

1,1-dimethoxy- and 1,1-diethoxy-2,4,6-trinitronaphthalene anionic σ complexes have a quinoid structure, and MO calculations³⁹⁻⁴¹ have indicated that in this complex most of one negative charge donated by the alkoxy nucleophile is located over the 4-nitro group (para to the sp^3 ring carbon).

Our MO calculations^{23,42} indicate that, in the ground state (S_0) of $1d^-$, 30% of one negative charge is located over each of the 2- and 4-nitro groups, whereas in the S_0 state of $1a^-$, the 2-nitro group bears 36% of one negative charge and the 4-cyano group 18%. The difference in electron-attracting character of the 4-substituents, therefore, is considered to affect the K_c values. Similar results have been observed in other cases.⁴³⁻⁴⁶ Terrier et al.⁴⁶ isolated

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some thiophenic and selenophenic anionic σ complexes, in which the K_c values for complex formation were larger than $490 M^{-1}$. It appears that a complex must have a K_c value larger than about $200 M^{-1}$ in order to be isolated.

From Table III it is clear that the differences between the k_1 and k_{-1} values for $1a^-$ and $1d^-$ are attributable to the entropy of activation rather than to the enthalpy of activation. Here, rigorous comparison is impossible, since the data of Fendler et al. were obtained in the absence of added salt, so that ion pairing must be taken into account. The results may indicate that the transition state for the formation of $1a^-$ is more solvated than that for the formation of $1d^-$, which seems reasonable, because the negative charge donated is less delocalized in $1a^-$ than in $1d^-$, and consequently the former should be more solvated. According to the principle of microscopic reversibility, this should also be the case for the transition state for the decomposition of $1a^-$. The result, however, is the opposite, which may be due to the ion pairing of $1d^-$ with sodium ion.

Registry No. 1a, 71436-13-0; sodium methoxide, 124-41-4; methanol, 67-56-1; KOMe, 865-33-8; LiOMe, 865-34-9.

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Kinetics and Mechanism of Hydrolysis of Chloro-1,3,5-triazines. Atrazine¹

Steven J. Plust, Joseph R. Loehe, Frank J. Feher, John H. Benedict, and H. F. Herbrandson*

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181

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Atrazine (1) in acid solution hydrolyzes through both its monoprotonated and diprotonated forms. At temperatures up to 100 °C there are only hydronium ion, hydroxide ion, and buffer catalyses; no uncatalyzed or water-catalyzed reaction with a rate constant greater than $3 \times 10^{-11} s^{-1}$ at 25 °C contributes to the hydrolysis. Phosphate buffer catalysis may be by a specific-acid-general-base mechanism. At 25 °C the minimum rate for hydrolysis in the absence of buffer catalysis is at a pH value of 6.97 with a pseudo-first-order rate constant of $1.24 \times 10^{-11} s^{-1}$. The thermodynamic pK_a value of atrazine at 20 °C is 1.62. Consideration is given to the consequences on the pK_a value and on the rates of the acid- and buffer-catalyzed reactions of protonation on the three different heterocyclic nitrogens of the triazine.

The hydrolysis of atrazine (1, 6-chloro-*N*-ethyl-*N'*-(1-methylethyl)-1,3,5-triazine-2,4-diamine) through 4-(ethylamino)-6-[(1-methylethyl)amino]-1,3,5-triazin-2-ol (2) to 4-(ethylamino)-6-[(1-methylethyl)amino]-1,3,5-triazin-2-(1*H*)-one (3) is the major pathway for chemical degradation of this herbicide.² The reaction, catalyzed by both acid and base,³ has been reported to be dependent on the hy-

drogen ion activity to the 0.6 power³ and subject to buffer catalysis with acetate and citrate buffers.^{3b} Propazine [6-chloro-*N,N'*-bis(1-methylethyl)-1,3,5-triazine-2,4-diamine], a homologue of atrazine, also has been reported to hydrolyze with a 0.6 power dependence on the hydrogen ion activity.⁴ The nonintegral dependence of the rates of hydrolysis on the hydrogen ion activity cannot be explained by any simple mechanism. Although it was reported from three different laboratories, this unusual kinetic order may have resulted from insufficient detail in the pH-rate profile. We have accomplished a more com-

(1) (a) Supported by Federal Funds from the U.S. Environmental Protection Agency under Grant R804820. The contents do not necessarily reflect the view and the policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use. (b) We express our gratitude to Dr. R. A. Park for encouragement of the research reported here.

