in the 1:9 chloroform–carbon disulfide solution for analysis. Recoveries attained by this method ranged from 96 to 99% and are also listed in Table I. An attempt was made to oxidize A and A-SO before the first extraction procedure, but recoveries were very poor. The solution at this point in the procedure is acidic, and it was thought that the peracetic acid might be decomposing to acetic acid and hydrogen peroxide under these conditions.

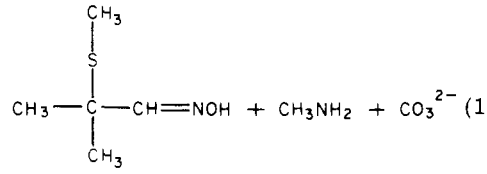
Analysis. All samples were analyzed by gas chromatography. A Micro Tek DSS series gas chromatograph with a flame ionization detector (FID) was used for all analyses, and in addition, some experiments were repeated with a newly purchased Tracor Instruments Model 702 nitrogen–phosphorus detector (NPD). Several columns were tried, but best results were attained with a 4 ft × 4 mm i.d. glass column containing 1.5% SP 2250/1.95% SP 2401 on 100–120-mesh Supelcoport. Nitrogen was used as the carrier gas at a flow rate of 150 mL/min. The detector was maintained at 260 °C with the hydrogen and air supplied at 65 and 283 mL/min, respectively. The injector and column temperatures were maintained at 300 and 130 °C, respectively. A standard curve for A-SO_2 determination was developed by making 5-μL injections of the standard in 1:9 $CHCl_3$–CS_2. One or two points on this linear curve were checked daily. Experiments performed with the NPD were carried out as follows. The

injection port, column, and detector temperatures were maintained at 300, 160, and 280 °C, respectively. Helium was selected as the carrier gas. Flow rates (mL/min) were as follows: helium, 38; hydrogen, 2.8; air, 120. A-SO_2 residues were redissolved in acetone for determination with this detector. Rate constants determined with the NPD were identical with those determined with the FID.

Calculations. It is well-known that carbamate pesticides such as aldicarb and its metabolites hydrolyze in basic solution according to eq 1. The progress of base



aldicarb



aldicarb oxime

hydrolysis was followed directly by measuring the disappearance of A, A-SO, or A-SO_2 with the gas chromatographic methods just described. The pseudo-first-order rate constant, k_{obsd}, was determined by plotting log C_{A_t}/C_{A_0} against time where C_{A_t} and C_{A_0} are the concentrations of A, A-SO, or A-SO_2 at time t and at the initial concentration, respectively. The second-order or reaction rate constant, k_r, was calculated from the plot of k_{obsd} values vs. initial concentrations of NaOH according to the usual equation

$$k_r = k_{obsd}/[OH^-] \quad (2)$$

The activation energy, E_A, was calculated from the slope of the straight line in the Arrhenius plot:

$$k_r = Ae^{-E_A/(RT)} \quad (3)$$

Regression analyses of all linear plots were made by using the computer program MINITAB (copyright Pennsylvania State University, 1981). Standard errors were computed from the standard deviation by using the relationship

$$\pm\text{error} = \sigma/\sqrt{n} \quad (4)$$

where σ = standard deviation and n = number of data points.

RESULTS AND DISCUSSION

Development of Analytical Method. Many gas chromatographic methods for carbamate pesticide analysis have been reported in the literature (Dorough and Thorstenson, 1975). The Union Carbide Corp. (1980) procedure to quantify aldicarb and its metabolites has involved preoxidation to the sulfone, pyrolysis in the injection port to the sulfone nitrile degradation product, and detection by a flame photometric detector (FPD). We have used procedures that depend on degradation to the nitrile, but found with preliminary experiments that detection by FPD was not sensitive enough and not reproducible. We followed the Union Carbide Corp. (1980) procedure, i.e., using a 5% SP 1000 column, but found it very difficult to analyze water samples on the order of 1–10 ppb with the GC/FPD instrument that was available to us. Consequently, we decided to adapt the Union Carbide methods to use with a flame ionization detector and eventually to purchase a nitrogen–phosphorus detector. The major problem that one encounters with the FID is the large solvent peak. Under normal conditions the retention time of the sulfone nitrile would be too short to allow separation. However, when a solvent mixture of 1:9 $CHCl_3$ to CS_2 was used (the $CHCl_3$ to dissolve the sample and the CS_2 for minimum detector response), the solvent peak was small enough so that there was complete resolution of the aldicarb sulfone nitrile peak at 1.6 min (Figure 1). A large injection of the aldicarb sulfone oxime standard gave a peak with a longer retention time (3.9 min). The results assured us that the oxime product of hydrolysis was not interfering with the measurement of the nitrile. Also, there was no indication that the oxime degraded to the nitrile under the GLC conditions used. When FID was used under these conditions, 10-ng quantities of aldicarb sulfone could be quantified. When the NPD method was substituted, quantities at least as small as 1 ng could be quantified. We did not need to quantify at lower levels for the experiments we were doing, so we chose to prolong the detector life and not run the detector at the higher temperatures required for smaller quantities.

