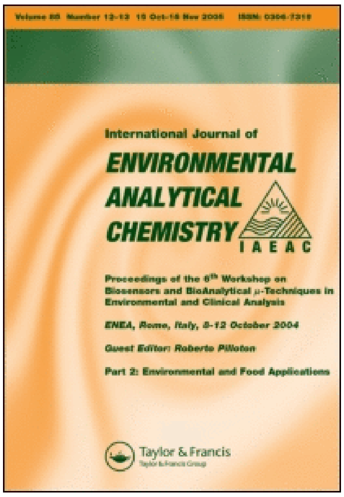

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ALKALINE AND NEUTRAL HYDROLYSIS OF FOUR PHENYLUREA HERBICIDES

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The kinetics of hydrolysis of four phenylurea herbicides – fenuron, monuron, diuron and chloroxuron – were measured in aqueous alkaline solutions at temperatures of 64°C and 84°C and extrapolated to 25°C. At hydroxide concentrations $\geq 8.6 \times 10^{-4}$ mol l^{-1}, alkaline hydrolysis dominates but the reaction does not obey second-order kinetics and approaches a maximum value at concentrations > 0.1 mol l^{-1}. The kinetic data support a mechanism of reaction proposed previously for the alkaline hydrolysis of trichloro- and trifluoroacetanilides. The mechanism is a hydroxide-ion-promoted equilibrium formation of a reactive tetrahedral intermediate anion that can either revert to the starting compound, decompose to products, or react with a second hydroxide to form a dianion prior to decomposition to products. Statistical analysis of the data suggests that the break-down of the reactive intermediate proceeds entirely via the path in which a second hydroxide removes a proton from the intermediate to yield a dianion that decomposes, whereas the path in which the intermediate breaks down without the assistance of OH^- is of no kinetic importance, even at hydroxide concentrations as low as 0.00086 mol l^{-1}. Our hydrolysis rate constant measurements suggest that neutral hydrolysis is a major route of environmental degradation of the herbicides. The half-lives in years of the four ureas at 25°C and pH 7 are estimated to be 89 for fenuron, 66 for monuron, 41 for diuron, and 41 for chloroxuron.

KEY WORDS: Phenylurea herbicides, fenuron, monuron, diuron, chloroxuron hydrolysis.

INTRODUCTION

Fenuron, monuron, diuron, and chloroxuron are four members of a group of aryl urea compounds used as herbicides. At low rates of application they display selective control of germinating broadleaf weeds and grasses in crops such as cotton and alfalfa, but the largest quantity used is at a high rate of application for nonselective (total) weed control on highway rights-of-way and for landscape maintenance. As a class, urea herbicides are relatively persistent in soils and this persistence has been attributed to resistance to both biological and abiotic degradation[1]. In a well water monitoring study covering the 20 year period of 1971–1991, the U.S. Environmental Protection Agency (EPA) found diuron in some ground waters at concentrations of 1–3 µg l^{-1}. In June 1992, diuron also was detected at concentrations of 1–3 µg l^{-1} in a surface water sample from the Meuse River (Belgium/The Netherlands)[3]. The amide bond of the urea herbicides is considered stable except under extreme acid or alkaline pH. However, abiotic hydrolysis may play an important role in the degradation of urea herbicides in underground water where

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residence time may be measured in decades. In this study, the neutral and alkaline hydrolysis of four urea herbicides was investigated in a laboratory setting.

MATERIALS AND METHODS

Equipment

A Model 332 Beckman high pressure liquid chromatograph equipped with a Model 164 variable wavelength UV detector set at 240 nm was used to monitor the disappearance of the phenylureas. The hydrolysate was analyzed on an Ultrasphere ODS 5 μm, 4.6 mm × 250 mm column. The mobile phase was acetonitrile/water 60/40 for analysis of monuron and fenuron and 70/30 for analysis of diuron and chloroxuron.

Chemicals

Fenuron and monuron were obtained from Aldrich Chemical Company (Milwaukee, Wisconsin USA). Diuron and chloroxuron were obtained from the U.S. EPA Chemicals Repository (Research Triangle Park, North Carolina USA). Their purity ranged from 98.5 to 99.9%. The structural formulae are shown in Figure 1. The acetonitrile (HPLC Grade) was obtained from the Merck Company (Germany). Sodium hydroxide (purity 98.4%) was obtained from Fisher Scientific (Philadelphia, Pennsylvania USA).

