

The Hydrolysis of Schiff Base Derivatives of p-Phenylazoaniline

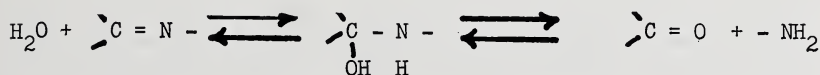
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Abstract

The rates of hydrolysis of N-benzylidene-p-phenylazoaniline, N-p-chlorobenzylidene-p-phenylazoaniline, and N-p-methoxybenzylidene-p-phenylazoaniline were investigated at 25° C. in unbuffered ethanol-water mixtures spectrophotometrically. The rate of the hydrolysis increases with increasing water concentration. For water concentrations ranging from 28.7 molar to 9.1 molar the apparent first order rate constants varied from $9.2 \times 10^{-4} \text{ sec.}^{-1}$ to $1.6 \times 10^{-4} \text{ sec.}^{-1}$ for N-benzylidene-p-phenylazoaniline, from $10.2 \times 10^{-4} \text{ sec.}^{-1}$ to $1.4 \times 10^{-4} \text{ sec.}^{-1}$ for N-p-chlorobenzylidene-p-phenylazoaniline, and $10.7 \times 10^{-4} \text{ sec.}^{-1}$ to $1.2 \times 10^{-4} \text{ sec.}^{-1}$ for N-p-methoxybenzylidene-p-phenylazoaniline. The substituent effect that was observed for these compounds was $\text{CH}_3\text{O} > \text{Cl} > \text{H}$ at higher concentrations of water while the order is reversed at lower concentrations of water. This anomaly can be explained by considering the effect of the changing dielectric constant of the medium with water concentration on the rate of the reaction.

Introduction

The hydrolysis of Schiff bases is postulated to involve the formation and subsequent decomposition of the unstable carbinolamine moiety.



For a discussion of the cleavage of the carbon-nitrogen double bond consult the review article (83 references), by Bruylants and Feytmantis-de Medicis (2). Experimentally a complex dependence of the rate of hydrolysis of aldimines on the pH of the medium is observed (5). In the case of the hydrolysis of a series of substituted benzalanilines Mesli and Tirouflet noted an acid catalyzed region, pH 3–9, a region in which the rate was independent of pH, pH 9–12, and a region in which the rate was dependent upon the hydroxide ion concentration, pH > 12 (7). To account for the complicated pH dependence, Reeves proposed a mechanism that involved proton addition equilibria to the neutral Schiff base or to the carbinolamine (strongly acid solutions) followed by the nucleophilic attack of water or the hydroxide ion on the protonated species with subsequent decomposition to products (8). Kinetic analysis of this reaction scheme led to an equation for the rate constant of the form,

$$k(\text{obs}) = \frac{A + B(\text{H}^+) + C(\text{H}^+)^2}{D + E(\text{H}^+) + F(\text{H}^+)^2}$$

which reduces to the form empirically observed by Willi—neglect of the quadratic term in the denominator—in those instances in which the system is weakly acid or weakly basic (9).

This particular study examined the dependence of the hydrolysis of Schiff bases on the water concentration in neutral, unbuffered ethanol-

water mixtures. The compounds studied were N-benzylidene-p-phenylazoaniline (I), N-p-chlorobenzylidene-p-phenylazoaniline (II), and N-p-methoxybenzylidene-p-phenylazoaniline (III).

Experimental

The Schiff bases were available in this laboratory. Prior to their use they were purified by recrystallization from absolute ethanol and vacuum dried. Their melting temperatures agreed with those cited in the literature. The kinetics of hydrolysis were followed spectrophotometrically using a Bausch and Lomb Spectronic 505 Spectrophotometer. All absorbance measurements were made using matched 1 cm. silica cuvettes at a temperature of $25.0 \pm 0.1^\circ$ C. In order to determine the optimum wave length to employ for the kinetic study the spectrum of each Schiff base p-phenylazoaniline, and the parent aldehyde was measured in absolute ethanol (benzene free) from 230-400 nm. At the wave length selected, 360 nm., the aldehydes were transparent; the molar absorbances expressed as $\log \epsilon$ are Schiff base I (4.56), II (4.40), and III (4.58). $\log \epsilon$ for p-phenylazoaniline is 4.24 at 360 nm.

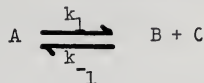
Since absorbance measurements as a function of time were determined with an external recorder, it was necessary to calibrate the chart paper of the instrument in absorbance units. It was verified that the recorder response was a linear function of the absorbance of the solution. A change in absorbance of 0.4 units was represented by a deflection of 200 divisions on the recorder chart paper. Prior to each kinetic run the chart paper was calibrated using two potassium chromate solutions of differing concentrations; the calibration was checked at the conclusion of the kinetic run.

