Hydrolysis Kinetic Studies of Schiff Bases Derived from Pyrrolic Aldehydes in Buffered Aqueous Ethanol and Sulfuric Acid Solutions: Structural Effects of Substitutes

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ABSTRACT: Two series of substituted N-pyrrolyl-2-methylene-aniline were synthesized and characterized to study their stability in a large domain of pH (0–14) and especially in the H₀ domain (–4 to 0). The hydrolysis kinetics of the azomethine group was established in homogeneous media using a thermostated UV–vis spectrophotometer. The hydrolysis mechanism was investigated, and the experimental kinetic constants were calculated. Then, the pH–rate diagram profile was determined and the structural effect of substitutes on the kinetic constants was clarified and discussed. © 2013 Wiley Periodicals, Inc. Int J Chem Kinet 45: 404–414, 2013

INTRODUCTION

A great number of Schiff bases have been synthesized and used as substrates for the preparation of industrially and biologically active compounds. Furthermore, their biological activities as antimicrobial, antifungal, and antitumor agents and herbicides have been largely proved [1-10]. Also, the stability of azomethine function has been discussed in numerous studies. Some empirical hydrolysis curves of some series of Schiff bases in the range of pH values from 0 to 14 and different mechanisms have been proposed by researchers [11-17]. Schiff bases were also used as ligands for the metal complex; their hydrolysis assisted by a metal catalyst was investigated [18,19], and they

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A series: Y = H, X = H: **1**, CH_3 : **2**, OCH_3 : **3**, OC_2H_5 : **4**, Cl: **5**, Br: **6** B series: $Y = CH_3$, X = H: **1'**, CH_3 : **2'**, OCH_3 : **3'**, OC_2H_5 : **4'**, Cl: **5'**, Br: **6'**

Scheme 1

were also used as acid-base indicators as reported by Khalil et al. [20].

Certain aldimines derived from pyrrole-2carbaldehyde and pyrrole derivatives were synthesized and used for the preparation of compounds with antimicrobial, antibacterial, and tuberculostatic activities [21–23].

The present study is focused on the hydrolysis study of two series of Schiff bases based on substituted N-pyrrolyl-2-methylene-aniline and their stability in a large domain of pH. The hydrolysis of some of these compounds has been previously described qualitatively by Dezelic et al. [24], showing their rapid and complete destruction in acidic, basic, and neutral media. This research has been succeeded by Mesli et al. for the complete hydrolysis from pH 0 to 14 using polarography and amperometry methods [25,26]. The present paper reports the systematic hydrolysis study of substituted N-pyrrolyl-2-methylene-aniline and Nmethyl pyrrolyl-2-methylene-aniline (Scheme 1) in a large range of pH including the H₀ domain of moderately concentrated aqueous acid. To our knowledge, this is the first hydrolysis kinetic investigation of these products using the UV-vis spectroscopy method particularly in the zone H_0 (from -4 to 0); obviously this domain of strong acidity was mainly explored [27,28]. Thus, the aim of the paper is to determine the morphology of the pH-rate profile of the hydrolysis reaction of these pyrrolic Schiff bases series (Scheme 1). So, the apparent rate constants have been calculated and the structural effect of substitutes discussed.

EXPERIMENTAL

Synthesis of Schiff Bases

Schiff bases were synthesized from mixtures of N-pyrrole-2-carbaldehyde or N-methylpyrrole-2-carbaldehyde and p-substituted anilines in a stoichiometric proportion by a classical method of condensation [29] in anhydrous benzene as a solvent and p-toluene sulfonic acid as a catalyst using the Dean–

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Starck apparatus. The products were recrystallized in ethanol, and the melting points were measured using the Totolli apparatus.

Characterization of Schiff Bases

IR spectra were registered on a FTIR-8300 Shimadzu spectrophotometer with samples dispersed in KBr pellets. The ¹H and ¹³C NMR spectra of A and B series of Schiff bases dissolved in deuteriated chloroform were recorded on Brucker DRX 500 MHZ and 300 MHz apparatus, respectively. The UV–vis spectrum (200–400 nm) of each imine in an absolute ethanol solution at $C = 10^{-4}$ mol L⁻¹ was carried out using a UV–vis Shimadzu UV-2401 PC; it presented four bands (λ_{max} in nm, ε in L cm⁻¹ mol⁻¹).