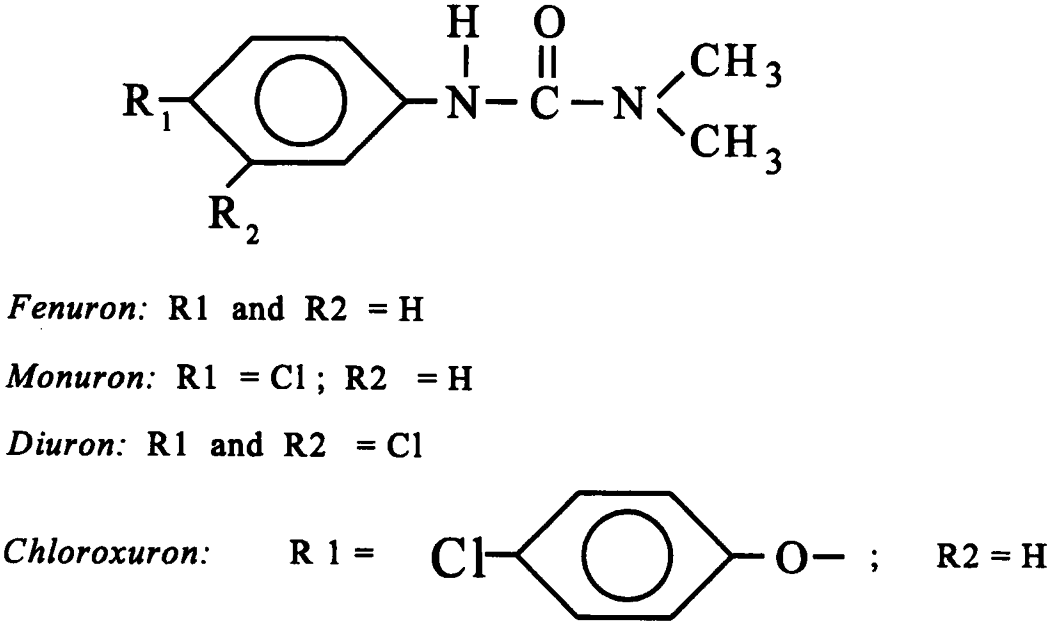

Figure 1 Chemical structure of the phenylurea herbicides.

Kinetic experiments

Aqueous solutions of sodium hydroxide that ranged in concentration from 8.6×10^{-4} to 4.5×10^{-1} mol l^{-1} were prepared by adding weighed amounts of solid sodium hydroxide to distilled water. The exact molarity was determined by titration against hydrochloric acid of known molarity. Solutions of the phenylureas (3–6 μg l^{-1}) for the hydrolysis experiments were prepared by adding the standardized solutions of sodium hydroxide to the weighed urea. This range of experimental concentrations for the ureas ensured a large excess of hydroxide ion present and produced pseudo first-order kinetics for their degradation. To perform a hydrolysis rate study, aliquots of these alkaline-urea solutions were transferred to 1-ml glass ampules and flamesealed. Typically, 12 "rate point" tubes were prepared for each experiment and incubated together in a thermostated oven with temperature controlled to ±1.6°C. The degradation of each herbicide was monitored over time by sacrificing individual ampules and measuring the amount of herbicide remaining. Prior to the HPLC analysis of the ampule samples, the hydrolyzate was adjusted to pH 6–7 by adding a predetermined amount of 1 mol l^{-1} HCl and 0.5 mol l^{-1} KH_2PO_4 to quench the reaction.

RESULTS AND DISCUSSION

Preliminary experiments confirmed the hydrolysis reaction was first order in herbicide concentration and a minimal rate law, neglecting any acid-promoted hydrolysis, was written

$$-\frac{d[F]}{dt} = (\Phi[OH^-] + k_n)\,[F] = k_{obs}[F] \qquad (1)$$

where [F] is the herbicide concentration, $\Phi[OH^-]$ is a function of the dependence of the reaction rate on hydroxide ion, k_n is the neutral hydrolysis rate constant, and k_{obs} is the observed reaction rate constant (pseudo first-order hydrolysis rate constant) at any specific $[OH^-]$ and temperature. Integration of this equation from time t_o to time t of an experimental measurement yields:

$$\ln[F]/[F_o] = -k_{obs}t \qquad (2)$$

Thus, k_{obs} is the negative slope of the data line plotted according to equation 2, where the ratio $[F]/[F_o]$ is the measured fraction of herbicide remaining at any time t. For convenience in plotting, the ratio was multiplied by 100 to give %F remaining and ln(%F remaining) was plotted against time. A typical plot is shown in Figure 2 for fenuron. To determine the contribution of the neutral hydrolysis process (k_n), hydrolysis rates were also measured in unbuffered, distilled, deionized and autoclaved water. The pH of this system was slightly below 7. The possible effect of salt on the hydrolysis rate was checked by performing some of the hydrolyses in distilled and deionized water made 0.1 mol l^{-1} in NaCl. Comparative data from two of these hydrolysis experiments are plotted in Figure 3, one experiment with and one without added sodium chloride. Significant salt effects were not observed as indicated by the similar slopes of the two lines.

