# The Addition of Protons to Schiff Bases of p-Phenylazoaniline. Tautomeric Equilibrium Between the Azonium and Ammonium Species

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Schiff base derivatives of p-phenylazoaniline form both a monoprotonated and a diprotonated species in acid solution (1). Since the base species, the monoprotonated species, and the diprotonated species absorb electromagnetic radiation of different wave lengths, the equilibrium constants that are associated with proton addition can be studied spectrophotometrically. In particular the addition of the first proton to the neutral base results in a tautomeric equilibrium between the species

Ammonium Form   Azonium Form
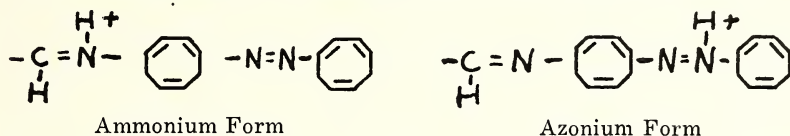
Consider the addition of a proton to a base species, B, which results in a mixture of monoprotonated acids, BH_1^+ and BH_2^+. If C is the stoichiometric concentration of the base plus the two acid species, and a_1 and a_2 represent the fractions of the base converted to $B + H_1$ and BH_2^+ respectively, then two separate acid dissociation constants exist,

$$K(1) = \frac{(1 - a_1 - a_2) \times a_{H_3O^+}}{a_1 \times f_\pm} \tag{1}$$

and

$$K(2) = \frac{(1 - a_1 - a_2) \times a_{H_3O^+}}{a_2 \times f_\pm} \tag{2}$$

where $a_{H_3O^+}$ refers to the activity of the hydronium ion in the solution and $f_\pm$ to the mean activity coefficient in the solution. The activity of the solvent has been assumed to be unity. Experimentally it is the total fraction of base converted to a protonated species that is measured and the equilibrium constant,

$$K = \frac{(1 - a_1 - a_2) \times a_{H_3O^+}}{(a_1 + a_2) \times f_\pm} \tag{3}$$

is determined. K is related to K(1) and K(2) by the equation,

$$\frac{1}{K} = \frac{1}{K(1)} + \frac{1}{K(2)} \tag{4}$$

The tautomeric equilibrium constant, K(T), is simply

$$K(T) = \frac{K(1)}{K(2)} \tag{5}$$

If K(T) is a true tautomeric equilibrium constant, it is independent of the acid concentration of the solution.

At a wave length at which B absorbs and BH_1^+ and BH_2^+ are relatively transparent, equation 3 becomes

$$pK = pH + \log \frac{(D - D_B)}{(D_{BH} - D)} + \log f_{\pm} \qquad (6)$$

D is the absorbance of the system at the pH of the solution, D_B is the absorbance at a pH at which only the base species is present, and D_{BH}^+ is the absorbance at the pH at which no base species is present. Since it is impossible to measure the molar absorbance of either BH_1^+ or BH_2^+ directly, it is necessary to determine $K(T)$ by an alternate method.

The following deduction is based upon the assumption that at the wave length of maximum absorption of either acid species, the other acid species is transparent. At any pH at which B, BH_1^+, and BH_2^+ are present, at the wave length of maximum absorption of BH_1^+

$$D - (1 - a_1 - a_2) D_B = a_1 D_{BH_1}^+ \qquad (7)$$

D is the experimental absorbance of the solution at the particular wave length, D_B is the absorbance of the system if it were entirely in the base form at this particular wave length, and $D_{BH_1}^+$ represents the absorbance of the system at this wave length if the entire concentration of the dye molecule was present as BH_1^+. At the wave length of maximum absorption of BH_2^+ at the same pH

$$D' - (1 - a_1 - a_2) D'_B = a_2 D'_{BH_2}^+ \qquad (8)$$

The prime denotes that a different wave length is involved. Using the value of K, the sum, $a_1 + a_2$, can be calculated at any given pH value. At that pH at which none of the base species is present—experimentally determined as that acid strength where the system displays its minimum absorbance at the wave length of maximum absorption by the base species—the relationships are

$$D_{max} = a_{1max} D_{BH_1}^+ \qquad (9)$$

and

$$D'_{max} = a_{2max} D_{BH_2}^+ \qquad (10)$$

with the sum, $a_{1max} + a_{2max}$, equal to unity. These equations can be solved for a_1 and a_2 at any acid strength and $K(T)$ determined.

If the monoprotonated acid species can add a second proton to form the diprotonated BH_2^+, the effective second acid dissociation constant is

$$pK' = pH + \log \frac{(D - D_{BH}^+)}{(D_{HB2}^{++} - D)} \qquad (11)$$

D is the absorbance of the solution at the wave length at which BH_2^+ absorbs, $D_{BH_2}^{++}$ is the absorbance when only the diprotonated species is present, and D_{BH}^+ is the absorbance when only the tautomeric monoprotonated forms are present.

Experimental

The Schiff bases N-benzal-p-phenylazoaniline, N-(p-chlorobenzal)-p-phenylazoaniline, and N-(p-methoxybenzal)-p-phenylazoaniline were prepared by the method of Guilhot (2). The appropriate aldehyde was reacted with a concentrated solution of p-phenylazoaniline in absolute ethanol at the temperature of melting ice. The Schiff bases, which precipitated, were then recrystallized three times from ethanol and vacuum dried. Stock solutions of the bases were made up in absolute ethanol.

