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Transformation Kinetics and Mechanism of the Sulfonylurea Herbicides Pyrazosulfuron Ethyl and Halosulfuron Methyl in Aqueous Solutions

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Pyrazosulfuron ethyl (PE) and halosulfuron methyl (HM) are two new highly active sulfonylurea herbicides that have been widely used for weed control in a variety of vegetables and other crops. These two herbicides have similar molecular structures, differing only in the substitutions on the pyrazole ring. Chemical hydrolysis is a primary process affecting the environmental fate of sulfonylurea pesticides. The hydrolytic transformation kinetics of PE and HM were investigated as a function of pH and temperature. For both herbicides, the hydrolysis rate was pH-dependent and increased with increasing temperature. The hydrolysis of both sulfonylureas was much faster in acidic or basic media than under neutral conditions. Identification of hydrolytic products by liquid chromatography−mass spectrometry (LC-MS) suggested that both PE and HM were subject to cleavage and contraction of the sulfonylurea bridge. The hydrolysis rate of HM was significantly higher than that of PE in alkaline solutions, despite their structural similarity. A chlorine substitution on HM's pyrazole ring makes HM more susceptible to bridge contraction than PE under basic conditions. The hydrolysis of HM and PE was relatively unaffected by the presence of cyclic oligosaccharides (cyclodextrins), indicating that natural OH-containing organic compounds occurring in aquatic environments may have little impact on the transformation of these sulfonylurea herbicides.

KEYWORDS: Sulfonylurea; pyrazosulfuron ethyl; halosulfuron methyl; cyclodextrin; hydrolysis

INTRODUCTION

Sulfonylureas, a modern class of herbicides, are extensively used to control a wide range of weeds in many crops. These herbicides exhibit a simple but effective biological mode of action through inhibiting acetolactate synthase, a key enzyme that participates in the protein synthesis of plants. Because of the high herbicidal activity of sulfonylureas, they are effective at application rates as low as g ha^{-1} (*1*), which are about 10−1000 times less than those of conventional herbicides such as triazines and chloroacetanilides. Also, sulfonylureas exhibit extremely low acute and chronic mammalian toxicities in comparison with most other herbicides (*2*). Therefore, the use of sulfonylurea herbicides is increasing steadily worldwide.

The occurrence of sulfonylurea herbicides in aquatic environments is receiving public attention (*3*). Residues of sulfonylureas have been detected in surface water and groundwater due to runoff and leaching after their application (*3, 4*). Because of their high herbicidal activity, some crops (e.g., legumes and pastures) are highly sensitivite to trace-level residues of sulfonylurea herbicides in soils (*2*). An increased understanding of the environmental fate and behavior of sulfonylureas is imperative to reduce their potential negative effects on agronomic systems.

Microbial degradation and chemical hydrolysis are two primary transformation mechanisms of sulfonylureas in the environment. Photolysis is a minor decomposition process for sulfonylureas and only occurs under UV light (*5*). The chemical hydrolysis kinetics and pathways of many sulfonylurea herbicides in soils and water have been previously reviewed by Sarmah and Sabadie (*6*). It has been well-demonstrated that the hydrolysis of sulfonylureas is pH- and temperature-dependent (*2, 6–10*). The dissipation of sulfonylureas is usually more rapid in acidic than in neutral or weakly basic conditions (*9–11*). The primary pathway of hydrolysis under mildly acidic conditions is the cleavage of the sulfonylurea bridge, producing CO_2 and the corresponding sulfonamide and heterocyclic amine (*6–8*). In addition to the cleavage of the sulfonylurea bridge, some sulfonylureas may undergo a base-catalyzed hydrolysis through