The observed hydrolysis rate constants were corrected for the contribution of the neutral process ($k_{corr} = k_{obs} - k_n$), to obtain the pseudo-first order rate constants for

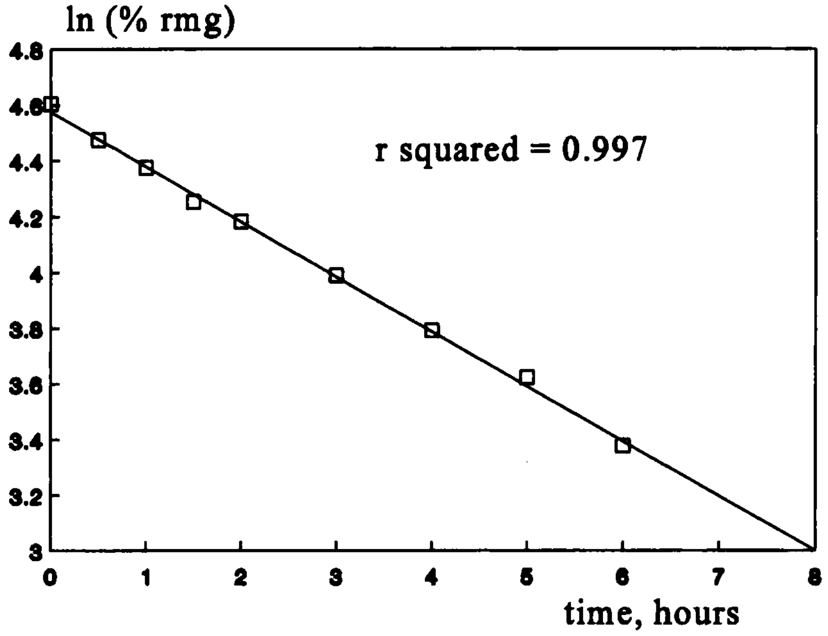

Figure 2 A typical plot of ln(percentage remaining) vs time for the hydrolysis of phenylureas.

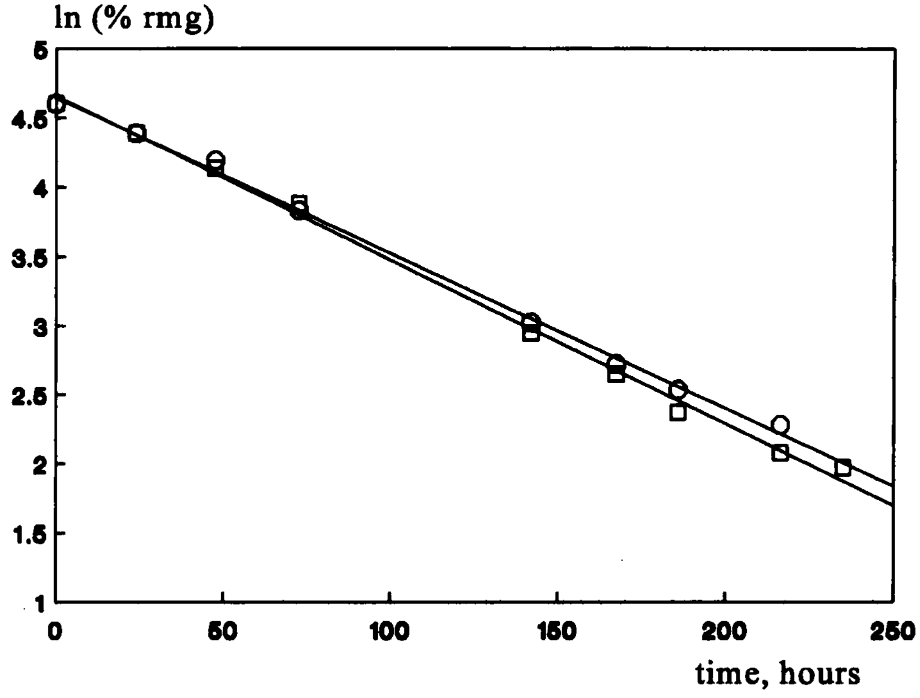

Figure 3 Plot of ln(percentage remaining) vs time for the hydrolysis of fenuron in distilled water (-○-) and 0.1 mol l^{-1} NaCl solution (-□-) at 85°C.

the alkaline hydrolysis process. The measured neutral (k_n) and specific hydroxide ion hydrolysis rate constants (k_{corr}) for fenuron, monuron, diuron, and chloroxuron are given in Table 1. At the lowest experimental hydroxide concentrations (0.00086 and 0.00091 mol l^{-1}), neutral hydrolysis accounts for 50–90% of the overall hydrolysis. The contribution of specific hydroxide ion hydrolysis below these concentrations quickly approaches zero. For all the hydrolysis experiments, the squared correlation coefficients of linear regressions of ln(%F remaining) against time were 0.950 or higher with the majority being greater than 0.990.