The spectrum of each base was determined in a solution of pH 5, in 1 molar HCl, and in 96 per cent H_2SO_4 solution in the range of 220 to 700 mu with a Bausch and Lomb Spectronic 505 recording spectrophotometer. These initial spectra presented the spectral characteristics of the base, the monoprotonated, and the diprotonated molecule. The effect of pH on the absorption characteristics of each Schiff base was studied using a Beckman DU Spectrophotometer. Matched silica cells were employed, and the cell compartment was thermostated to $25.0 \pm 0.2°C$. The range of acidities covered was from a pH 7 through concentrated H_2SO_4. In the pH range 1 through 7, buffer solutions of ionic strength 0.1 were employed; the pH of each buffer was determined with a Beckman Model G pH meter. The pH values of the various H_2SO_4 solutions were estimated using the extended pH scale of Michaelis and Granick (3). At each pH 2 ml. of stock ethanolic Schiff base was diluted to 25 ml. with the appropriate solution and the absorbance was measured at three wave lengths about each maximum. In order to determine the absorbance of the solution when only the monoprotonated species was present, the absorbance of the solution was taken at the wave length of maximum absorption of the base species in dilute H_2SO_4 solutions until the absorbance at this wave length reached its minimum value. The concentration of H_2SO_4 at which the minimum absorbance was found varied between 1.5 and 3.1 normal, depending upon the particular base.

Results and Discussion

Table 1 summarizes the spectral characteristics of the Schiff bases as well as listing the first and second acid dissociation constants for the protonated species. Data for p-dimethylaminoazobenzene has also been included, since tautomeric equilibria in the case of the monoprotonated Schiff bases is best explained by their similar spectral behavior to this molecule.

In the case of substituted p-dimethylaminoazobenzenes the existence of tautomeric equilibrium between monoprotonated cationic species has been postulated by many, notably Badger (4), Sawicki (5), and Jaffe (6). These workers assign the absorption band at 320 mu to the ammonium species and the absorption band at 515 mu to the azonium form. This assignment is based upon a spectral comparison with substituted azobenzene molecules and their monoprotonated forms. The most conclusive evidence is afforded by Jaffe (7), who studied the addition of protons to p-dimethylaminoazobenzene and to the monomethyl sulfate salt of p-trimethylammoniumazobenzene. In 5 per cent H_2SO_4 the ammonium salt had only one absorption band with a maximum at 320 mu while p-dimethylaminoazobenzene has two separate bands at 320 mu and 515 mu. In stronger H_2SO_4 solutions the ammonium salt absorbs at 408 mu, its monoprotonated species, while the dimethylaminoazobenzene absorbs at 415 mu, its diprotonated species.

The spectral behavior of the Schiff bases in acid solution is similar to p-dimethylaminoazobenzene. The most striking difference is a twin peak associated with the diprotonated Schiff base. This absorption band seems due to the a single diprotonated species since the second acid dissociation constant had the same value regardless of which absorption

TABLE 1

Spectral Characteristics and Acid Dissociation Constants of the Schiff
Bases of p-Phenylazoaniline

Compound	Wave length mu.	Molar Absorbance x 10⁻³	pK	pK'
N-Benzal-p-phenyl-azoaniline			2.75± .02	—3.39± .05
Base	375	20.3		
Monoprotonated	320	21.2		
	495	54.8		
Diprotonated	295	25.4		
	415	32.0		
N-(p-Methoxybenzal)-p-phenylazoaniline			2.83± .03	—3.84± .02
Base	375	20.1		
Monoprotonated	290	25.9		
	495	45.6		
Diprotonated	350	42.3		
	415	29.2		
N-(p-Chlorobenzal)-p-phenylazoaniline			2.74± .02	—3.85± .03
Base	375	19.7		
Monoprotonated	320	23.0		
	495	41.7		
Diprotonated	320	28.8		
	415	30.6		
p-Dimethylamino-azobenzene			3.16± .03	—4.56± .01
Base	415	20.0		
Monoprotonated	320	22.6		
	515	64.2		
Diprotonated	415	35.0		

maximum was used. It was observed that in those H_2SO_4 solutions in which the diprotonated form began to appear that the absorbance associated with the ammonium species decreases and simultaneously the absorbance of the azonium species increases. This experimental evidence indicates definitely that the two monoprotonated species are different. If a tautomeric equilibrium does exist between monoprotonated Schiff bases, another effect besides the simple addition of a second proton to the acid cations must be occurring.

Table 2 summarizes the tautomeric equilibrium constants associated with monoprotonation as calculated using equations 7-10. The constancy of these values indicates that a tautomeric equilibrium does exist. In the case of the Schiff bases the relative order of magnitude of K(T) is that expected. The chloro group would inductively decrease the electron

TABLE 2

Tautomeric Equilibrium Constants for the Monoprotonated Species

Compound	pH	$K(T) = \dfrac{\text{Azonium}}{\text{Ammonium}}$
N-Benzal-p-phenyl azoaniline	2.45	0.198
	2.15	0.201
	1.74	0.209
	1.23	0.205
N-(p-Methoxybenzal)-p-phenylazoaniline	2.45	0.0180
	2.15	0.0189
	1.74	0.0195
	1.23	0.0198
N-(p-Chlorobenzal)-p-phenylazoaniline	2.45	0.265
	2.15	0.381
	1.74	0.295
	1.23	0.286
p-Dimethylaminoazobenzene	2.45	1.28
	2.15	1.28
	1.74	1.31
	1.23	1.29

density at the azomethine nitrogen while the methoxy group should enhance the electron density at the azomethine nitrogen through a resonance effect. The value of 1.3 for $K(T)$ in the case of p-dimethylaminoazobenzene is especially interesting since Yeh (8) by assuming that the molar extinction coefficients for the monomethyl sulfate salt of p-trimethylammoniumazo benzene and the ammonium form of the monoprotonated p-dimethylaminoazobenzene were identical, determined $K(T)$ to be 1.4 in 6.6 per cent H_2SO_4.

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