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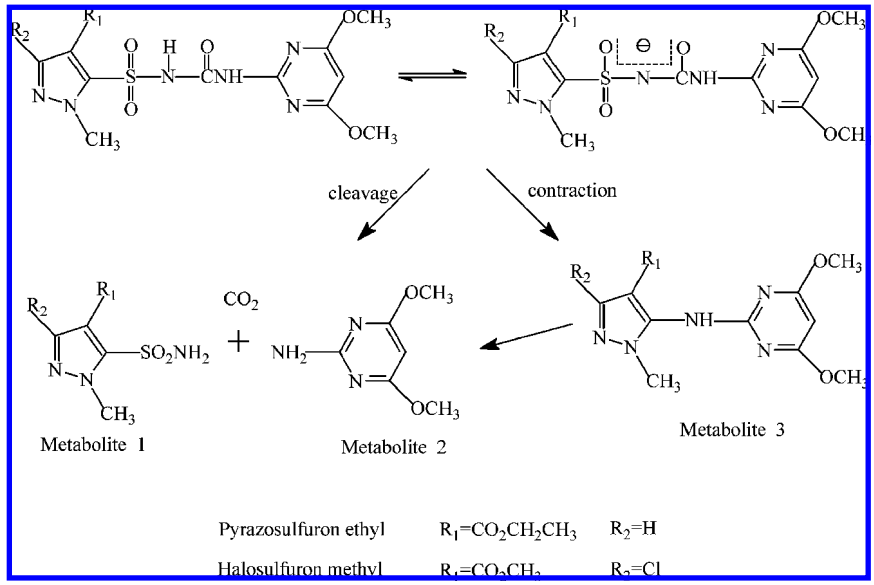

Figure 1. Molecular structures of PE and HM and their hydrolysis pathways.

bridge contraction and rearrangement, which results in high hydrolysis rates in alkaline conditions (*6, 12*). Under strong alkaline conditions, some sulfonylureas with ester groups are also subject to ester hydrolysis to form corresponding acids (*6, 9*).

A variety of minerals and organic materials usually exist in natural soil and aquatic systems. Minerals have been well-documented to affect the hydrolysis of sulfonylureas (*6, 13*). Organic matters in aquatic environments include polysaccharides and humic substances that contain a large amount of phenolic hydroxyl groups. The presence of these polyhydroxy compounds may induce an alcoholysis reaction (*14*) and thereby alter the environmental fates of pesticides. There are few reports on the effects of these natural hydroxyl compounds on sulfonylurea hydrolysis (*15*). Cyclodextrins are cyclic oligosaccharides consisting of six or more cyclically linked glucopyranose units with numerous primary and secondary hydroxyl groups. Previous studies have shown that cyclodextrins may catalyze the hydrolysis of the pesticides malathion (*16*) or prevent rimsulfuron hydrolysis and photolysis (*17*).

Pyrazosulfuron ethyl (PE) and halosulfuron methyl (HM) are two relatively new postemergence sulfonylurea herbicides. They share the same basic structure (**Figure 1**): a pyrazole ring linked to an identical pyrimidine through a sulfonylurea bridge. The only structural distinction of these two sulfonylurea herbicides lies in the substitutions on the pyrazole ring. This class of sulfonylureas does not include a triazinic and pyridinic ring (*6*). Therefore, some common degradation pathways occurring on sulfonylureas, such as O- and N-dealkylation of the group on the triazine ring or triazine ring opening to form a triuret (*18, 19*), would not be expected for PE and HM. Information pertaining to the metabolism or transformation of these two novel herbicides in the environment is poorly documented (*20*). To date, very few studies are available on their hydrolysis kinetics and mechanisms, especially for PE. Moreover, their hydrolysis products have not been fully investigated.

The objectives of this study are (i) to comprehensively investigate the stability of the herbicides PE and HM in aqueous solutions under different hydrolytic conditions including different pH values and temperatures, (ii) to characterize their hydrolysis mechanisms and pathways, (iii) to compare the distinct chemical hydrolysis processes of these two sulfonylureas, and (iv) to assess the potential effect of cyclodextrins on the transformation of PE and HM in aquatic environments.

MATERIALS AND METHODS

Chemicals. Standards of PE {ethyl 5-[(4,6-dimethoxypyrimidin-2-ylcarbamoyl)sulfamoyl]-1-methylpyrazole-4-carboxylate, purity 98%} and HM [methyl 3-chloro-5-(4,6-dimethoxypyrimidin-2-ylcarbamoyl-sulfamoyl)-1-methyl-pyrazole-4-carboxylate, purity 99%] were purchased from Chem Service (West Chester, PA). Stock solutions of these two sulfonylurea herbicides were prepared in acetonitrile. α-Cyclodextrin and β-cyclodextrin were obtained from Sigma-Aldrich (St. Louis, MO). All chemicals were used as received.