The relationship between k_{corr} and $[OH^-]$ was found to be hyperbolic over the range of $[OH^-]$ covered (Figure 4A). The log-log plot of k_{obs} against $[OH^-]$ (Figure 4B) shows clearly the nonlinear dependence of the hydrolysis on hydroxide ion. Nonlinear dependence of the experimental pseudo-first-order hydrolysis rate constant for the base hydrolysis of amides has been attributed to the formation of a tetrahedral intermediate and a change in the rate-determining step[4]. Similar hyperbolic dependence of hydrolysis on $[OH^-]$ has been reported for trifluoroacetanilides[5,6], para substitued acetanilides[7,8], meta and para substituted formanilides[9], and the organophosphorothioate insecticide chlorpyrifos[10].

The scheme in Figure 5 summarizes theoretically feasible pathways for the alkaline hydrolysis of phenylureas. The figure is based on previously described hydrolysis mechanisms of the secondary amide bond[5-9,11-14]. The hydroxide-ion-mediated hydrolysis of the amidic bond is proposed as a two-step process in which the tetrahedral intermediate (FH^-) formed by addition of hydroxide to the carbonyl carbon can either revert back to starting material or proceed to products[13]. If FH^- is not sufficiently reactive, the assistance of a second hydroxide may be required to remove a proton from FH^- to yield the dianion FH^{2-}, which breaks down to the final products. The pK_a values for fenuron, monuron, diuron and chloroxuron at 25°C are 9.7, 9.1, 8.2 and 9.1, respectively[15]. Consequently, under alkaline conditions significant amounts of the urea herbicides should exist in solution as the conjugated base F^-. Elimination of dimethylamine from F^- to form the phenylisocyanate (not shown) is unlikely because dimethyl amine is a poor leaving group. Theoretically, F^- could hydrolyze to products via step k_4 $[OH^-]$; however, most authors agree that the activation energy of this step is too high to make it a feasible pathway, and F^- should be considered an unreactive side product[5,9,14].

This seems likely for at least three reasons. First, in some secondary amides where the hydrogen on nitrogen is not acidic enough to make K_a important for hydrolysis, and in the hydrolysis of tertiary amides where this step is excluded, hydrolysis takes place readily; therefore, the formation of F^- is not necessary for hydrolysis. Second, conjugation in the anion F^- is expected to increase the double bond character of the C–N bond compared to the primary compound and, thereby, stabilize F^- against cleavage. Third, if most of the reaction flux proceeded via k_4 $[OH^-]$ step, the reaction rate, as it will become apparent from the considerations below, would change from first to second order in hydroxide, which contradicts the present experimental data. Similarly, we can exclude the k_5 step, suggested previously for acetanilides[6].

Use of the steady-state approximation for the concentration of the tetrahedral intermediate leads to the following expression for the pseudo-first-order rate constant in unbuffered solutions:

$$k_{alk} = \frac{k_1 K_w}{K_a + [H^+]} \, \frac{k_2 + k_3[OH^-]}{k_{-1} + k_2 + k_3[OH^-]} \qquad (3)$$

where k_{alk} is the specific $[OH^-]$ -mediated pseudo-first-order hydrolysis and corresponds to k_{corr} in Table 1.