A Series.



X=H (*N*-pyrrolyl-2-methylene-aniline), mp = 94°C; IR: 1625 (C=N), 3220 (N–H); ¹H NMR (ppm): H₃ (6.68 m), H₄ (6.26 m), H₅ (6.79 m), H_i (8.26 s), H_{2'} and H_{6'} (7.16 m), H_{3'} and H_{5'} (7.34 m), H_{4'} (7.16 m), H₁ (10.25 s); ¹³C NMR (ppm): C_i (152.16), C_{1'} (150.53), C_{2'} and C_{6'} (117.37), C_{3'} and C_{5'} (129.67), C_{4'} (121.40), C₂ (131.12), C₃ (123.97), C₄ (110.81), C₅ (125.9). UV–vis: band I (325, 19281), band II (295, 11667), band III (225, 6213), band IV (202, 10105).

X=CH₃ (N-pyrrolyl-2-methylene-*p*-methylaniline), mp = 101°C; IR: 1615 (C=N), 3246 (N–H); ¹H NMR (ppm): H₃ (6.63 m), H₄ (6.22 m), H₅ (6.75 m), H_i (8.25 s), H_{2'} and H_{6'} (7.08d), H_{3'} and H_{5'} (7.09 d), H(CH₃) (2.20 s); ¹³C NMR (ppm): C_i (149.57), C_{1'} (149.92), C_{2'} and C_{6'} (117.07), C_{3'} and C_{5'} (130.24), C_{4'} (129.80), C₂ (131.17), C₃ (121.23), C₄ (110.65), C₅ (123.89). UV–vis: band I (328, 20,961), band II (296, 12,118), band III (233, 6261), band IV (203, 12007). X=OCH₃ (*N*-pyrrolyl-2-methylene-*p*-methoxyaniline), mp = 94.5°C; IR: 1615 (C=N), 3232 (N–H), ¹H NMR (ppm): H₃ (6.89 m), H₄ (6.29 m), H₅ (6.91 m), H_i (8.23 s), H_{2'}, _{6'} (7.17 d), H_{3'}, _{5'} (7.24 d), H (–CH₃) (3.80 s); ¹³C NMR (ppm): C_i (158.22), C_{1'} (145.12), C_{2'} and C_{6'} (116.41), C_{3'} and C_{5'} (114.86), C_{4'} (148.59), C₂ (131.34), C₃ (122.34), C₄ (110.74), C₅ (123.15), C (OCH₃) (21.36). UV–vis: band I (337, 19,131), band II (297, 11,266), band III (227, 7205), band IV (203, 11,993).

X=OC₂H₅ (*N*-pyrrolyl-2-methylene-*p*-ethoxyaniline), mp = 118.5°C; IR: 1618 (C=N), 3232 (N–H); ¹H NMR (ppm): H₃ (6.63 m), H₄ (6.24 m), H₅ (6.78 m), H_i (8.28 s), H_{2'} and H_{6'} (6.90 d), H_{3'} and H_{5'} (7.17 d), H(–CH₂–) (4.03 q), H (–CH₃)(1.41 t); ¹³C NMR (ppm): C_i (157.61), C_{1'} (145.02), C_{2'} and C_{6'} (116.66), C_{3'} and C_{5'} (115.48), C_{4'} (148.85), C₂ (131.30), C₃ (122.40), C₄ (110.64), C₅ (123.55), C (–CH₂–) (64.13), C(–CH₃) (15.31). UV–vis: band I (336.4, 23,296), band II (296, 13,393), band III (226, 7819), band IV (203, 13,017).