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plete kinetic study which leads to a clearer understanding of the mechanism for the acid-catalyzed hydrolysis of atrazine.

Atrazine is subject also to basic hydrolysis,^{3a} but there has been no demonstration of its hydrolysis in the pH range 4–11. Separation of the factors contributing to the rate in this intermediate pH range at temperatures up to 100 °C has permitted us to assess the importance of any uncatalyzed or water-catalyzed hydrolysis reaction.

Experimental Section

Materials. Atrazine, kindly provided by the Ciba-Geigy Corp., was twice recrystallized from acetone and stored in a desiccator. Phosphate buffers were prepared from reagent grade potassium dihydrogen phosphate and standard solutions of sodium hydroxide. Citrate buffer was prepared from reagent grade citric acid and standard sodium hydroxide solution. Reagent grade pyridine was diluted with distilled water to give a 70% (v/v) solution.

Kinetic Measurements. The analytical method for atrazine, a refinement of that reported by Armstrong et al.,⁵ provided a sensitivity at 436 nm, a Beer–Lambert slope, of about 7.5×10^4 absorbance units $\times M^{-1}$.

Atrazine solutions to be hydrolyzed were prepared from saturated aqueous solutions that had been diluted with 0.25 part of boiled, distilled water. For reactions in strongly acidic solutions, the appropriate amount of 2.0 N hydrochloric acid together with sufficient solid potassium chloride and boiled, distilled water to adjust the chloride ion concentration to 0.4 M were added to the atrazine solution. For runs in the mid pH range, phosphate buffer, potassium chloride, and boiled, distilled water to provide an ionic strength of 0.4 were used. For short kinetic runs, the bulk solution was thermostated; for runs extending up to 3 months, portions of the solution were sealed in glass vials. For each kinetic point, a 20.00-mL aliquot was diluted to 50.00 mL with distilled water after adding 20 mL of citrate buffer of pH 6.5 and 9 mL of 70% pyridine/water. The resulting solution could be stored at 5 °C for at least 48 h with no apparent change in the atrazine concentration. About 25 mL of the solution was sealed in a glass ampule and immersed in a boiling water bath for 30 min. Two 10.00-mL aliquots then were transferred from the ampule to two 50-mL volumetric flasks. To these were added approximately 15 mL of distilled water and, rapidly, 10.00 mL of 9 N sodium hydroxide. The solutions then were quickly diluted to the mark with distilled water and mixed. Samples were transferred to 1-cm cuvettes, and within 1 min of addition of the alkali, the absorbance at 436 nm was measured with a Beckman DL 25 spectrophotometer. The absorbance was compared to that in a Beer–Lambert plot from a serially diluted atrazine solution in 1 part ethanol/99 parts water, which had been analyzed by using the same procedure. Reported values are the average of the two analyses. The products from the hydrolysis of atrazine do not interfere with this analysis.⁵

pK_a Value of Atrazine. The absorbance at 222 nm of freshly prepared saturated solutions of atrazine diluted with distilled water was obtained by using a Bausch and Lomb Spectronic 200 spectrophotometer with a 0.5-nm slit width and 1-cm cells. The titration of the atrazine over a pH range of 0.1–7 was carried out rapidly to minimize hydrolysis, initially with dilute hydrochloric acid but with concentrated hydrochloric acid at the extremity of the pH range. pH measurements were made with a Beckman Research Model pH meter and a Fisher combined glass–Ag|AgCl electrode. Calibrations were made with Fisher Certified buffers at pH 1.00, 2.00, and 3.00. Temperatures of the solutions were 20 ± 2 °C.