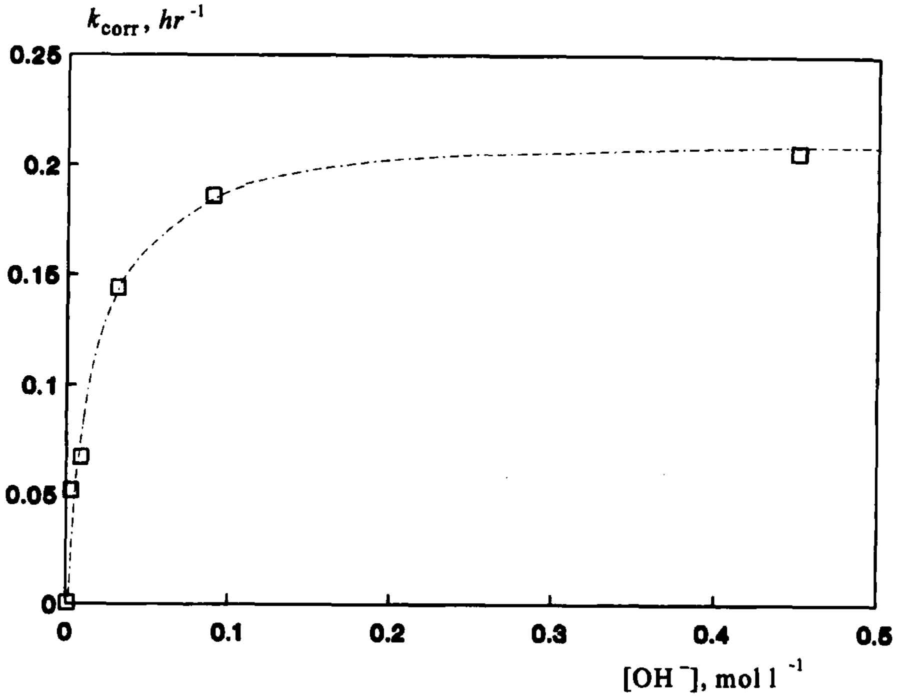

Figure 4A Plot of k_{corr} for the hydrolysis of fenuron at 85°C. The dotted line is the regression line (range of pH ≈ 9–13).

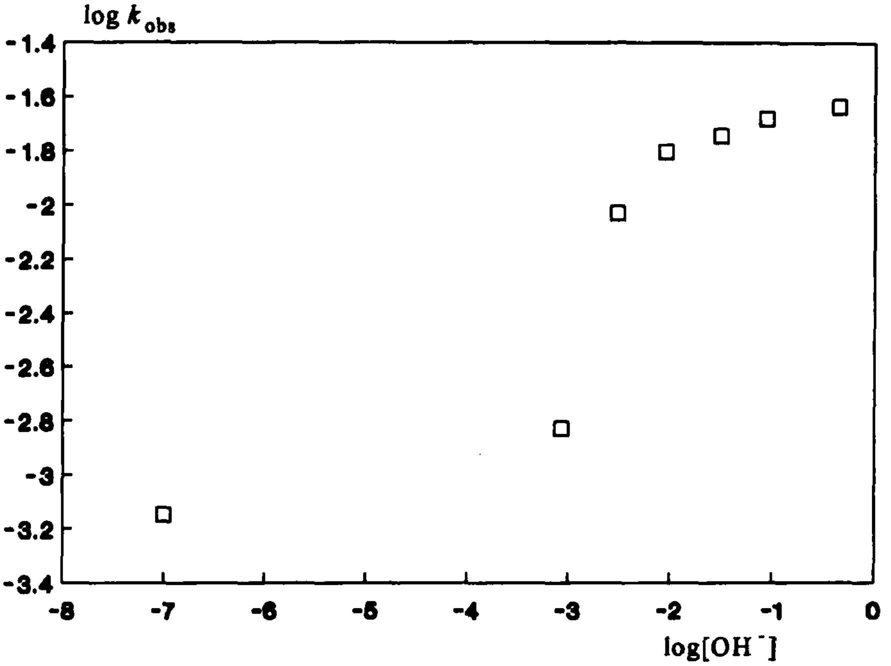

Figure 4B Plot of log(k_{obs}) against log[OH⁻] for the hydrolysis of fenuron at 64°C.

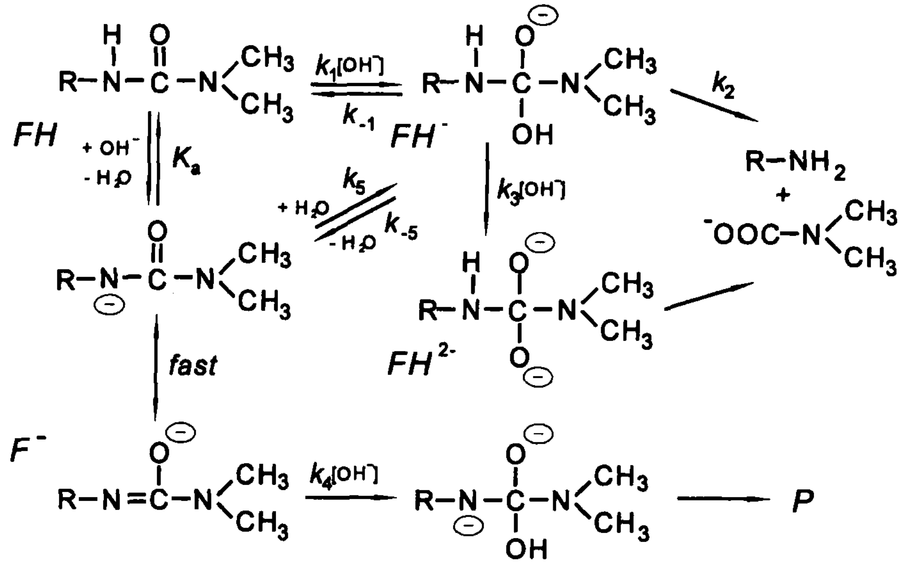

Figure 5 Theoretically possible paths for the hydroxide ion-promoted hydrolysis of phenylureas.