X=Cl (*N*-pyrrolyl-2-methylene-*p*-chloro-aniline), mp = 97.5°C; IR: 1614 (C=N), 3232 (N–H), ¹H NMR (ppm): H₃ (6.71 m), H₄ (6.28 m), H₅ (6.72 m), H_i (8.25 s), H_{2'} and H_{6'} (7.15 d), H_{3'} and H_{5'} (7.32 d), NH (10.25); ¹³C NMR (ppm): C_i (150.67), C_{1'} (151.00), C_{2'} and C_{6'} (118.14), C_{3'} and C_{5'} (130.91), C_{4'} (129.78), C₂ (131.38), C₃ (122.77), C₄ (111.05), C₅ (124.56). UV–vis: band I (331, 14,658), band II (294.6, 13,967), band III (241.6, 14,264), band IV (204, 25,345).

X=Br (*N*-pyrrolyl-2-methylene-*p*-bromo-aniline), mp = 107.5°C; IR: 1614 (C=N), 3232 (N–H); ¹H NMR (ppm): H₃ (6.70 m), H₄ (6.28 m), H₅ (6.92 m), H_i (8.22 s), H_{2'} and H_{6'} (7.04 d), H_{3'} and H_{5'} (7.40 d), NH (9.80); ¹³C NMR (ppm): C_i (150.56), C_{1'} (149.87), C_{2'} and C_{6'} (117.24), C_{3'} and C_{5'} (130.50), C_{4'} (118.69), C₂ (132.22), C₃ (122.56), C₄ (110.71), C₅ (123.60). UV– vis: band I (332, 19,281), band II (295, 9827) band III (225, 6740), band IV (203, 12,159).

B Series.



X=H (*N*-methyl-*N*-pyrrolyl-2-methylene-aniline), mp = 120°C; IR: 1624 (C=N); ¹H NMR (ppm): H₃ (6.78 m), H₄ (6.30 m), H₅ (6.85 m), H_i (8.37 s), H_{2'} and H_{6'} (7.26 m), H_{3'} and H_{5'} (7.43 m), H_{4'} (7.26 m), H₁ (4.11 s). UV-vis: band I (325, 13,855), band II (297,13723), band III (220, 11,157), band IV (203, 18,286).

X=CH₃ (*N*-methyl-*N*-pyrrolyl-2-methylene-*p*-methyl-aniline), mp = 45°C; IR: 1622 (C=N); ¹H NMR (ppm): H₃ (6.72 m), H₄ (6.23 m), H₅ (6.81 m), H_i (8.33 s), H_{2'} and H_{6'} (7.12 d), H_{3'} and H_{5'} (7.20 d), H(-CH₃) (4.20 s), H₁ (4.07 s). UV-vis: band I (329, 14,382), band II (294, 10,217), band III (220, 8939), band IV (204, 14,487).

X=OCH₃ (*N*-methyl-*N*-pyrrolyl-2-methylene-*p*-methoxy-aniline), mp = 60° C; IR: 1618 (C=N); ¹H NMR (ppm): H₃ (6.8 m), H₄ (6.23 m), H₅ (6.8 m), H_i (8.34 s), H_{2'} and H_{6'} (6.95 d), H_{3'} and H_{5'} (7.20 d), H(-CH₃) (3.85 s), H₁ (4.07 s). UV-vis: band I (336, 18,577), band II (297, 12,688), band III (219, 8624), band IV (202, 12,419).

X=OC₂H₅ (*N*-methyl-*N*-pyrrolyl-2-methylene-*p*ethoxy-aniline), mp = 48°C; IR: 1618 (C=N); ¹H NMR (ppm): H₃ (6.80 m), H₄ (6.30 m), H₅ (6.90 m), H_i (8.34 s), H_{2'}, _{6'} (6.95 d), H_{3'} and H_{5'} (7.20 d), H(-CH₂-) (4.09 q), H(-CH₃) (1.45 t), H₁ (4.07 s). UV-vis: band I (337, 18,511), band II (295, 12,503), band III (222, 8425), band IV (203, 12,973).

X=Cl (*N*-methyl-*N*-pyrrolyl-2-methylene-*p*chloro-aniline), mp = 40°C; IR: 1612 (C=N); ¹H NMR (ppm): H₃ (6.85 m), H₄ (6.24 m), H₅ (7.13 m), H_i (8.30 s), H_{2'}, $_{6'}$ (7.15 d), H_{3'} and H_{5'} (7.35 d), H₁ (4.07 s). UV-vis: band I (329, 13,604), band II (297, 11,741), band III (227, 8338), band IV (203, 16,925).