Experimental Systems. All aqueous solutions were prepared using high-purity deionized water (E-pure, Barnstead, Dubuque, IA). To avoid microbial degradation, all glassware and solutions were autoclaved prior to use.

The effect of pH on the kinetics of PE and HM hydrolysis was determined in aqueous buffer solutions of different pH values at 25 ± 0.5 °C. Aqueous buffer solutions (pH 3−10) were prepared according to ref *21*, using KCl and HCl for pH 3, acetate buffer for pH 5, phosphate buffer for pH 7, and borate buffer for pH 9 and 10. Stock solutions containing 1.0 mM PE or HM were spiked to buffer solutions in serum bottles, yielding initial herbicide concentrations of 50 μM. Bottles were capped with Teflon-faced butyl rubber septa and incubated at 25 ± 0.5 °C in the dark. At regular time intervals, aliquots were removed from each bottle, adjusted pH to 7, and stored at −20 °C until analysis via high-performance liquid chromatography (HPLC).

The effect of temperature on the rate of hydrolysis of PE and HM was determined in sterile aqueous buffer solutions at pH 3 and 9. The kinetic experiments were initiated by spiking stock solution of PE or HM to buffer solutions to generate initial herbicide concentrations of 50 μM and were then incubated at 15, 25, 35, and 45 °C in the dark. Aliquots were periodically sampled using the procedure described above. The activation energies of hydrolysis for PE and HM were calculated using the data obtained from this experiment.

To investigate the effect of cyclodextrins on sulfonylurea hydrolysis, PE and HM stock solutions were added into deionized water and pH 7 buffer solutions containing 1.0 or 5.0 mM cyclodextrins, respectively. The initial concentrations of herbicides were 50 μM. After 7 days of incubation in the dark at 25 ± 0.5 °C, the solutions were sampled as described above and analyzed by HPLC. Control experiments were concurrently performed in deionized water and buffer solution containing 50 μM PE or HM without cyclodextrin.

HPLC and LC/MS Analysis. The disappearance of PE and HM and appearance of their hydrolysis products were analyzed using an Agilent 1100 series HPLC/diode array detector (DAD) and LC/mass selective detector (MSD) equipped with an electrospray ionization (ESI) source (Agilent Technologies, Palo Alto, CA). Separation for HPLC/DAD analysis was performed using an Eclipse C18 column (250 mm

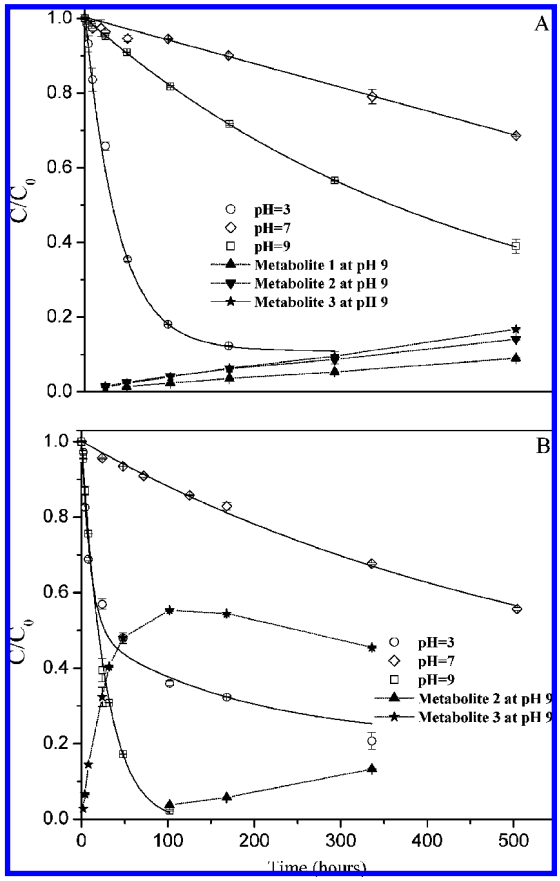

Figure 2. Example time courses for hydrolysis of sulfonylureas at 25 °C and pH 3, 7, and 9 buffer solutions: (A) PE and (B) HM. C_0 (50 μmol/L) is the initial concentration of herbicide in solution. The formations of metabolites 1−3 vs time in the aqueous solution at pH 9 are presented as relative values (chromatographic peak area for metabolite/peak area of herbicide at the initial concentration, C_0; the detector wavelength was 242 nm). Error bars represent standard deviations of triplicate samples.