Results

Acid-Catalyzed Hydrolysis of Atrazine. Rates of the acid-catalyzed hydrolysis of atrazine were measured at 25

Table I. Pseudo-First-Order Rate Constants for the Hydrolysis of Atrazine in Aqueous Solution

at 25.00 \pm 0.05 °C		at 39.90 \pm 0.05 °C	
pH	10 ⁶ k', s ⁻¹	pH	10 ⁶ k', s ⁻¹
0.46	4.60	0.4	19.9
0.74	2.78	0.4	16.4
1.0	2.36 ^a	0.48	22.0
1.07	1.60	0.7	12.7
1.3	1.58 ^b	0.7	11.6
1.36	1.08	0.88	11.8
1.66	0.704 ^c	0.97	9.92
1.68	0.699	1.0	9.75
2.0	0.578 ^a	1.0	8.57
2.06	0.497	1.0	8.50 ^f
2.2	0.438 ^b	1.13	8.39
3.1	0.121 ^d	1.36	5.83
4.0	0.0329 ^a	1.58	4.08
11.1	0.0990 ^e	1.6	4.41
11.9	0.529 ^e	1.61	3.61
12.9	4.29 ^e	2.0	1.77 ^f
		2.1	1.84
		2.6	0.85
		2.6	0.76
		3.1	0.26
		4.0	0.165 ^g

^a Determined from Figure 1 in ref 3b. ^b At 25 ± 2 °C as determined from eq 1 in ref 3a. ^c In this experiment glass beads were added to increase the surface area by a factor of 5. ^d At 25 ± 2 °C in the presence of a citrate buffer and as determined from eq 1 in ref 3a. ^e At 25 ± 2 °C as determined from eq 2 in ref 3a. ^f At 40 °C as determined from Figure 1 in ref 3b. ^g At 40 °C, ref 3b.

and 39.9 °C over the pH range 0.4–3.1. It was unnecessary to buffer the solutions since the hydrogen chloride formed in the course of the reaction in the solutions that were initially about 10^{-4} M in atrazine was insufficient to change measurably the pH. The ionic strength was maintained at 0.4 M even though, in control experiments, variations in the ionic strength did not significantly influence the measured rates. The rate constants, including those measured by Armstrong et al.^{3a} and by Li and Felbeck,^{3b} are summarized in Table I. The data, as shown in Figure 1, demonstrate that our rate constants are in near agreement with those earlier reported to give a slope of 0.6.

Atrazine at 25 °C has a pK_a value of 1.61. If the hydrolysis of protonated atrazine is the rate-determining step, as has been suggested for chloro-1,3,5-triazines by Horrobin⁶ and for atrazine by Armstrong et al.,^{3a} at pH 1.61 with one-half of the atrazine protonated, the rate should be one-half that achievable at high acidity with all of the atrazine protonated. Li and Felbeck^{3b} reported for pH 1.0 at 25 °C a measured pseudo-first-order rate constant of 2.36×10^{-6} s⁻¹ and at pH 0.46 the rate constant is 4.60×10^{-6} s⁻¹ (Table I). The rate at pH 1.0 is more than twice that calculated from the equation of Li and Felbeck^{3b} for a pH value of 1.61, 1.08×10^{-6} s⁻¹, and that at a pH value of 0.46 is more than 4 times larger. These observations require that an additional acid-catalyzed reaction contribute to the hydrolytic process.

A much more rapid hydrolysis of diprotonated atrazine, present in a small amount in strongly acidic solutions, can account for the fast reaction (Scheme I).⁷ The pseudo-first-order rate constant for hydrolysis through both the mono- and diprotonated atrazine is given by eq 1. In eq

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(7) We have found no chemical or spectral evidence for any kinetically important participation in the reaction of a Meisenheimer-type intermediate.