A solid sample of the Schiff base was dissolved in absolute ethanol. Initial studies demonstrated that these solutions were spectrally stable for at least thirty minutes. The solution was filtered and the appropriate volume of Schiff base solution and the appropriate volume of water were mixed. The reaction mixture was introduced into the absorption cuvette. The absorbance was measured at 360 nm. as a function of time until no change in the absorbance was noted over a time interval of at least fifteen minutes. This value represented the "time infinity" absorbance; the value for the initial absorbance was obtained by extrapolation to zero time. The time required to dissolve the solid sample, add water, introduce the sample into the spectrophotometer, and begin measurements was no greater than five minutes. Absorbance measurements on the reaction mixture were begun within one minute after water was added. In order to realize reproducible results it was necessary to free both the ethanol and the water from CO_2 and to minimize solution contact with air during the preparation of the reaction mixture.

Results and Discussion

In the case of the hydrolysis of the chlorosubstituted and the methoxy-substituted Schiff bases the expected first order kinetics were observed. The plot of $\log (D_{inf}-D_t)$ versus time was linear. D_{inf} is the final absorbance of the reaction mixture, and D_t is its absorbance

at any arbitrary time. However, in the case of N-benzylidene-p-phenylazoaniline the expected linear plot was not obtained; D_{int} was greater than the value that was calculated if the hydrolysis reaction were assumed to proceed to completion. This result is expected if the hydrolysis was reversible. For a reversible reaction of the type,



starting with pure A, one form of the integrated rate expression is (3),

$$\ln \left[\frac{f + f_e - ff_e}{f_e - f} \right] = k_1 \left[\frac{2 - f_e}{f_e} \right] t \quad [2]$$

f_e is the fraction of the reaction completed at "time infinity," and f is the fraction completed after t . Since the water concentration was essentially constant during the reaction, equation [2] can be applied. A represents the Schiff base, B the free amine, C the aldehyde, and k_1 , the product k (H_2O)ⁿ, where k is the specific rate constant associated with the hydrolysis and n the order with respect to water. Since the aldehyde is spectrally inert at 360 nm.,

$$f = \frac{(D_t - D_0) \epsilon_A}{(\epsilon_B - \epsilon_A) D_0} \quad [3]$$

ϵ_A and ϵ_B are the molar absorbances of the Schiff base and free amine at 360 nm., D_t the absorbance of the reaction mixture at time t , and D_0 the extrapolated value of the absorbance of the mixture to time zero.

Table 1 summarizes the values for the apparent first order rate constant for the hydrolysis of the three Schiff bases. At least fifteen experimental points were used to ascertain the value of k_1 for a given kinetic run. In the case of simple first order kinetics the method of least squares was employed; for the reversible case an average value for k_1 was calculated. The initial concentration of Schiff base which was determined by the initial value, D_0 , for the absorbance varied within the

TABLE 1. *The hydrolysis rate constants for Schiff bases in ethanol-water.*

Schiff Base	Molarity H ₂ O	k_1 (avg.) $\times 10^{+4}$ sec. ⁻¹	Number Runs	Average Deviation
N-benzylidene- p-phenylazo- aniline (I)	28.71	9.24	8	0.6
	19.24	3.55	5	0.04
	14.28	3.01	5	0.2
	9.13	1.61	4	0.07
N-p-chloroben- zylidene-p- phenylazoaniline (II)	28.71	10.2	5	0.4
	19.24	3.93	5	0.2
	14.28	2.32	5	0.05
	9.13	1.41	4	0.02
N-p-methoxyben- zylidene-p- phenylazoaniline (III)	28.71	10.7	5	0.4
	19.24	4.36	4	0.02
	14.28	2.48	4	0.2
	9.13	1.23	4	0.05

range of $2 - 3 \times 10^{-5}$ molar. The molarity of the ethanol-water solutions with respect to water were calculated using the experimentally determined density of the solution in conjunction with the data in the literature (6).

From the results it appears impossible to make any conclusions concerning the effect of the substituent on the rate of hydrolysis since at the higher water concentration the order is $\text{CH}_3\text{O} - > \text{Cl} - > \text{H}^-$ while the order is reversed at the lower water concentration. For water-ethanol mixtures the dielectric constant changes from a value of 24.3 in pure ethanol to 78.54 in pure water; the data in Harned and Owen can be used to determine the value for the dielectric constant in the solutions that were used in this research (4). The influence of the dielectric constant on reaction rates is extensively discussed by Amis in *Solvent Effects on Reaction Rates and Mechanisms* (1). The effect can be treated using the approximate equations,

$$\ln k_D = \ln k_{\text{inf}} + \frac{Z_A |e_o| u_B}{r_{AB}^2 D k T} \text{ (ion-dipole)} \quad [4]$$