Table II. Observed Base Hydrolysis Rate Constants of Aldicarb Sulfone, Aldicarb Sulfoxide, and Aldicarb at 15 °C in DDD Water

name of compound	concn of NaOH × 10^2, mol L^{-1}	k_{obsd} × 10, min^{-1}	±	r^2, %
aldicarb sulfone	0.18	0.55	0.001	99.1
	0.22	0.76	0.001	99.9
	0.28	0.93	0.001	99.8
	0.36	1.16	0.002	99.6
	0.44	1.46	0.001	99.9
aldicarb sulfoxide	0.31	0.39	0.001	98.7
	0.43	0.56	0.001	99.5
	0.62	0.76	0.001	99.9
	0.81	0.92	0.001	99.8
	1.05	1.22	0.001	99.8
aldicarb	1.67	0.18	0.001	98.5
	2.85	0.32	0.001	98.4
	4.77	0.56	0.001	99.6
	6.20	0.73	0.001	99.6
	8.05	0.91	0.001	99.6

Table III. Reaction Rate Constants for Aldicarb Sulfone, Aldicarb Sulfoxide, and Aldicarb at 15 °C in DDD Water

name of compound	k_r, L mol^{-1} min^{-1}	±	r^2, %
aldicarb sulfone	33.0	0.6	99.3
aldicarb sulfoxide	11.4	0.2	99.5
aldicarb	1.15	0.02	99.6

Hydrolysis in Distilled Water. The rate of disappearance of A, A-SO, and A-SO_2 in aqueous solution (25 ppb in DDD water) at 15 °C was studied as a function of NaOH concentration. The observed rate constants, k_{obsd}, for each species are reported in Table II. In each case a straight line with high correlation coefficient was obtained, confirming pseudo-first-order behavior.

The k_{obsd} values obtained from regression analyses of the slopes were plotted vs. hydroxyl ion concentrations. These plots yielded straight lines passing through the origin for each species, indicating that the reaction is first order with respect to hydroxide ions. The second-order reaction rate constant, k_r, was computed for each species as the slope of the line. The results are listed in Table III. The order of rate of hydrolysis is

$$\text{A-}SO_2 > \text{A-SO} > \text{A}$$

These results are in agreement with those obtained pre-

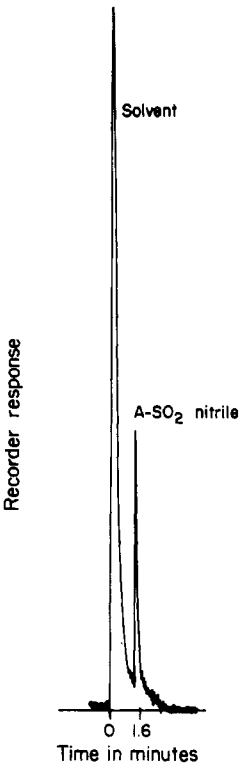


Figure 1. Typical chromatogram of 10 ng of aldicarb sulfone.

Table IV. Effect of Temperature on the Hydrolysis of Aldicarb Sulfone in DDD Water

temperature, °C	k_r, L mol^{-1} min^{-1}	±	r^2, %
5	1.13 × 10	0.4	98.4
10	1.91 × 10	0.4	98.9
15	3.30 × 10	0.6	99.3
25	8.05 × 10	0.5	99.9
35	1.70 × 10^2	1.0	99.9

E_A = 15.6 ± 0.4 kcal mol^{-1}; r^2 = 99.1%

viously (Lemley and Zhong, 1983) in ppm solutions. The experimental behavior described above indicates that aldicarb and its environmental metabolities like other *N*-methyl carbamate pesticides such as carbaryl and Baygon (Aly and El Dib, 1972) are sensitive to hydryoxyl ion in aqueous solution. In fact, the rate results obtained for aldicarb sulfone are very similar to those obtained for Baygon (Aley and El-Dib, 1972); this despite the fact that Baygon hydrolyses to a phenol rather than an oxime.