× 4.6 mm i.d.; particle size, 5 μm). The mobile phase consisted of acetonitrile/water with 0.1% trifluoroacetic acid (60:40, v/v), the flow rate was 1.0 mL min^{-1}, and the detector wavelength was 242 nm. Under these conditions, the retention times for PE and HM were 6.3 and 7.4 min, respectively.

Analyses by LC/MSD were performed using the same chromatographic conditions described above, except that the flow rate was 0.8 mL min^{-1}. LC/MS total ion current (TIC) chromatograms were recorded between *m/z* 50 and 500 at a rate of 2 scans per second. Positive polarity ionization mode was operated to obtain mass spectra for the identification of hydrolysis products of PE and HM. The electrospray source parameters were optimized by infusion of analyte standard solutions. The operating conditions for ESI were as follows: capillary voltage, 4000 V for positive mode; drying gas (nitrogen) flow rate, 10 L min^{-1} at 350 °C; and nebulizer gas pressure, 60 psi.

RESULTS AND DISCUSSION

Acid- and Base-Catalyzed Hydrolysis Kinetics. Initial experiments focused on the hydrolysis kinetics of PE and HM in aqueous solutions of different pH values. Example time courses for hydrolysis of these two herbicides at pH 3, 7, and 9 are depicted in **Figure 2**, which represent their hydrolytic transformations in acidic, neutral, and basic media. As shown in **Figure 2**, the dissipation of PE and HM was slower at neutral pH than at acidic and basic pH. This result suggests that these two sulfonylureas are more susceptible to chemical hydrolysis in acidic and basic solutions than in neutral media.

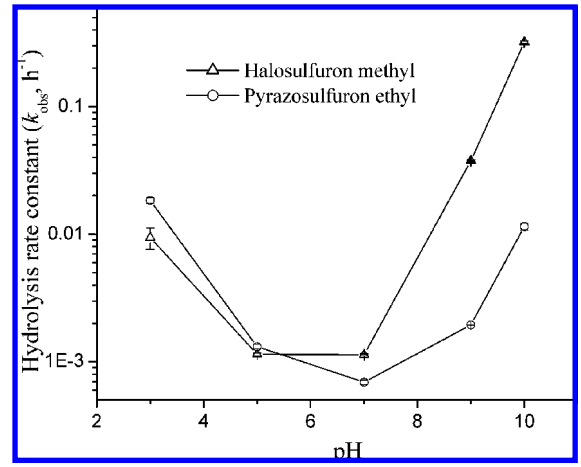

Figure 3. Hydrolysis rate constants of PE and HM in aqueous buffer solutions as a function of pH. Error bars represent standard deviations of means (triplicate samples).

Generally, the hydrolysis of pesticides is treated as a pseudo-first-order reaction (*22*). In the experiment, a pseudo-first-order kinetic model was applied for the sulfonylurea hydrolysis:

$$d[SU]/dt = -k_{obs}[SU] \quad (1)$$

Upon rearrangement and integration, eq 1 becomes

$$\ln([SU]) = -k_{obs}t + \ln([SU]_0) \quad (2)$$

where k_{obs} is the observed pseudo-first-order rate constant at a fixed pH, [SU] is the concentration of PE or HM, and $[SU]_0$ is the initial concentration of PE or HM. Values of k_{obs} were calculated from the slope of semilogarithmic plots of sulfonylurea concentration vs time using data collected over at least two half-lives (for acidic and basic solutions) and over one half-life (for neutral solutions). Actually, k_{obs} represents the sum of three separate reactions: the acid-catalyzed, neutral, and base-catalyzed hydrolysis (*23*). At a constant pH, k_{obs} can be expressed as:

$$k_{obs} = k_a[H^+] + k_n + k_b[OH^-] = k_a[H^+] + k_n + k_b(K_w/[H^+]) \quad (3)$$

where k_a, k_n, and k_b represent the rate constants for acid-catalyzed, neutral, and base-catalyzed hydrolysis reactions and K_w is the equilibrium constant for the dissociation of pure water.