X=Br (*N*-methyl-*N*-pyrrolyl-2-methylene-*p*bromo-aniline), mp = 37° C; IR: 1612 (C=N); ¹H NMR (ppm): H₃ (6.82 m), H₄ (6.22 m), H₅ (7.10 m), H_i (8.30 s), H_{2'}, _{6'} (7.10 d), H_{3'} and H_{5'} (7.40 d), H₁ (4.07 s). UV-vis: band I (330, 14,118), band II (297, 10,043), band III (227, 9365), band IV (204, 16,858).

UV–Vis Analysis and Hydrolysis Kinetics

The hydrolysis of imines was studied at a temperature of $37 \pm 0.1^{\circ}$ C using a UV–vis spectrophotometer (Shimadzu UV-2401 PC; Tokyo, Japan) equipped with a thermostatically controlled cell holder, in homogeneous media, i.e., 33% (V/V) of ethanol buffer mixtures, where the ionic strength is maintained at 0.15. A Tacussel digital pH meter was used for the pH measurements.

- For pH 4–12, the hydrolysis media were prepared using the buffered aqueous solution/ethanol, according to the method of Michaelis and Mizutani [30].
- For pH <4 and >12, hydrochloride and sodium hydroxide solutions were used, respectively, instead of the buffer solution.



Figure 1 Time-resolved absorption spectra for N-methylpyrrolyl-2-methylene-aniline in pH solution = 7.36.

• For the H₀ zone (-4 to 0), aqueous sulfuric acid solutions (from 2% to 54%)/ethanol were prepared as described by Johnson et al. [31].

To follow the hydrolysis kinetics, the buffer (2 mL) and ethanolic Schiff base solution (1 mL) were poured into the UV–vis cell and shaken; for all experiments, the initial concentration of imine in the UV–vis cell is equal to 10^{-4} mol L⁻¹.

In general, complete UV spectra of solution were registered over time intervals consistent with the advancement of the reaction state. However, when the kinetics was rapid, only the change in UV absorption with time at the selected wavelength was recorded.

RESULTS AND DISCUSSION

Schiff Bases Hydrolysis in pH Media from 0 to 14

First, it should be noted that the UV–vis spectra of all compounds (A and B series) in absolute ethanol showed four bands, which are described in the Experimental section. The same UV behavior was noted for the substituted biphenyl Schiff bases $XC_6H_4CH = NC_6H_4Y$ [32,33], where the band I corresponding to $\pi - \pi^*$ electronic transition is affected by the Y substitute. For the A and B pyrrolic series, the four bands appeared in the same regions whatever be the substitutes; nevertheless, the molar coefficient of extinction ε is affected by both X and Y substitutes.

Concerning the hydrolysis kinetics of A and B series of *N*-pyrrol-2-methylene aniline (YNC₄H₃CH = NC₆H₄X), examples of UV spectra of slow and fast kinetics are shown in Figs. 1 and 2, respectively.



Figure 2 Hydrolysis of 1: *N*-pyrrolyl-2-methylene aniline at pH 3.35 ($\lambda_{max} = 345$ nm).

As a matter of fact, the hydrolysis reaction of the imine functional group passes inevitably through the carbinolamine group [34]. So, the presence of isobestic "i" points as mentioned in Fig. 1 indicated that there was no accumulation of any intermediate, especially the α -amino alcohol, during the hydrolysis process.

The present results showed that the hydrolysis kinetics of these Schiff bases in ethanol buffer mixtures is considered as a first-order reaction as indicated by the linearity of plot of $\log(D^{t,c})$ versus time (Eq. (1)):

$$\log D^{t,c} = \log D^{0,c} - \frac{k_{\exp}}{2.3}t$$
 (1)

where $D^{t,c}$ is the corrected optical density at time *t*, $D^{t,c} = D^t - D^\infty$; D^t is the optical density at time *t*; and D^∞ is the optical density at the end of hydrolysis (infinite time). So, the experimental kinetic constant (k_{exp}) is calculated from the slope of the $\log(D) =$ f(t) equation. Also, the initial corrected optical density $(D^{0,c})$ is determined by extrapolation at t = 0.