The pK_a values ($-\log K_a$) stated previously for fenuron, monuron, diuron and chloroxuron at 25°C mean that at this temperature $K_a \gg [H^+]$ even at the lowest experimental hydroxide concentration (0.00086 mol l^{-1}, ≈ pH 11). The $[H^+]$ can be calculated at elevated temperatures, but at least two factors determine the change in pK_a values of the ureas at elevated temperatures: (1) solvation of the hydrogen ion decreases (increase in pK_a); (2) higher temperatures weaken the N–H bond (decrease in pK_a). The net change in pK_a thus depends upon the relative importance of these two factors.

The pK_a values of the phenylureas were inferred from the pK_a values of the hydrochloride salt of alpha-propyl-2-methyl-propionanilide. The pK_a values of the propioanilide were determined at 25, 40, 60, 80 and 95°C by titration of the solutions with 0.1 mol l^{-1} sodium hydroxide[16]. The pK_a of the side-chain amine-hydrochloride was observed to drop from 7.94 at 25°C to 6.6 at 95°C, while the pK_a of the amidic bond of the propionanilide dropped from 9.8 at 25°C (fenuron amide pK_a =9.7) to approximately 8.1 at 95°C . The amidic bond of the propioanilide is similar to the amidic bond of the phenylureas. The authors concluded that the drop in pK_a with increase in temperature was equal to the decrease in pH with increase in temperature. Given the structural similarity of propionanilide and phenylureas, the pK_a of the ureas should decrease by approximately 1.5 units at 85°C and by approximately 1 unit at 65°C. At the higher temperatures, $K_a \gg [H^+]$ is still valid and equation (3) can be simplified by excluding $[H^+]$ from the denominator of the first term:

$$k_{\text{alk}} = \frac{k_1 K_w}{K_a} \frac{k_2 + k_3[\text{OH}^-]}{k_{-1} + k_2 + k_3[\text{OH}^-]} \tag{4}$$

Rearranging equation 4 for statistical analysis,

$$k_{\text{alk}} = \frac{k_1 K_w}{K_a} \frac{k_2/k_3 + [\text{OH}^-]}{(k_{-1} + k_2)/k_3 + [\text{OH}^-]} \tag{5}$$

Table 1 The neutral and specific hydroxide ion hydrolysis rate constants for fenuron, monuron, diuron and chloroxuron.

$10^4[OH^-]^a$	$10^4 k_{corr}$, (hr^{-1})
Fenuron	
64 ± 1°C ($k_n = 7.1 \times 10^{-4}\ hr^{-1}$)^b	
8.6	6.7
30.4	86.2
90.4	150.0
311.0	173.0
880.0	201.0
4510.0	224.0
84 ± 1°C ($k_n = 112.0 \times 10^{-4}\ hr^{-1}$)	
8.6	3.9
30.4	518.0
90.4	670.0
311.0	1440.0
902.0	1860.0
4510.0	2060.0
Monuron	
64 ± 1°C ($k_n = 5.4 \times 10^{-4}\ hr^{-1}$)	
8.6	6.4
29.3	69.2
90.4	127.0
311.0	136.0
902.0	160.0
4500.0	189.0
84 ± 1°C ($k_n = 71.0 \times 10^{-4}\ hr^{-1}$)	
8.6	5.5
29.3	444.0
90.4	865.0
311.0	1410.0
902.0	1430.0
4500.0	1500.0
Diuron	
64 ± 1°C ($k_n = 5.8 \times 10^{-4}\ hr^{-1}$)	
9.1	4.8
30.4	22.2
90.1	99.0
311.0	118.0
910.0	124.0
4480.0	143.0
84 ± 1°C ($k_n = 61.0 \times 10^{-4}\ hr^{-1}$)	
9.1	48.0
30.4	202.0
90.1	759.0
311.0	1283.0
910.0	1097.0
4480.0	1421.0

Table 1 *(Continued).*

$10^4[OH^-]^a$	10^4k_{corr}, (hr^{-1})
Chloroxuron	
64 ± 1°C ($k_n = 6.1 \times 10^{-4}$ hr^{-1})	
9.1	6.5
26.2	50.5
90.4	71.4
263.0	121.0
910.0	159.0
4520.0	183.0
84 ± 1°C ($k_n = 66.0 \times 10^{-4}$ hr^{-1})	
9.1	5.5
26.2	229.0
90.4	557.0
263.0	1320.0
910.0	1420.0
4520.0	1520.0

(a) mol l^{-1}, The pH can calculated from the relationship pH = pK_w − pOH. K_w varies with temperature and follows the relation log K_w = −6013.79/T − 23.6521 log T + 64.7013 (ref. 17).