To better demonstrate pH effects on hydrolysis, the logarithm of hydrolysis rate constants (k_{obs}) of PE and HM was plotted against the pH values (**Figure 3**). The hydrolytic dissipation of these two herbicides shows a similar tendency in the studied pH range (pH 3−10). The hydrolysis rates of both PE and HM decreased significantly from pH 3 to 7, then substantially increased at pH > 7. The hydrolysis half-lives of PE and HM at different pH values are available in the Supporting Information. The reaction rate constants for the acid-catalyzed, neutral, and base-catalyzed hydrolyses (k_a, k_n, and k_b) of PE and HM were estimated using nonlinear regression according to eq 3 (**Table 1**). The observed hydrolysis rate constants (k_{obs}) from different pH buffer solutions were well-described by eq 3 (r^2 > 0.99). These model-calculated kinetic parameters varied widely, which indicates that acid-catalyzed, neutral, and base-catalyzed hydrolyses of PE and HM are three totally different reactions resulting from different degradation mechanisms (*23*).

Table 1. Rate Constants for Acid-Catalyzed, Neutral-, and Based-Catalyzed Hydrolyses of the Sulfonylurea Herbicides PE and HM in Buffer Solutions (pH 3−10) at 25 °C

herbicides	hydrolysis rate constants		
	acid-catalyzed (k_a) (M^{-1} h^{-1})	neutral (k_n) (h^{-1})	based-catalyzed (k_b) (M^{-1} h^{-1})
PE	$1.75 \times 10^1 \pm 0.03 \times 10^1$	$9.01 \times 10^{-4} \pm 1.37 \times 10^{-4}$	$1.06 \times 10^2 \pm 0.03 \times 10^2$
HM	6.90 ± 3.35	$2.48 \times 10^{-3} \pm 1.72 \times 10^{-3}$	$3.17 \times 10^3 \pm 0.31 \times 10^3$

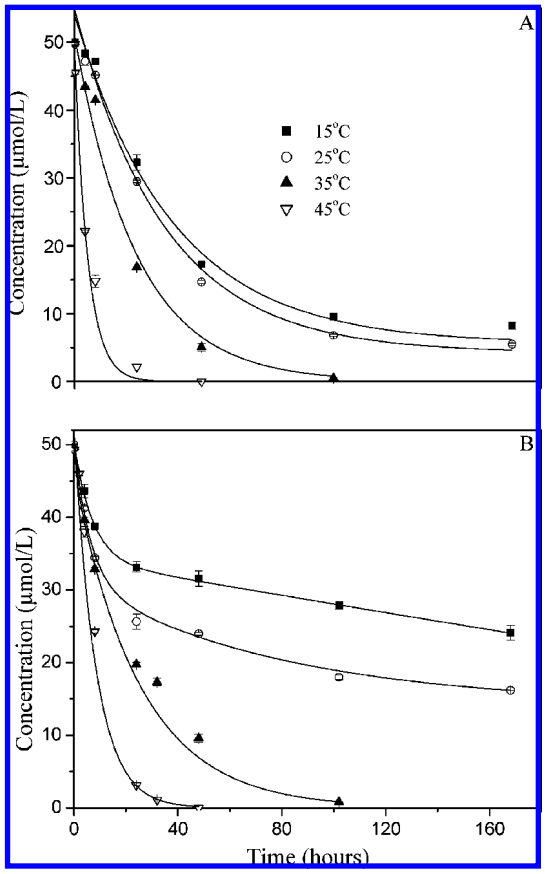

Figure 4. Example time courses for hydrolysis of sulfonylureas in pH 3 buffer solutions at different temperatures: (A) PE and (B) HM. Error bars represent standard deviations of triplicate samples.

Temperature Effects on Hydrolysis. Temperature generally plays an important role in hydrolysis of pesticides. Example time courses for hydrolysis (pH 3) of PE and HM at different temperatures are shown in **Figure 4**. Hydrolysis of these herbicides consistently increased with increasing temperature at a fixed pH. Hydrolysis of PE and HM followed pseudo-first-order kinetics for each temperature with correlation coefficients (r) of more than 0.90 (**Table 2**).