Examples of straight lines of the hydrolysis data of A series are given in Fig. 3. The imine absorption band, i.e., the analytical wavelength λ_a , is selected from the free imine band at each pH; it disappears completely at infinite time, suggesting that the reaction is complete in the present operating conditions.

Schiff Bases Hydrolysis in Sulfuric Acid Solution ($H_0 = -4$ to 0)

In these experimental conditions, we have obtained the same behaviors. Figure 4 presents the hydrolysis of *N*-methylpyrrolyl-2-methylene-aniline at $H_0 = -1.03$ (20% of H_2SO_4), where $\lambda_a = 400$ nm. As mentioned



Figure 3 Typical first order of the hydrolysis reaction of A series of compounds at pH 2.66.



Figure 4 Time-resolved absorption spectra for *N*-methylpyrrolyl-2-methylene-aniline in the H_0 solution = -1.03 (20% of H_2SO_4).

previously, we tested Eq. (1) to identify the hydrolysis mechanism and, consequently, to calculate the apparent kinetic constants (k_{exp}). In this case (H₀ zone), λ_a is selected from the protonated imine band. Thus, we present in Fig. 5 plots log $D^{t,c}$ versus time for A series hydrolysis at H₀ = -1.03.

Morphology of Hydrolysis Curves and Structural Effects of Substitutes

The experimental kinetic constants of the hydrolysis reaction of all products in the pH and H_0 ranges were

investigated and calculated. Figures 6 and 7 show hydrolysis curves of A and B series, respectively. Some examples of kinetic constant values are given in Tables I and II. All H₀ and pH–rate profiles, i.e., $\log k_{exp} = f(H_0, pH)$, are bell shaped, and they can be divided into four zones (Fig. 6).

As reported in the literature [11-13,35-39], the hydrolysis curve of Schiff bases derived from aromatic and aliphatic amines can be divided into different domains. In the current study, we have numbered only four domains: H₀, P', A, and P as mentioned in Fig. 6.

The proposed mechanism of imine hydrolysis in the H_0 domain (from $H_0 = -4$ to 0) is presented in Scheme 2, and the general mechanism of hydrolysis in P', A, and P zones (from pH 0–14) is described in Scheme 3.

First, in the H_0 domain, the water base catalyzed decomposition of the cationic form (SH₂OH⁺) of the carbinolamine intermediate corresponds to the hydrolysis-limiting step (step c in Scheme 2). Then, the apparent kinetic constant is given by

$$\log k_{\rm obs} - \alpha \log(a_{\rm H_2O}) + \log k_h k \tag{2}$$

where

$$k_{h} = [SH_{2}OH^{+}]/[SH^{+}][H_{2}O]$$
 (3)



Figure 5 Typical first order of the hydrolysis reaction of A series of compounds at $H_0 = -1.03$ (20% of H₂SO₄).



Figure 6 General hydrolysis curve: $\log k_{\exp} (s^{-1}) = f(pH, H_0)$ of A pyrrolic series.

 $a_{\rm H_2O}$ is the water activity, and α is a number of water molecules involved in the transition state [34].

In this zone, only the hydrolysis of *N*-*p*-chlorobenzylydene-aniline has been previously discussed by Cordes and Jenks [36]; they demonstrated a linear relationship between the kinetic constant and H_0 value, and the slope of log k_{obs} versus H_0 was equal to 1.24.

For A and B series of pyrrolic Schiff bases, linear relationships have been obtained too and the slope values are summarized in Tables III and IV. The results showed slope values close to 1.27 for A series and 1.20 for B series; we concluded that the pyrrolic and benzylic Schiff bases have practically the same hydrolysis behavior in the H_0 zone.

Also, Cordes and Jenks [36] presented a linear relationship between log k_{exp} and log a_{H_2O} (Eq. (2)) and the slope (α) was equal to 3.12, indicating the involvement of at least three water molecules in the transition state.