(b) k_n is the neutral hydrolysis rate constant and $k_{corr} = k_{obs} - k_n$; r squared of regression line of plot of ln(% urea remaining) against time ranged from 0.951 to 0.999.

The Levenberg-Marquardt algorithm for nonlinear regression was used to calculate k_1/K_a, k_2/k_3 and $(k_{-1} + k_2)/k_3$. Analysis showed that the experimental data fitted the above equation well with the standard errors not exceeding 10% of the estimate for the parameter k_1K_w/K_a and 30% of the estimate for the parameter $(k_{-1} + k_3)/k_3$. Most interestingly, the ratio k_2/k_3 for all the series was in the 10^{-8}–10^{-11} range. The very small value of the ratio k_2/k_3 indicated that degradation defined by k_2 was insignificant and that hydrolysis was controlled by k_3. Equation 5 was, therefore, simplified by eliminating k_2:

$$k_{alk} = \frac{k_1K_w}{K_a}\,\frac{[OH^-]}{k_{-1}/k_3 + [OH^-]} \qquad (6)$$

From a mathematical point of view, equations (5) and (6) are similar, with k_{-1}/k_3 of (6) being equivalent to $(k_{-1} + k_2)/k_3$ of (5). The results from analysis of equation 6 by the Levenberg-Marquardt algorithm supported the simplification. The coefficients k_1K_w/K_a and k_{-1}/k_3 were almost identical to the respective coefficients calculated from equation (5), and even the standard errors were similar. Calculated values of k_1K_w/K_a and k_{-1}/k_3, as well as the squared correlation coefficients from the nonlinear regression, are given in Table 2. It is obvious that, at the hydroxide concentration where the rate has become constant, $k_3[OH^-] >> k_{-1}$ and $k_{alk} = k_1K_w/K_a = k_{max}$ and formation of the tetrahedral

Table 2 Reaction rate parameters for the alkaline hydrolysis of phenylureas, calculated using the Marquardt-Levenberg algorithm for nonlinear regression.

	k_1K_w/K_a		k_{-1}/k_3		k_1/K_a	*r squared*
	Estimate	*Standard Error*	*Estimate*	*Standard Error*		
Fenuron						
64°C	0.0219	0.0013	0.0054	0.0015	1.95×10^{11}	0.962
84°C	0.2153	0.0110	0.0159	0.0033	7.45×10^{11}	0.983
Monuron						
64°C	0.0178	0.0012	0.0052	0.0017	1.59×10^{11}	0.952
84°C	0.1582	0.0084	0.0073	0.0018	5.47×10^{11}	0.974
Diuron						
64°C	0.0144	0.0012	0.0075	0.0028	1.28×10^{11}	0.940
84°C	0.1413	0.0133	0.0091	0.0037	4.89×10^{11}	0.934
Chloroxuron						
64°C	0.0184	0.0009	0.0125	0.0026	1.64×10^{11}	0.980
84°C	0.1632	0.0127	0.0126	0.0040	5.65×10^{11}	0.962

intermediate (k_1) is the rate determining step. In the linear portion of the rate profile (Figure 4B), $k_{-1} >> k_3[OH^-]$, and $k_{alk} \approx k_1K_wk_3\,[OH^-]/K_ak_{-1}$.

An equation identical to equation 3 has been reported for the alkaline hydrolysis of trichloroacetanilide and trifluoroacetanilide[7]. However, contrary to our phenylurea hydrolysis data where the rate is proportional to the hydroxide ion concentration over just one order of magnitude, the hydrolysis of the acetanilides were proportional to hydroxide ion over four orders of magnitude (10^{-2}–10^{-6}). The pK_a values for trichloro- and trifluoroacetanilide were 9.51 and 9.98, respectively at 25°C. At the lower hydroxide concentrations where $[H^+] >> K_a$, k_2 was assumed to be $>> k_3[OH^-]$ and equation 3 reduces to $k_1k_2[OH^-]/(k_{-1} + k_2)$ with the slope equal to $k_{alk} = k_1k_2/(k_{-1} + k_2)$. Based on these assumptions, Eriksson and Holst calculated the parameters k_2/k_{-1} and k_3/k_{-1}. The fact that the pH-rate plot for the acetanilides maintained linearity up to 10^{-2} mol l^{-1} in hydroxide, where $[H^+] << K_a$, was not explained.