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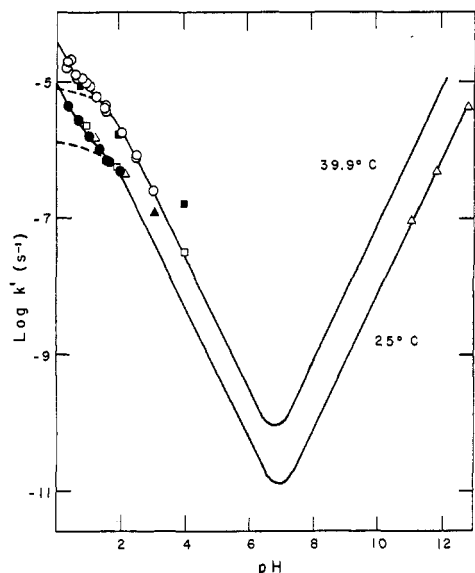
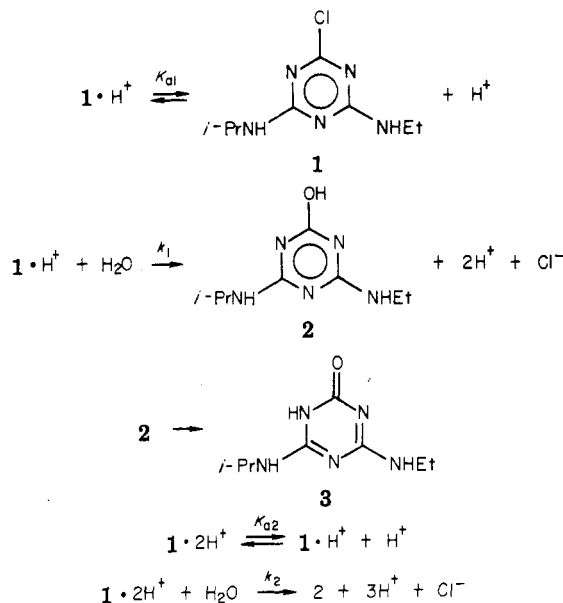


Figure 1. The pH-rate profile for the hydrolysis of atrazine. The dashed lines represent the rates that would result if there were no contribution from diprotonated atrazine. The rate at 39.9 °C under alkaline conditions is interpolated from the rates observed at 25 (ref 3a), 60, 80, and 100 °C. (●) At 25 °C, this work; (○) at 39.9 °C, this work; (Δ) at 25 ± 2 °C, ref 3a; (▲) at 25 ± 2 °C in the presence of citrate buffer, ref 3a; (□) at 25 °C, ref 3b; (■) at 40 °C, ref 3b.

Scheme I



$$k' = \frac{k_1[\text{H}^+] + (k_2/K_{a2})[\text{H}^+]^2}{K_{a1} + [\text{H}^+] + ([\text{H}^+]^2/K_{a2})} \quad (1)$$

1, the term $[\text{H}^+]/(K_{a1} + [\text{H}^+] + [\text{H}^+]^2/K_{a2})$ represents the fraction of atrazine in the monoprotonated form and the term $([\text{H}^+]^2/K_{a2})/(K_{a1} + [\text{H}^+] + [\text{H}^+]^2/K_{a2})$ represents the fraction that is diprotonated.

For the acid-catalyzed reactions, the solid lines of Figure 1 give the best fit of our data obtained by minimizing the sums of the squares of the residuals in the log form of eq 1. The last term in the denominator in eq 1, which provides a measure of the ratio of concentrations of diprotonated to monoprotonated atrazine, was treated as being negligibly

Table II. Equilibrium and Rate Constants for Reactions of Atrazine at 25.00 ± 0.05 and 39.90 ± 0.05 °C

	25.00 ± 0.05 °C	39.90 ± 0.05 °C
$10^6 k_1, \text{s}^{-1}$	1.44	8.3
K_{a1}, M	0.0247	0.0267
K_{a2}, M	>30	>30
$10^6 k_2/K_{a2}, \text{s}^{-1} \text{M}^{-1}$	9.1	32

small in deriving the curves of Figure 1. This is justified because of the excellent fit to the experimental data. The estimated limit on the magnitude of K_{a2} given in Table II is fixed by this assumption. The best values for the rate and equilibrium constants and for the ratio of the rate constant for reaction of diprotonated atrazine to its first ionization constant are given in Table II.