Additional experiments were designed to study the effect of temperature on the base hydrolysis of aldicarb sulfone. Rate studies identical with those described above were performed at five temperatures between 5 and 35 °C. The results are shown in Table IV. The values for k_{obsd} and k_r were calculated as before for each temperature. The results show an increased rate of hydrolysis with increased temperature and a 15-fold increase of k_r in the range of temperatures studied. The activation energy, E_A, calculated as the slope of the Arrhenius plot had a value of 15.6 ± 0.4 kcal/mol. Rate studies were also made for A and A-SO at a second temperature, 5 °C, and estimated activation energies for these species were found to be in the range of 14–16 kcal/mol. The activation energies of the three aldicarb species are essentially the same and are in the range of those reported by other investigators for hydrolysis of *N*-methylcarbamates (Aly and El-Dib, 1972; Fukuto et al., 1967). In addition, satisfactory agreement can be seen between the present study and previous work by Lemley and Zhong (1983) with respect to the activation energy calculated for ppm solutions of aldicarb sulfone.

Although there appeared to be close agreement for values of k_r and E_A between ppm and ppb concentrations, several studies were made at 10- and 50-ppb concentrations, and the results were compared to those obtained for 25-ppb solutions. This study was done in order to ensure that treatment methodology developed for contaminated drinking water would be effective for a range of concentrations of aldicarb species. The majority of the contaminated wells identified on Long Island had concentrations in the range from 10 to 50 ppb (Suffolk County Department of Health Services, 1981). The results of the studies with A-SO_2 are shown in Table V, and they confirm that concentration differences at these dilute levels do not influence hydrolysis reaction rates.

The series of investigations described above establishes base data for aldicarb/aldicarb metabolite hydrolysis with which reactive ion exchange results can be correlated. The fact that the most highly oxidized species degrades at the fastest rate is important to the concept of in situ degradation in that it suggests that a preoxidation column should be put in series with the reactive ion exchange column for most efficient performance. In addition, accurate and precise data in distilled water have been obtained with which to compare results from other experiments in chlorinated and well water.

Hydrolysis in Chlorinated Water. There were two types of studies done with degradation of aldicarb metabolites in chlorinated water. The purpose of the first study described here was to determine the stability of low levels of aldicarb sulfone in chlorinated drinking water. This was accomplished by preparing solutions of DDD water containing 0.5 and 1.0 ppm of free chlorine residual after 5 min of contact time. The degradation of A-SO_2 in this solution was compared with the degradation in pure DDD water. The results are depicted in Figure 2. No obvious hydrolysis of A-SO_2 was observed after 10 h at 25 °C in DDD water, but a slight degradation did appear in

Table V. Effect of Aldicarb Sulfone Concentration on Its Hydrolysis in DDD Water

concn of A-SO_2, ppb	concn of NaOH, M, × 10^3	k_{obsd} × 10, min	±	r^2, %	k_r, L mol^{-1} min^{-1}
10	1.33	0.50	0.001	99.6	37.7
	1.77	0.64	0.001	99.9	36.0
	2.22	0.81	0.002	99.8	36.5
	2.88	1.06	0.001	99.9	36.8
	3.55	1.26	0.001	99.9	35.7
				99.7	35.8 ± 0.4
50	0.89	0.31	0.001	99.5	34.5
	1.55	0.49	0.001	99.6	31.4
	2.22	0.74	0.001	99.2	33.2
	2.88	1.03	0.001	99.5	35.6
	3.77	1.31	0.001	99.4	34.8
				99.3	35.2 ± 0.7

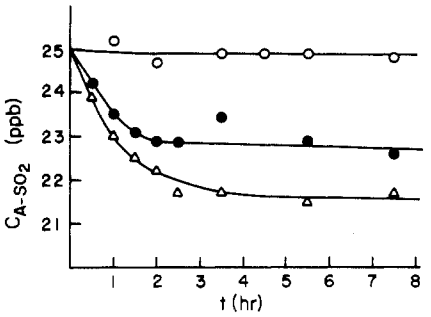


Figure 2. Influence of chlorination on degradation of aldicarb sulfone at 25 °C. (○) Doubly distilled deionized water; (●) 0.5 ppm of free chlorine; (△) 1.0 ppm of free chlorine.

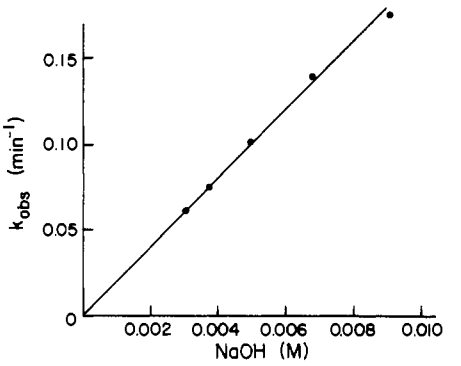


Figure 3. Base hydrolysis of aldicarb sulfone in well water at 15 °C.