The results displayed in Tables III and IV show that the slope value of log $k_{exp} = f(\log a_{H_2O})$ plots varied



Figure 7 General hydrolysis curve: $\log k_{\exp} (s^{-1}) = f(pH, H_0)$ of B pyrrolic series.

practically from 9.3 to 10.4 for A series and from 10.0 to 13.7 for B series. We concluded that for A and B series, respectively, 10 and 11 water molecules on average participate in the transition state but only one of them had a nucleophilic reactive role.

Nevertheless, we must specify that Bunnett [40] did not observe correlations between kinetic constants and water activity; he found anomalous and high slope values. Consequently, he considered that Eq. (2) remained as an empirical relationship and the water molecule does not have a significant activity on the hydrolysis mechanism in concentrated acid media [40].

$$C = N - + H^{+} - C = NH^{+} - (a)$$
(S)
(S)

$$C = NH^{+} + H_2O \xrightarrow{k_h} - CH - NH_2 - (b)$$

 $(SH_2OH^+) + H_2O \xrightarrow{k} H_3O^+ + (Products)$ (c)

Scheme 2

Regarding the structural effect of the X substitute in the H₀ zone, the Hammett correlation (Fig. 8) gave positive values of reaction constants equal to 1.53 (r = 0.980) and 1.55 (r = 0.985) for A and B series, respectively. So, the destruction of protonated α aminoalcohol intermediate is favored when X had an electron-withdrawing effect. In addition, we noted that the Y substitute (H or CH₃) did not modify the reaction constants of Hammett.

Second, for P', A, and P zones (pH 0–14) and from Scheme 3, the general observed kinetic constant can be expressed by Eq. (4) [26]:

$$k_{\rm obs} = \frac{k_1 k_5 [{\rm H}^+] + K_e k_2 k_5}{([{\rm H}^+] + K_{\rm SH}^+) (k_{-1} [{\rm H}^+] + k_{-2} + k_5)} \qquad (4)$$

where K_e is the autoprotolysis constant of water.

The acidic plateau P' or the bell summit in the hydrolysis curve (pH 0-4) corresponded to the transition in the limiting step of the hydrolysis reaction. In this case, the kinetic constant of hydrolysis is independent of pH as indicated by Eq. (5). The rate-limiting step

Table I Some Values of Experimental Hydrolysis Kinetic Constants of A series (Y = H)

	$k_{\rm obs}~({\rm s}^{-1})$								
Zone, pH	$X = OCH_3$	$X = OC_2H_5$	$X = CH_3$	X = H	X = Cl	X = Br			
H ₀ , -0.76 P', 2.25 A, 5.04 P, 12.38	$\begin{array}{c} 1.43 \times 10^{-3} \\ 6.47 \times 10^{-3} \\ 4.90 \times 10^{-3} \\ 0.69 \times 10^{-4} \end{array}$	$\begin{array}{l} 1.31 \times 10^{-3} \\ 7.19 \times 10^{-3} \\ 4.76 \times 10^{-3} \\ 0.77 \times 10^{-4} \end{array}$	$\begin{array}{c} 2.21 \times 10^{-3} \\ 9.57 \times 10^{-3} \\ 5.88 \times 10^{-3} \\ 0.91 \times 10^{-4} \end{array}$	$\begin{array}{l} 3.68 \times 10^{-3} \\ 2.96 \times 10^{-2} \\ 1.45 \times 10^{-2} \\ 0.99 \times 10^{-4} \end{array}$	$\begin{array}{l} 6.98 \times 10^{-3} \\ 6.75 \times 10^{-2} \\ 1.65 \times 10^{-2} \\ 0.48 \times 10^{-4} \end{array}$	$8.75 \times 10^{-3} \\ 6.60 \times 10^{-2} \\ 2.34 \times 10^{-2} \\ 0.50 \times 10^{-4} \\ \end{array}$			

Table II Some Values of Experimental Hydrolysis Kinetic Constants of B Series ($Y = CH_3$)