The Arrhenius equation offers a simple and direct method to characterize the effects of temperature into a mathematical relationship:

$$\ln k_{obs} = \ln A - E_a/RT \quad (4)$$

where A is called the preexponential factor, E_a is the activation energy, R is the universal gas constant, and T is the absolute temperature. The activation energies of PE and HM were calculated by fitting the hydrolysis rates (k_{obs}) to the Arrhenius equation (**Table 2**). The magnitude of activation energy corresponds to the effect of temperature on hydrolysis rate constants. The calculated values of the activation energy (55−110 kJ mol^{-1}) for PE and HM at pH 3 and 9 indicate that an increase of 10 °C accelerates the rate of hydrolysis by a factor of 2.2−4.7 at typical environmental temperatures (*23*). In these experiments, each 10 °C increase in temperature increased the average rate of PE hydrolysis by 2.4 times at pH 3 and 4.5 times at pH 9. For HM, the average rate of hydrolysis increased by 2.9 (pH 3) and 3.2 times (pH 9) with each 10 °C increase in temperature.

Hydrolysis Mechanism and Pathway. To elucidate the pathways of PE and HM hydrolysis, aliquots of hydrolysis solutions at different pH values were periodically withdrawn and monitored by HPLC/DAD and LC/MS. Representative HPLC/DAD chromatograms after the hydrolysis of PE and HM in acidic and basic solutions are shown in the Supporting Information (Figures 1S and 3S). Peak identification was performed by LC/MS. Prior to the identification of the hydrolysis products, PE and HM standards were run to verify chromatographic separation and mass spectra with desired fragmentations. In these hydrolysis experiments, three products of each sulfonylurea were characterized based on their mass spectra and retention times. The mass spectra (Figure 2S and 4S) and a description of the interpretation of fragmentation used to identify PE, HM, and their hydrolysis products are available in the Supporting Information.

For PE, two primary products were detected and identified in acidic and neutral solutions: 1-methyl-4-ethylcarboxylate pyrazolesulfonamide (metabolite 1) and 2-amino-4,6-dimethoxypyrimidine (metabolite 2) (**Figure 1**). The latter was also detected as a hydrolysis product for other sulfonylureas with a pyrimidine ring, for example, azimsulfuron (*7*) and rimsulfuron (*24*). The concentrations of these two products increased gradually with the dissipation of the corresponding parent compound. Like all sulfonylureas, the cleavage of the sulfonylurea bridge was a predominant hydrolysis pathway for PE, especially in acidic water and soils. In this case, the hydrolysis process occurs through an acid catalysis ($A_{AC}2$) mechanism involving a protonation of the carbonyl oxygen initially (*22*), producing carbon dioxide, the pyrazolesulfonamide, and pyrimidine amine (**Figure 1**). The mechanism differs from the normal behavior observed for carbonate derivatives, which exhibit base catalysis ($B_{AC}2$) (*22*). Generally, sulfonylureas are weak acids and have pK_a values ranging from 3 to 5. The sulfonyl group may significantly enhance the acidity of the proton on the adjacent nitrogen atom. Deprotonation of the sulfonylurea bridge results in a distribution of the negative charge throughout the sulfonylurea moiety (**Figure 1**), which largely deactivates the direct nucleophilic attack of H_2O or OH to the carbonyl group. The transformation process pertaining to the cleavage of the sulfonylurea bridge is relatively slow under neutral and basic conditions as compared to acidic media, which is similar to previous observations of the hydrolysis of azimsulfuron (*7*).

In addition to the cleavage of the sulfonylurea bridge, another transformation mechanism of PE is the contraction of the sulfonylurea bridge in alkaline solutions, yielding metabolite 3 (**Figure 1**). This contraction mechanism is suggested to proceed through an intramolecular S_NAr reaction (*25*). Unlike the cleavage of sulfonylurea bridge, the contraction only occurs in

Table 2. Hydrolysis Pseudo-First-Order Rate Constants (h^{-1}) and Activation Energies (kJ mol^{-1}) of Sulfonylurea Herbicides PE and HM in Buffer Solutions (pH 3 and 9) at Different Temperatures