Table VI. Influence of Water Chlorination on Base Hydrolysis of Aldicarb Sulfoxide and Aldicarb Sulfone at 15 °C

compound	free chlorine, ppm	concn of NaOH, M	k_r, L mol^{-1} min^{-1}
aldicarb sulfoxide	0	0.003098	10.3
	0.5	0.003098	12.1
aldicarb sulfone	0	0.003098	33.5
	0.5	0.003098	32.9

the first few hours in both chlorinated solutions. The degradation rate was faster in the solution with the higher chlorine content. These results are most likely due to the fact that the pH is raised when hypochlorite is added to the solution. The time scale of this hydrolysis is such that significant detoxification of drinking water containing A-SO_2 would not occur due to chlorination.

The study of A-SO and A-SO_2 degradation in chlorinated water was performed in order to determine whether chlorination would interfere with the strong base hydrolysis to be used in the reactive ion exchange method. Table VI shows the results of base hydrolysis of A-SO andd A-SO_2 in DDD water containing 0.5 ppm of free chlorine at 15 °C. The values calculated for k_r in each case are not significantly different from those obtained in the previously described studies in distilled water.

Hydrolysis in Long Island Well Water. Base hydrolysis studies identical with those described above were carried out with A-SO and A-SO_2 at 15 °C by using actual well water from Oakdale, NY. The results of these experiments are illustrated in Figure 3 and Table VII. As before, a straight line through the origin was obtained by plotting k_{obsd} vs. [NaOH]. However, the slopes were different, and k_r values of 5.9 ± 0.2 and 19.8 ± 0.2 L mol^{-1} min^{-1} were calculated for A-SO and A-SO_2, respectively. These values are lower than those obtained in DDD water, 11.4 and 33.0 L mol^{-1} min^{-1}, indicating that the rate of hydrolysis is slower. This phenomenon was predicted by previous work (Lemley and Zhong, 1983) where slower rates of hydrolysis were obtained in 1 M NaCl solutions. Although water on Long Island does not have high salt content, it does have enough ionic strength to slow base hydrolysis. The results from the chlorinated water experiments and from the well water experiments will provide an important base for prediction and comparison of detoxification results by means of reactive ion exchange columns. Chlorination should not interfere with detoxification by hydrolysis, whereas well water will slow it down.

Extrapolation to Environmental pH. In addition to the concern about treating drinking water that contains carbamate pesticides, there is also interest in determining how long the affected groundwater will remain contaminated. It is of interest to look at some of the data reported in this work and extrapolate to hydroxide ion concentrations equivalent to environmental pH values. Since the plots of k_{obsd} values vs. [OH^-] are straight lines with high correlation coefficients and which go through the origin, one can obtain reliable values for k_{obsd} using eq 2. Table VIII shows values for $t_{1/2}$ (days) ($t_{1/2} = 0.693/k_{obsd}$; k_{obsd} converted to days) at hydroxide ion concentrations equivalent to pH values of 6.0, 7.0, and 8.0 for A-SO and A-SO_2 in DDD water at 15 °C, for A-SO_2 in DDD water at 25 °C, and for A-SO and A-SO_2 in well water at 15 °C. This extrapolation is not valid at pH <1.0 since an acid-catalyzed hydrolysis mechanism takes over at very low pH values (Armstrong and Moodie, 1969; Lemley and Zhong, 1983). A problem with an extrapolation such as this one is that the rates and half-life values calculated are for a given hydroxide ion concentration and not for a buffered solution at a given pH. The mole ratio, [OH^-]/[A-SO_2], at a hydroxide ion concentration equivalent to pH 6.0 can be calculated to be 88.5; thus, the comparison to a buffered solution should be reasonable. The half-life values do represent an approximate upper limit for a given pH at the temperature studied, 15 °C, and it would be interesting to compare these values with experimental data.