The dashed lines in Figure 1 result from the use of eq 2, which represents hydrolysis of atrazine only through its

$$k' = (k_1[\text{H}^+])/(K_{a1} + [\text{H}^+]) \quad (2)$$

monoprotonated form; the terms k_2 and $1/K_{a2}$ in eq 1 are set equal to zero. In strongly acid solutions the hydrolysis of diprotonated atrazine makes a substantial contribution to the rate: at a pH of 1, 39% of the hydrolysis at 25 °C takes place through the diprotonated form even though less than 0.3% of the atrazine is diprotonated.

Uncatalyzed and Buffer-Catalyzed Hydrolysis of Atrazine. At 40 °C, atrazine has a half-life of 50 days to acid-catalyzed hydrolysis at pH 4.0^{3b} and at pH 11.1 its half-life is 117 days at 25 °C.^{3a} Any attempt to measure an uncatalyzed or water-catalyzed rate in the intermediate pH region, where acid- and base-catalyzed reactions would be exceedingly slow, requires that the hydrolysis be studied at elevated temperatures. Rates of hydrolysis were measured over the pH range of 5.8–7.6 at 60–100 °C in phosphate-buffered solutions (Table III).

The pH at 60 °C was determined by use of constants for the buffer at that temperature⁸ after corrections were made for thermal expansion of the solvent. For 80 and 100 °C, the equation provided by Bates and Acree⁸ relating the $\text{p}K_a$ of the dihydrogen phosphate anion to temperature was extended. Application to 80 and 100 °C of the equation of Alner et al.,⁹ which they proposed for use only up to 60 °C, suggests that the pH value of a phosphate-buffered solution at these temperatures differs by less than 0.05 unit from its value at 25 °C. Our extrapolation from the equation of Bates and Acree⁸ tends to confirm this, but because of the uncertainties in the extrapolations, the pH values are considered to be accurate to only two significant figures. All pOH values are based on the $\text{p}K_w$ for water at the appropriate temperature.¹⁰

In addition to a possible uncatalyzed reaction, reactions catalyzed by the hydronium and hydroxide ions and by buffer acids and bases may be detectable in this intermediate pH range (eq 3). The second term on the right

$$k' = k_w + (k_1/K_{a1})[\text{H}^+] + k_{\text{OH}^-}[\text{OH}^-] + k_{\text{H}_2\text{PO}_4^-}[\text{H}_2\text{PO}_4^-] + k_{\text{HPO}_4^{2-}}[\text{HPO}_4^{2-}] \quad (3)$$

in eq 3 derives from eq 2 at low hydrogen ion concentrations. With the rate constants as adjustable parameters, the squares of the deviations were minimized in fitting the

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Table III. Hydrolysis of Atrazine at Elevated Temperatures

temp, °C	pH	pOH	H ₂ PO ₄ ⁻ , M	HPO ₄ ²⁻ , M	10 ⁷ k', s ⁻¹	
					exptl	calcd ^a
60	5.7 ₈	7.2 ₄	0.038 ₁	0.00147	0.119	0.119
80	6.9 ₀	5.7 ₀	0.025 ₉	0.013 ₀	0.525	0.641
80	7.1 ₀	5.5 ₀	0.0054 ₁	0.0043	0.174	0.267
80	7.5 ₀	5.1 ₀	0.0065 ₁	0.0013	0.466	0.504
80	7.5 ₁	5.0 ₉	0.012 ₈	0.026 ₂	0.998	0.642
100	5.7 ₇	6.4 ₉	0.037 ₂	0.0013 ₈	3.90	3.77
100	5.7 ₇	6.4 ₉	0.018 ₆	0.0006 ₉	2.57	2.53
100	7.1 ₇	5.0 ₉	0.0049 ₅	0.0046 ₂	2.93	2.91
100	7.5 ₂	4.7 ₄	0.006 ₂	0.013	6.13	6.09
100	7.5 ₆	4.7 ₀	0.011 ₇	0.026 ₇	6.82	7.01

^a From use of the rate constants of Table IV in eq 3.