In our studies, fenuron (0 chlorine) exhibited the fastest hydrolysis rate under all conditions, followed by monuron (1 chlorine) and diuron (2 chlorines). The order of decreasing reactivity of the ureas matches the order of decrease of their pKa values (increasing acidity). This is an indication that the rate of hydrolysis of the ureas is controlled to a large extent by the stability of the nonreactive conjugate base (F^- in Figure 5). An increase in stability of the anion shifts the equilibrium to the ionic form and decreases the fraction of the reactive, nonionized form of the urea available to form the tetrahedral intermediate via k_1. This is evident in equation 6 where the hydrolysis rate is inversely related to K_a. The stability of the urea anions is explained by the differences in conjugation (resonance) effect of the phenyl ring-N=C–O^- bonds (see Figure 5). The chlorine atoms have a positive conjugation effect and, therefore, they contribute positively to the stabilization of F^- and determine the order of reactivity: fenuron > monuron = chloroxuron > diuron. The hydrolysis rate of chloroxuron agrees with this structure-reactivity relationship since the 4-chlorphenoxy- group has about the same conjugation effect as a chlorine. The hydrolysis rate of this compound is similar to that of the mono-chlorine-substituted monuron.

Although the reaction rates in our study were measured at two temperatures, it was not possible to calculate activation energies of separate reaction steps because the values of individual rate constants of those steps were not known. However, the activation energies at two extreme points were calculated... the first where the reaction rate leveled off (ie. at k_{max}) and the second when the reaction rate was directly proportional to the hydroxide concentration in the linear portion of the rate profile (Table 3). In the first case, the activation energy was determined by the values of the activation energies of the k_1 and K_a processes ($k_{alk} = k_1K_w/K_a$). In the second case, it was determined by activation energies of the k_1, k_{-1}, k_3 and K_a steps ($k_{alk} = k_1K_wk_3[OH^-]/K_a k_{-1}$). These values plus the activation energies for neutral hydrolysis are reported in Table 3. The k_n activation energies in Table 3 were used to extrapolate the neutral hydrolysis rate constants to 25°C.

CONCLUSIONS

The hydrolysis data for the phenylureas are consistent with only one of the accepted pathways for alkaline hydrolysis of acetanilides. Hydrolysis of both classes of chemicals proceeds via addition of hydroxide ion to the carbonyl carbon of the amide group to form a tetrahedral intermediate. It has been reported that the hydrolysis of acetanilides proceeds mainly via the k_2 path at lower concentrations of hydroxide ion and shifts to the k_3 path mediated by a second hydroxide ion at higher hydroxide ion concentrations. Analysis of our phenylurea data indicated k_3 was the only distinguishable path for alkaline hydrolysis and that neutral hydrolysis is an important degradation process below pH 10. This is contrary to the data reported for trifluoroacetanilides[7]. Hydrolysis of trifluoroacetanilide (fenuron is the dimethyl amino analog of this compound) at pH 7 was estimated to be 80% mediated by hydroxide ion. In contrast, the calculated alkaline contribution to hydrolysis of the phenylureas at pH 7 in our study is less than 1%. or in other words, the neutral contribution to phenylurea hydrolysis at pH 7 can be considered as 100%. The electron-donating dimethyl amino group of the phenylurea apparently retards the alkaline hydrolysis of fenuron in comparison to the electron-withdrawing trifluoromethyl group of the acetanilide.

The importance of the observed pH independent hydrolysis to degradation of the phenylureas in the environment is evident from a comparison of calculated half-lives for fenuron at pH 7 and 25°C both with and without inclusion of k_n. The half-life calculated at pH 7 and 25°C using $k_{alk} = k_1K_wk_3[OH^-]/K_a k_{-1}$ and E_{act} as the activation energy was 4700 years. Including k_n yielded a half-life of 89 years for fenuron at pH 7 and 25°C. The calculated half-lives in years of the remaining ureas at pH 7 and 25°C were 66 for monuron, 41 for diuron, and 41 for chloroxuron. Thus, in groundwater where residence

Table 3 Estimated activation energies of base-promoted hydrolysis of phenylureas.

kcal mol^{-1}	*Fenuron*	*Monuron*	*Diuron*	*Chloroxuron*
$E_{act'}$	30.4 ± 2.1	28.7 ± 2.5	30.8 ± 2.7	29.5 ± 2.2
$E_{act''}$	16.3 ± 2.7	24.2 ± 2.9	28.2 ± 3.0	29.4 ± 2.7
E_{act}^{n}	34.0 ± 3.4	31.7 ± 3.2	29.0 ± 2.9	29.3 ± 2.9

Legend: E_{act} is the activation energy calculated from k_{max}, estimated at two temperatures. $E_{act''}$ is the activation energy calculated from the linear portion of the rate profile. E_{act}^{n} is the activation energy calculated of neutral hydrolysis.

time may be decades, abiotic hydrolysis of the ureas could be an important degradation pathway.

Acknowledgements

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