$$\ln k_D = \ln k_{\text{inf}} - \frac{Z_A Z_B |e_o|^2}{r_{AB} D k T} \text{ (ion-ion)} \quad [5]$$

$$\ln k_D = \ln k_{\text{inf}} - \frac{2 u_A u_B}{r_{AB}^3 D k T} \text{ (dipole-dipole)} \quad [6]$$

which predict a linear semi-log k_D versus $1/D$ relationship. In equations [4] - [6], k_D is the value for the specific rate constant in a medium of dielectric constant D , k_{inf} is the specific rate constant in the reference state of infinite dielectric constant, $|e_o|$ is the absolute value for the electronic charge, Z is the valence of the ion, T is the absolute temperature, k the Boltzmann constant, u is the dipole moment, and r_{AB} is the distance of closest approach of reacting species A and B in forming the activated complex.

Figure 1 is a graph of $\log k_D$ versus $1/D$ for the kinetic results for the hydrolysis of the three Schiff bases. The negative slope of these graphs precludes ion-ion interaction being involved in the rate determining step, i.e., the attack on hydroxide ion on the protonated Schiff base. A consideration of possible ion-dipole interactions forces the conclusion that, if ion-dipole interaction is involved, the attack of water on the protonated Schiff base is not rate determining; however, the attack of hydroxide ion on the carbinolamine is compatible with the results. Dipole-dipole interaction predicts a negative slope; hence, one can postulate the attack of the carbinolamine by water as being involved in the rate determining step.

The experimentally determined specific rate constant k_1 , equals the product of the true specific rate constant and the concentration of water raised to some power, the order with respect to water; i.e., $k_1 = k (\text{H}_2\text{O})^n$. However, the graph of $\log k_1$ versus $\log (\text{H}_2\text{O})$ is not linear. This result is expected since the concentration of water has a dual effect on the kinetics, the change of the dielectric constant and the concentration effect within the rate equation itself.

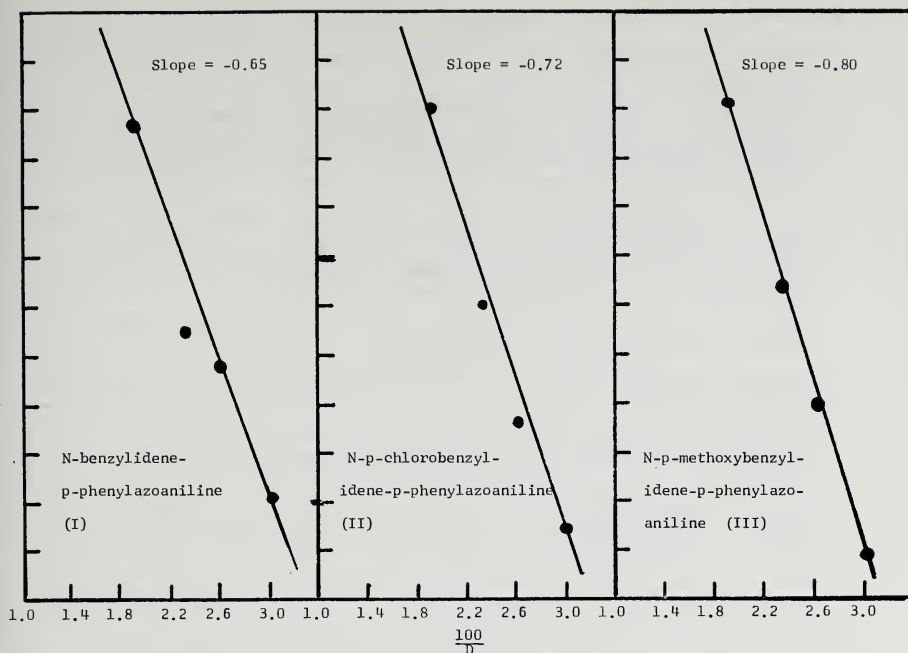


FIGURE 1. The effect of the dielectric constant of the medium on the rate of hydrolysis.

If it is assumed that k is independent of the dielectric constant, the value for the order can be calculated from the following equation

$$\frac{k_1}{k_{\text{pure}}} = \left[\frac{(\text{H}_2\text{O})}{55.36} \right]^n \quad [7]$$

k_{pure} represents the specific rate constant in pure water as determined from Figure 1. The values are $24.1 \times 10^{-4} \text{ sec}^{-1}$ for I, $25.7 \times 10^{-4} \text{ sec}^{-1}$ for II, and $31.2 \times 10^{-4} \text{ sec}^{-1}$ for III. The average value for the order with respect to water using the experimental values for k_1 are 1.48 for I, 1.68 for II, and 1.81 for III. These values indicate a complex dependence on the water concentration. In order to separate the concentration dependence from the dielectric constant dependence one might vary the water concentration while holding the dielectric constant of the media constant which could be accomplished using different organic solvents.

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