Table IV. Second-Order Rate Constants for the Catalyzed Hydrolysis of Atrazine

temp, °C	10 ⁵ (k ₁ /K _{a1}), M ⁻¹ s ⁻¹	10 ⁵ k _{OH⁻} , M ⁻¹ s ⁻¹	10 ⁵ k _{H₂PO₄⁻} , M ⁻¹ s ⁻¹
25	5.81	6.57 ^b	
39.9	31.2	25.2 ^c	
60	238 ^a	140 ^c	0.0207
80	1420 ^a	459	0.205
100	7040 ^a	3110	0.666

^a Extrapolated value; see Table V. ^b From Armstrong et al.,^{3a} see text. ^c Interpolated value; see Table V.

Table V. Activation Parameters for the Catalyzed Hydrolysis of Atrazine

reaction	E _a , kcal mol ⁻¹	ln A	r
k ₁ /K _{a1} ^a	20.9	25.6	
k _{OH⁻} ^b	17.6	20.1	0.996
k _{H₂PO₄⁻} ^c	21.5	17.3	0.989

^a Using rate constants at 25 and 39.9 °C. ^b Using rate constants at 25, 80, and 100 °C. ^c Using rate constants at 60, 80, and 100 °C.

data of Table III at each temperature to eq 3. The inclusion of numerical values for the rate constants k_1/K_{a1} , k_{OH^-} , and $k_{H_2PO_4^-}$ was necessary, but k_w and $k_{HPO_4^{2-}}$ provided no contribution to the pseudo-first-order rate constant. Table IV gives the best values for the rate constants at all temperatures. Armstrong et al.^{3a} reported a 0.91 power dependence on the hydroxide ion activity over the pH range 11.1–12.9 at 25 °C. The rate constant in Table IV at 25 °C for the hydroxide ion catalyzed hydrolysis has been calculated from the best fit of their data to a first-order dependence. The temperature coefficients for the rate constants and the correlation coefficients of the corresponding Arrhenius equations in their linear form are given in Table V.

Use of the rate constants from Table IV in eq 3 gives the calculated values for the pseudo-first-order rate constants recorded in Table III. The calculated value for the rate constant at 60 °C is identical with the experimental value as there was only a single experiment at that temperature; the numerical value for $k_{H_2PO_4^-}$ was chosen so that when it was combined in eq 3 with the extrapolated value for k_1/K_{a1} and with the interpolated value for k_{OH^-} exact agreement resulted. The excellent correlation for the activation parameters, for k_{OH^-} over the temperature range 25–100 °C, and for $k_{H_2PO_4^-}$ over the temperature range 60–100 °C and the agreement of the calculated values with the experimental values for the pseudo-first-order rate constants without the use of the terms in k_w and $k_{HPO_4^{2-}}$

in eq 3 exclude the possibility of any important contribution to the rate by uncatalyzed or monohydrogen phosphate catalyzed reactions at temperatures up to 100 °C.

pK_a Value of Atrazine. The pK_a value of atrazine was determined spectrophotometrically at 20 ± 2 °C by titration. Two sharp isosbestic points were observed. Since the molar absorptivity of protonated atrazine cannot be measured directly, the pK_a value was determined from the pH value at the half-neutralization point. The measured pK_a value, 1.68 ± 0.03 (the average of two determinations ± the standard deviation), was converted to the thermodynamic value by correcting for the activity of the protonated atrazine by using the extended form of the Debye–Hückel equation. This correction at the half-equivalence point was relatively small, -0.06 pK_a unit, giving a thermodynamic pK_a 1.62 ± 0.03 at 20 ± 2 °C. The value is in good agreement with a published value of 1.68,¹¹ but since it is unclear if the published pK_a value is the thermodynamic value¹² and since the temperature at which the measurement was made was not reported, our value has been used as the basis for all calculations. From this, the method of Perrin¹³ permits calculation of the pK_a value of atrazine to be 1.61 at 25 °C and 1.57 at 39.9 °C.