		$k_{\rm obs}~({\rm s}^{-1})$								
Zone, pH	$X = OCH_3$	$X = OC_2H_5$	$X = CH_3$	X = H	X = Cl	X = Br				
H ₀ , -0.66 P', 2.28 A, 5.00 P, 12.10	$\begin{array}{c} 1.03 \times 10^{-3} \\ 1.44 \times 10^{-2} \\ 1.14 \times 10^{-2} \\ 0.23 \times 10^{-3} \end{array}$	$\begin{array}{c} 1.63 \times 10^{-3} \\ 1.80 \times 10^{-2} \\ 1.11 \times 10^{-2} \\ 0.22 \times 10^{-3} \end{array}$	$\begin{array}{c} 2.74 \times 10^{-3} \\ 2.15 \times 10^{-2} \\ 1.49 \times 10^{-2} \\ 0.22 \times 10^{-3} \end{array}$	$\begin{array}{c} 4.60 \times 10^{-3} \\ 4.39 \times 10^{-2} \\ 2.32 \times 10^{-2} \\ 0.26 \times 10^{-3} \end{array}$	$7.49 \times 10^{-3} \\ 1.19 \times 10^{-1} \\ 3.71 \times 10^{-2} \\ 0.13 \times 10^{-3} \end{cases}$	$\begin{array}{c} 1.06 \times 10^{-2} \\ 1.02 \times 10^{-1} \\ 3.94 \times 10^{-2} \\ 0.13 \times 10^{-3} \end{array}$				

$$\sum_{\substack{K \in \mathbb{N} \\ (S)}} C = N + H^{+} \xrightarrow{K_{SH^{+}}} C = N H^{+}$$
(a')

$$\sum_{C=NH^{+} + H_{2}O} \underbrace{k_{1}}_{k_{-1}} - \underbrace{CH-NH}_{OH} + H^{+}$$
(b')

$$C = NH^{+} + OH^{-} \qquad \begin{array}{c} (SHOH) \\ \hline k_{2} \\ \hline k_{-2} \end{array} \qquad \begin{array}{c} CH - NH \\ OH \end{array} \qquad (c')$$

$$\sum_{\substack{C = N \\ (S)}}^{C = N} + OH^{-} \xrightarrow{k_{3}} - CH^{-} N^{-} \xrightarrow{(d')} OH^{-} OH$$

$$(SHO^{-})$$

$$(SHO^{-})$$

$$(SHO^{-})$$

$$(SHO^{-})$$

$$(SHO^{-})$$

$$(SHO^{-})$$

$$(SHOH)$$

$$(SHOH)$$

$$(CH - NH - \frac{k_{5}}{2} C = 0 + H_{2}N - (f')$$

(Products)

Scheme 3

corresponds to step b', i.e., the addition of water molecule on the protonated imine:

(SHOH)

$$k_{\rm obs} = k_1 \tag{5}$$

Concerning the substitute effect, good Hammett correlations, i.e., $\log k_{obs} = f(\sigma_x)$, were obtained for both the A and B series (Fig. 9). The reaction constants (ρ) were equal to 1.75 (where the coefficient of

Table III Values of Slope and Coefficient of Correlation (*r*) for Equations $\log k_{exp} = f(H_0)$ and $\log k_{exp} = f(\log a_{H_2O})$ for A Series

		A Series					
Parameter	1	2	3	4	5	6	SD
Slope of log $k_{\exp} = f(H_0)$	1.305	1.284	1.274	1.251	1.278	1.274	0.0159
r	0.993	0.993	0.991	0.995	0.993	0.991	-
Slope of log $k_{exp} = f(\log a_{H_2O})$	9.322	9.742	10.418	10.252	10.279	10.364	0.398
r	0.976	0.986	0.977	0.982	0.988	0.988	_

r: Coefficient of correlation.

SD: Standard deviation.