	PE		HM	
temperature	pH 3	pH 9	pH 3	pH 9
15 °C	$1.76 \times 10^{-2} \pm 0.19 \times 10^{-2}$	$3.57 \times 10^{-4} \pm 0.19 \times 10^{-4}$	$4.24 \times 10^{-3} \pm 0.75 \times 10^{-3}$	$8.22 \times 10^{-3} \pm 0.16 \times 10^{-3}$
25 °C	$1.99 \times 10^{-2} \pm 0.20 \times 10^{-2}$	$1.95 \times 10^{-3} \pm 0.01 \times 10^{-3}$	$9.40 \times 10^{-3} \pm 1.78 \times 10^{-3}$	$3.76 \times 10^{-2} \pm 0.06 \times 10^{-2}$
35 °C	$4.27 \times 10^{-2} \pm 0.32 \times 10^{-2}$	$1.04 \times 10^{-2} \pm 0.01 \times 10^{-2}$	$3.50 \times 10^{-2} \pm 0.18 \times 10^{-2}$	$1.26 \times 10^{-1} \pm 0.06 \times 10^{-1}$
45 °C	$1.69 \times 10^{-1} \pm 0.11 \times 10^{-1}$	$2.91 \times 10^{-2} \pm 0.04 \times 10^{-2}$	$9.39 \times 10^{-2} \pm 0.70 \times 10^{-2}$	$2.16 \times 10^{-1} \pm 0.24 \times 10^{-1}$
activation energy	56.8 ± 16.2	113.7 ± 6.7	80.7 ± 6.1	84.4 ± 10.0

some sulfonylureas, indicating that this transformation is structurally dependent. Example time courses for the formation of three hydrolysis products of PE in the pH 9 buffer solution are represented in **Figure 2**A. The decrease in concentration of PE was accompanied by a simultaneous increase of all three products at pH 9, suggesting that the cleavage and contraction of PE's sulfonylurea bridge occur simultaneously in alkaline solutions.

Similarly, a cleavage of HM's sulfonylurea bridge was observed in acid and neutral aqueous buffer solutions (pH ≤ 7), producing carbon dioxide and the corresponding pyrazole-sulfonamide and pyrimidine amine (metabolites 1 and 2 in **Figure 1**). Unlike PE, however, only the contraction product (metabolite 3) was detected shortly after HM was spiked to basic solutions (**Figure 2**B and Figure S3 of the Supporting Information). This result suggests that the cleavage of HM's sulfonylurea bridge is insignificant and that the bridge contraction is a predominant hydrolysis mechanism for HM in basic solution. The maximum concentration of the contraction product was observed when HM had completely disappeared (**Figure 2**B). The concentration of the contraction product then decreased gradually, with a concurrent gradual increase in the pyrimidine amine (metabolite 2). This result indicates that the contraction product of HM is not stable and it may decompose to its corresponding products, for example, pyrimidine amine, via further hydrolysis (**Figure 1**).

Although PE and HM have very similar structures, their hydrolysis rates in alkaline solutions are markedly different (**Figure 3**). The rate constant of base-catalyzed hydrolysis for HM is approximately 30-fold greater than that for PE (**Table 1**). This difference may be attributable to a minor structural distinction in the pyrazole ring. Pyrazole is an electron-poor heterocycle (electrophilic group), which may lead to the bridge contraction of sulfonylureas under basic conditions via a five-member transition state (*7, 25*). The sulfonylurea HM contains a chlorine on the pyrazole ring, which is a strong electron-withdrawing group that enhances the electrophilicity of HM's pyrazole ring. The increase in electrophilicity will favor the occurrence of the five-member transition state in the basic hydrolytic process of HM and thereby facilitate its bridge contraction. The difference in substitutions on the pyrazole ring in PE (H rather than Cl) makes PE less electrophilic and less susceptible to bridge contraction than HM. Therefore, the hydrolysis rates of HM were much higher than those of PE in alkaline solutions.

Saponification reactions often occur in some sulfonylureas with ester groups under alkaline conditions (*6, 26*). Although the saponification reactions related to the ester groups present in PE and HM were not observed in our experimental systems (pH ≤ 10), the hydrolysis pathway can not be neglected, especially in strong alkaline solutions (pH > 10) (*6, 9*). Collectively, both sulfonylurea herbicides may decompose to small molecular weight products through chemical hydrolysis reactions (**Figure 1**). The herbicidal activity and potential environmental effects of these daughter products should be considered to provide a better understanding of the environmental effects of these herbicides.