Discussion

It may be that earlier reports³ of a 0.6 power dependence on hydrogen ion activity for atrazine hydrolysis resulted from limited measurement of the rates at pH values near the point of inflection in the region where reaction takes place through both the monoprotonated and the diprotonated atrazine. The hydrogen ion concentration at this point of inflection, determined from the second derivative of the log form of eq 1 with neglect of the last term in the denominator, is given by eq 4. Substitution into

$$[H^+] = \sqrt{(k_1 K_{a1} K_{a2})/k_2} \quad (4)$$

eq 4 of the values for 25 °C from Table II gives a pH value of 1.20 at the point of inflection. From this and from eq 5, which represents the slope for the entire curve relating log k' to pH, Figure 1, the slope at the point of inflection is -0.57. For 39.9 °C, the pH value is 1.08 and the slope is -0.49 at the point of inflection. Armstrong et al.,^{3a} who determined rates in solutions of pH 1.3, 2.2, and 3.1, at the highest pH in the presence of a citrate buffer, reported a

(11) Gunther, F. A.; Gunther, J. D., Eds. *Residue Rev.* 1970, 32, viii.

(12) The pK_a's of 1.85 reported for the related triazines 6-chloro-*N,N'*-bis(1-methylethyl)-1,3,5-triazine-2,4-diamine and 6-chloro-*N,N'*-diethyl-*N,N'*(1-methylethyl)-1,3,5-triazine-2,4-diamine are nonthermodynamic values; Weber, J. B. *Spectrochim. Acta, Part A* 1967, 23, 458–461.

(13) Perrin, D. D. *Aust. J. Chem.* 1964, 17, 484–488.

$$\frac{d \log k'}{dpH} = 1 + \frac{[H^+]}{K_{a1} + [H^+]} - \frac{k_{OH}K_w[H^+] + 2k_1[H^+]^2 + 3\frac{k_2}{K_{a2}}[H^+]^3}{k_{OH}K_{a1}K_w + k_{OH}K_w[H^+] + k_1[H^+]^2 + \frac{k_2}{K_{a2}}[H^+]^3} \quad (5)$$

slope of -0.62 at 25°C . Li and Felbeck^{3b} reported slopes of -0.63 at 25°C and -0.58 at 40°C from measurements at pH values of 1.0, 2.0, and 4.0.

By titration, the pK_a of monoprotonated atrazine is 1.62 at 20°C , and from our kinetic results the first pK_a value of diprotonated atrazine must be less than -1.5 . The difference between these first and second pK_a values, $\Delta pK_a > 3.1$, may be contrasted with differences of about 8 pK_a units for pyrimidine,¹⁴ 4.3–5.1 for some 2,4- and 4,6-diaminopyrimidines,¹⁵ and 1.5–2.6 for some symmetrical 2-substituted 4,6-diaminotriazines.¹⁶ The ΔpK_a values for atrazine and other appropriately substituted aminopyrimidines and aminotriazines undoubtedly are much less than that of pyrimidine because delocalization of the positive charges in the protonated forms to the amino substituents of the heterocycles results in much lower charge densities. A consequence is diminished charge repulsion and smaller energy differences between mono- and diprotonated aminopyrimidines or aminotriazines than between mono- and diprotonated pyrimidine.

That the titration of atrazine with acid, followed spectrophotometrically, led to two sharp isosbestic points suggests that only atrazine and monoprotonated atrazine were being observed. The monoprotonation of atrazine will lead to an equilibrium distribution of three monoprotonated forms with the protonation taking place on the ring nitrogens; the spectrum for the monoprotonated form will be the weighted average of the individual spectra of the three. The measured pK_a , $pK_a(\text{obsd})$, would be related to the pK_a values for the three heterocyclic nitrogens, pK_a' , pK_a'' , and pK_a''' , as shown by eq 6. In the unlikely event

$$pK_a(\text{obsd}) = pK_a' + pK_a'' + pK_a''' + \log(K_a'K_a'' + K_a'K_a''' + K_a''K_a''') \quad (6)$$

that the pK_a 's for the three heterocyclic nitrogens were identical, the equation for the observed pK_a would reduce to eq 7 and the pK_a value for any one of the heterocyclic nitrogens would be 1.14 ± 0.03 at $20 \pm 2^\circ\text{C}$, 1.13 ± 0.03 at 25°C , and 1.09 ± 0.03 at 39.9°C .