Table VII. Rate of Base Hydrolysis of Aldicarb Sulfoxide and Aldicarb Sulfone in Well Water at 15 °C

compound	concn of NaOH × 10^3, M	k_{obsd} × 10, min	±	r^2, %	k_r, L mol^{-1} min^{-1}
aldicarb sulfoxide	5.03	0.24 × 10^{-1}	0.001	97.9	4.71
	8.04	0.44 × 10^{-1}	0.001	99.5	5.52
	10.1	0.61 × 10^{-1}	0.001	99.7	6.09
	17.3	0.89 × 10^{-1}	0.002	99.8	5.16
	19.5	1.20 × 10^{-1}	0.002	99.5	6.14
					5.86 ± 0.2
aldicarb sulfone	3.10	0.61	0.001	99.8	19.7
	3.72	0.75	0.001	99.8	20.2
	4.96	1.01	0.001	99.7	20.4
	6.77	1.39	0.001	99.9	20.5
	9.05	1.76	0.001	99.9	19.5
					19.8 ± 0.2

Table VIII. Half-Life Values of Aldicarb Sulfoxide and Aldicarb Sulfone at Environmental Hydroxide Ion Concentrations

name of compound	half-life, days, at indicated [OH^-], M		
	10^{-8} (pH 6.0)	10^{-7} (pH 7.0)	10^{-6} (pH 8.0)
aldicarb sulfoxide, 15 °C (distilled water)	4221	422	42.2
aldicarb sulfoxide, 15 °C (well water)	8212	821	82
aldicarb sulfone, 15 °C (distilled water)	1458	146	14.6
aldicarb sulfone, 25 °C (distilled water)	597	59.7	5.97
aldicarb sulfone, 15 °C (well water)	2431	243	24.3
aldicarb sulfone, 25 °C (Chapman and Cole, 1982)	420	77	9.8

Hydrolysis half-life values for aldicarb and its metabolites in buffered solutions have been reported by Chapman and Cole (1982) and by Hansen and Spiegel (1983). The Chapman and Cole (1982) experiments were conducted at 25 °C, 10-ppm concentrations, and 0.2 M ionic strength. Their results (Table VIII) compare very well with extrapolated half-life values determined from this work, with their value of 420 days (pH 6.0) slightly less than the extrapolated value of 597 days. At pH 7.0, the Chapman value is 77 days compared to an extrapolated value of 59.7 days, and for pH 8.0 the experimental value is 9.8 days, with an extrapolated value of 6 days. Hansen and Spiegel (1983) report a half-life value of 12 days at pH 8.0 and 25 °C. For solutions of aldicarb sulfone kept at 15 °C, Hansen and Spiegel get half-life values of 450 days at pH 5.5 and 25 days at pH 7.5. These compare to calculated values in this work of 4627 days and 46 days, respectively, at these same pH values. The discrepancy between these experimental values and the calculated values could be due to a high degree of uncertainty in the former (r^2 values are low) or to the assumption that extrapolation will work in this pH range. Hansen and Spiegel are repeating these experiments with different sampling intervals, and future comparisons will be made.

Another comparison of half-life values can be made between aldicarb sulfone and the *N*-methylcarbamate pesticide Baygon. Aly and El-Dib (1972) reported both k_{obsd} vs. [OH^-] and half-life values in buffered pH solutions for Baygon. The second-order rate constant that they calculated for base hydrolysis at 20 °C was 30 ± 2 L mol^{-1} min^{-1}, which is almost the same as that reported here for A-SO_2 at 15 °C. The half-life value that was measured for Baygon at 20 °C in a solution buffered at pH 8.0 was 16.0 days. The value calculated for A-SO_2 at 15 °C at a hydroxide ion concentration equivalent to pH 8 can be seen in Table VIII to be 14.6 days.

Although the extrapolation attempted here might not be valid for all pesticides over a wide range of pH values, there appears to be good agreement with the Chapman and Cole (1982) results for aldicarb sulfone. Their results with aldicarb sulfoxide indicate a similar dependence of half-life on pH. These experimental results, although performed at environmental pH values, were not conducted at groundwater temperatures. The aldicarb sulfone and aldicarb sulfoxide experiments reported in this paper in actual well water at 15 °C better approximate the Long Island groundwater conditions except for pH. Using the extrapolation technique described above, the half-life values reported in Table VIII for the experiments at this temperature might be the best approximation for environmental hydrolysis.

ACKNOWLEDGMENT

We thank Union Carbide Corp. for providing standards, A. Guerrera for providing a sample of well water, and G. E. Janauer for collaboration on this project.

Registry No. Aldicarb, 116-06-3; aldicarb sulfoxide, 1646-87-3; aldicarb sulfone, 1646-88-4.

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Received for review August 10, 1983. Revised manuscript received March 22, 1984. Accepted April 3, 1984. Portions of this work were presented at the 184th National Meeting of the American Chemical Society, Kansas City, MO, Sept 1982. This research was supported in part by Research Grant R809867 from the U.S. Environmental Protection Agency and by the U.S. Department of Agriculture.