Effect of Cyclodextrins on Hydrolysis. A large number of polyhydroxy molecules such as polysaccharides, polyphenols, and humic substances exist in aqueous and soil environments. These components may react with sulfonylureas to form transformation products not observed in pure water (*14*) and thereby impact the herbicide hydrolysis. The effect of cyclodextrin on the hydrolysis of PE and HM in deionized water and buffer solutions is summarized in **Figure 5**. Results show that the presence of either α- or β-cyclodextrin did not promote or decelerate the dissipation of either PE or HM in buffer solutions. In addition, no extra products were detected in the experimental system, suggesting that no nonhydrolysis reactions for PE and HM occurred in pH 7 buffer solution.

In unbuffered deionized water, the dissipation of PE was relatively rapid in the presence of β-cyclodextrin (**Figure 5**), which may be attributable to a slight decrease in pH after the addition of β-cyclodextrin. Only hydrolysis products were detected in the control solution (without cyclodextrin addi-

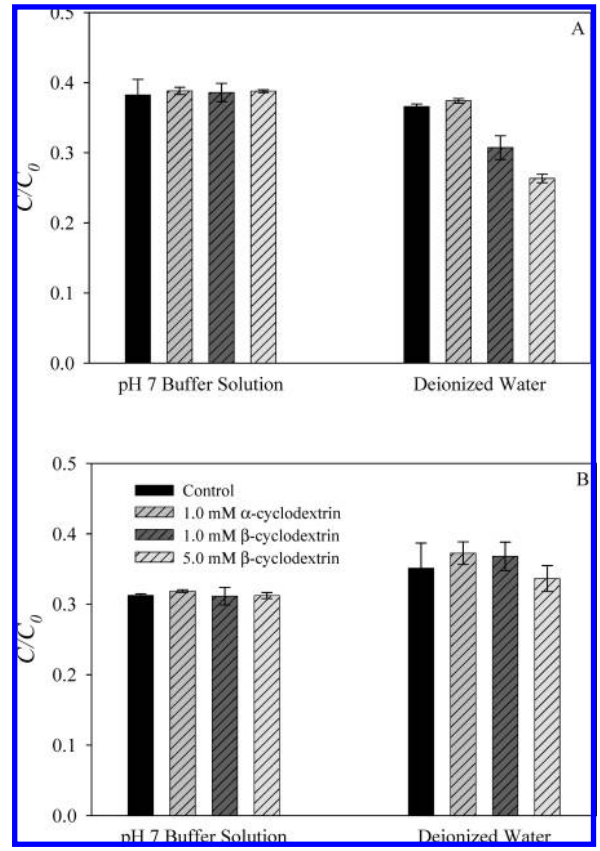

Figure 5. Effect of cyclodextrins on the hydrolysis of sulfonylureas after 7 days of incubation at 25 ± 0.5 °C: (A) PE and (B) HM. C_0 (50 μmol/L) is the initial concentration of two herbicides in aqueous solutions.

tion) and in the sulfonylurea unbuffered solutions with α- or β-cyclodextrin. These results suggested that cyclodextrin would not react with the sulfonylureas in unbuffered deionized water.

Cyclodextrin can reversibly host a variety of guest molecules to form inclusion complexes by noncovalent interaction. Therefore, there is interest in incorporating cyclodextrin into insoluble materials, for example, zeolite (*17*) and silica (*27*), to adsorb pesticide residues for the treatment of drinking water sources. Whereas cyclodextrin has been reported to affect the hydrolysis of some pesticides (*16, 17*), our results suggest that cyclodextrin is not expected to react with PE and HM in aqueous solutions, providing very useful information for the further evaluation of using cyclodextrin-coated sorbents to remove pesticide residues from contaminated water.

Supporting Information Available: Hydrolysis half-lives of PE and HM at different pH values, representative HPLC chromatograms of PE and HM after hydrolysis, electrospray LC/MS mass spectra, and a description concerning identification of hydrolysis products. This material is available free of charge via the Internet at http://pubs.acs.org.

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