$$pK_a' = pK_a'' = pK_a''' = pK_a(\text{obsd}) - \log 3 \quad (7)$$

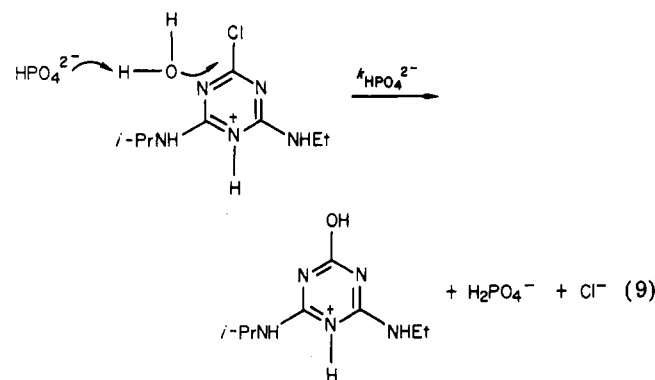
It also is unlikely that hydrolysis in acid solution takes place solely from atrazine monoprotonated on any single nitrogen—each form of the monoprotonated atrazine would react at a characteristic rate and the observed rate constant would be a composite. Equation 8 gives the re-

lationship between the observed first-order rate constant, $k_1(\text{obsd})$, for the hydrolysis of protonated atrazine and rate constants for reaction through the three monoprotonated forms, k_1' , k_1'' , and k_1''' . The observed rate constant is

$$k_1(\text{obsd}) = \frac{k_1'K_a''K_a''' + k_1''K_a'K_a''' + k_1'''K_a'K_a''}{K_a'K_a'' + K_a'K_a''' + K_a''K_a'''} \quad (8)$$

the average of the rates for each of the three protonated forms, the contribution from each weighted according to the fraction it represents of the atrazine protonated. That said above concerning the acid-catalyzed hydrolysis through three differently protonated atrazines applies as well to the buffer-catalyzed reactions.

Workers in two laboratories have reported the buffer catalysis of the hydrolysis of atrazine^{3b} and other chloro-1,3,5-triazines.⁶ That no products of nucleophilic substitution by buffer components have been found and that there is catalysis by phosphate, a poor nucleophile, suggest that the buffer catalysis may be through a specific-acid-general-base sequence (eq 9). The pseudo-first-order rate



constant of eq 3 would then more accurately be given by eq 10. Sufficient data are not available on different

$$k' = \frac{k_1}{K_{a1}}[H^+] + k_{OH}[OH^-] + \frac{k_{HPO_4^2-}K_{aH_2PO_4^-}}{K_{a1}}[H_2PO_4^-] \quad (10)$$

buffers to permit a Brønsted analysis.

The demonstration that there is no uncatalyzed hydrolysis of atrazine even at elevated temperatures leads, by extrapolation in the absence of buffer catalysis, to the complete pH-rate profile of Figure 1. If there were a water-catalyzed reaction contributing at the limit of detectability at 100°C , 3% of the observed rate, a reasonable extrapolation suggests that its contribution to the rate at 25°C would be less than $3 \times 10^{-11} \text{ s}^{-1}$. With no water contribution, the minimum value for the pseudo-first-order rate constant results when the hydrogen ion concentration is that quantity given by eq 11. At 25°C , the pH value

$$[H^+] = \sqrt{(k_{OH}K_{a1}K_w)/k_1} \quad (11)$$

for the minimum is 6.97 with a pseudo-first-order rate constant of $1.24 \times 10^{-11} \text{ s}^{-1}$ and a half-life of 1800 years in the absence of any buffer catalysis.

Registry No. 1, 1912-24-9.

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