Table IV Values of Slope and Coefficient of Correlation (*r*) for Equations $\log k_{exp} = f(H_0)$ and $\log k_{exp} = f(\log a_{H_2O})$ for B Series

		B Series					
Parameter	1'	2'	3'	4′	5'	6′	SD
Slope of log $k_{exp} = f(H_0)$	1.024	1.241	1.274	1.222	1.194	1.215	0.080
r	0.993	0.987	0.991	0.990	0.993	0.988	-
Slope of log $k_{exp} = f(\log a_{H_2O})$	10.707	10.832	11.176	10.002	11.510	13.777	1.186
r	0.998	0.995	0.990	0.998	0.983	0.996	_

r: Coefficient of correlation.

SD: Standard deviation.



Figure 8 Hammett correlation for A and B series of pyrrolic Schiff bases in the H₀ zone.



Figure 9 Hammett correlation for A and B series in the P' zone.

correlation, r = 0.997) and 1.92 (r = 0.976) for the A and B series, respectively. Then, the positive values of ρ confirmed the water nucleophilic attack on the protonated imine, which is favored by the electron-withdrawing effect of X substitutes [26,36].

In zone A, i.e., the pH range of 4–8, on the one hand, the hydrolysis reaction is catalyzed by acidity since the observed rate constants decrease markedly with an increase in pH whatever the substitute X. On the other hand, the kinetic constant value increased slightly when X is an electron-withdrawing substituent (Tables I and II).

If we considered the protonated imine (SH^+) attacked only by water molecules (step b'), the theoretical equation (4) can be simplified to Eq. (6):

$$k_{\rm obs} = \frac{k_1 [\rm H^+]}{K_{\rm SH^+}} \tag{6}$$

where the slope of the plot $log(k_{obs}) = f(pH)$ is equal to 1.

But, for these substituted pyrrolic series, the experimental slopes of the linear plots of log $k_{exp} = f(pH)$ varied from 0.5 to 0.8. So, Eq. (6) is not sufficient to describe the hydrolysis behavior of A and B series of *N*-Y-pyrrolyl-2-methylene-X-aniline and in this case the step c' (Scheme 3) cannot be neglected. Consequently, Eq. (4) becomes Eq. (7), where the hydrolysis reaction is simultaneously specific acid and base-catalyzed:

$$k_{\rm obs} = \frac{k_1[{\rm H}^+] + K_e k_2}{([{\rm H}^+] + K_{\rm SH^+})}$$
(7)

The basic plateau P appeared from pH 8–13, and in this domain Reeves [41] demonstrated that the ratelimiting step corresponded to the nucleophile attack of hydroxide anion on the protonated imine. The hydrolysis constant is then given by Eq. (8), where the kinetic constant is independent from pH:

$$k_{\rm obs} = \frac{K_e k_2}{K_{\rm SH^+}} \tag{8}$$



Figure 10 Hydrolysis curves of **1** and **1'** Schiff bases (*N*-2-pyrrolylmethylene-aniline and *N*-methyl-*N*-2-pyrrolylmethylene-aniline, respectively).



Figure 11 Hydrolysis curves of **5** and **5'** Schiff bases (*N*-2-pyrrolylmethylene-*p*-chloro-aniline and *N*-methyl-*N*-2-pyrrolylmethylene-*p* chloro-aniline, respectively)

Regarding the X substitutes, from the results, the kinetic constant decreased when X was an electronwithdrawing substituent; this is in agreement with the conclusions of Reeves [41] and Cordes and Jencks [36] about the substituted aromatic Schiff bases.

Finally, about the effect of Y substitute, examples of comparison are shown in Figs. 10 and 11. The results demonstrated that the kinetic constants increased when $Y = CH_3$ in all pH zone. However, in the H₀ zone, the curves are almost merged.

CONCLUSION

The present investigation is focused on the kinetic hydrolysis studies of two series of *N*-pyrrolyl-2-

methylene-aniline derivatives. The experimental kinetic constants were calculated, and the results showed bell-shaped hydrolysis curves of log $k_{exp} = f(pH, H_0)$. Good Hammett correlations were obtained in the zone P' of pH from 0 to 4 and in the H₀ zone (from -4 to 0). In the zone of H₀ of interest, linear relationships were obtained both between log k_{exp} and H₀ and between log k_{exp} and log a_{H_2O} . Finally, the hydrolysis mechanism was elucidated in each zone of pH and H₀.

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