

Effect of Partially Aqueous Solutions of Different pH's on the Hydrolysis Rate of Some Schiff Bases

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The mechanism of the hydrolysis of a series of Schiff bases derived from *p*-phenylenediamine and various aromatic aldehydes has been examined in aqueous media containing 40 wt% methanol, in the presence of NaOH. The base hydrolysis reaction of these compounds is strictly second-order kinetics, first-order with respect to the Schiff base and also to hydroxide ion, and the hydroxide ion attack on the free base becomes the rate-determining step under these basic conditions. The work is extended to include a systematic kinetic study on the hydrolysis reaction of the Schiff bases under investigation, in partially aqueous solutions of different pH's, in media containing 40 wt% methanol. A rate profile diagram of pH vs. hydrolysis rate constant for all of the Schiff bases shows that the rate is minimal at alkaline region (pH > 8.96), and too rapid at strongly acidic media (pH < 3.53).

Key words: Schiff bases, kinetics, base hydrolysis

Schiff bases are considered as a very important class of organic compounds. Azomethine compounds have wide applications in many biological aspects, i.e., proteins [1], visual pigment [2], enzymic aldolization [3], decarboxylation reactions [4], in pyridoxal phosphate degradation [5] and in the field of color photography [6]. These wide applications of Schiff bases have generated a great deal of interest in metal complexes, kinetics of formation and hydrolysis as well as electronic spectra and acidity constants.

In general, hydrolysis of Schiff bases is considered to be one of the most significant reactions in many pharmacological and biological processes [7–9]. Mechanisms of formation and hydrolysis of imines have been investigated in great detail and are now understood very well. However, analysis of the kinetic data has shown that the mechanism of hydrolysis of the aldimine linkage undergoes a transition from the rate-determining decomposition of the carbinolamine (to aldehyde and amine) under strongly acidic conditions to the rate-determining formation of the carbinolamine in mild acidic or basic medium. In other publications, the rate-limiting step was the attack of a water molecule on the protonated Schiff base in acidic or neutral solutions, while the attack of hydroxide ion on the free one is the predominant reaction in basic medium.

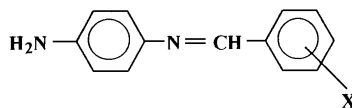
Hydrolysis of mono- and bi-functional Schiff bases has been the subject of some investigations [10–12], but no previous kinetic studies have been reported on the hydrolysis of double Schiff bases. This drew our attention and motivated the present study, whose objective is to shed light on the nature of some mono-, bi-functional or

double Schiff bases derived from *p*-phenylenediamine and certain aromatic aldehydes through their kinetic hydrolysis under base, neutral and acid conditions in aqueous media containing 40 wt% methanol.

EXPERIMENTAL

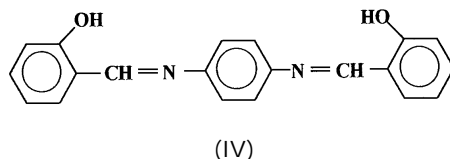
Materials: All the chemicals used in the present work were of the highest purity available (A.R. reagents) from BDH. They were used without further purification. The organic solvent employed, methanol, was spectroquality grade.

Synthesis of solid Schiff bases: Mono-functional Schiff bases: Equimolecular proportions (0.01 mol) of *p*-phenylenediamine and aromatic aldehyde were dissolved in ethanol (100 ml), to which piperidine (0.5 ml) was added. The reaction mixture was refluxed for about 3–5 h. The product was recrystallized from methanol. The synthesized mono-functional Schiff bases are

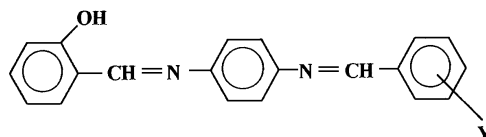


X = *p*-F-OH (compound I); -OH (compound II); -NO₂ (compound III).

Bi-functional Schiff base: The solid bi-functional Schiff base (IV) was prepared by refluxing *p*-phenylenediamine and salicylaldehyde (in 1:2 molar ratio) in absolute ethanol as described before [13].



Double Schiff bases: These compounds (V and VI) were prepared by reactions of two different aldehydes and *p*-phenylenediamine in a way similar to that previously described [14].



Y = -OH (compound V); -NO₂ (compound VI).

The purity of the compounds synthesized was checked by micro-chemical analysis, IR and ¹H NMR spectroscopy. The colour, melting points, yield percentage, molecular formula, molecular weight, elemental analysis, IR and ¹H NMR data of the synthesized compounds (I–VI) are listed in Table 1.

Working solutions: Schiff base solutions: Stock solutions (1 × 10⁻³ mol dm⁻³) of each of the Schiff bases (I–VI) were prepared by dissolving the accurate weight of the recrystallized solid compound in the required volume of methanol. Solutions of low molarity were prepared by appropriate dilution of the stock solutions. The concentration of the solutions prepared could not be higher than approximately 1 × 10⁻³ mol dm⁻³, because of the low solubility of some of the compounds used.

Table 1. Elemental analysis data, colour, melting point, yield percentage, some IR and ¹H NMR frequencies of the imine compounds under investigation.

Comp. No.	Colour	M.P. (°C)	Yield (%)	Mol. Formula (Mol. Wt.)	Calcd./(found) %			ν _{IR} (cm ⁻¹)			¹ H NMR (Chloroform) (ppm)
					C	H	N	OH	N=CH		
I	Orange	198	91	C ₁₃ H ₁₂ N ₂ O (212)	73.59 (73.41)	5.66 (5.20)	13.21 (12.33)	3446	1612	3.8 [s, 2H, (NH ₂)], 7.2-7.7 [m, 8H, aromatic] 8.4 [s, 1H, (CH)] 12.8 [s, 1H, (OH)]	
II	Brown	185	82	C ₁₃ H ₁₂ N ₂ O (212)	73.59 (73.20)	5.66 (5.22)	13.21 (12.20)	3454	1610	3.7 [s, 2H, (NH ₂)], 7.2-7.9 [m, 8H, aromatic] 8.4 [s, 1H, (CH)] 12.8 [s, 1H, (OH)]	
III	Reddish-brown	160	68	C ₁₃ H ₁₁ N ₃ O ₂ (241)	64.73 (65.10)	4.56 (4.30)	17.43 (16.91)	-	1625	3.8 [s, 2H, (NH ₂)], 7.1-7.7 [m, 8H, aromatic] 8.4 [s, 1H, (CH)]	
IV	Orange	205	88	C ₂₀ H ₁₆ N ₂ O ₂ (316)	75.95 (75.41)	5.06 (4.80)	8.86 (8.01)	3484	1609	7.2-7.8 [m, 12H, aromatic] 8.5 [s, 2H, (CH) ₂] 12.9 [s, 2H, (OH) ₂]	
V	Deep orange	200	74	C ₂₀ H ₁₆ N ₂ O ₂ (316)	75.95 (75.33)	5.06 (4.78)	8.86 (7.88)	3515	1620	7.2-7.7 [m, 12H, aromatic] 8.5 [s, 2H, (CH) ₂] 12.9 [s, 2H, (OH) ₂]	
VI	Yellow	170	70	C ₂₀ H ₁₅ N ₃ O ₃ (345)	69.56 (69.33)	4.34 (4.19)	12.17 (11.66)	3500	1610	7.1-7.9 [m, 12H, aromatic] 8.4 [s, 2H, (CH) ₂] 12.8 [s, 1H, (OH)]	

All the melting points are uncorrected.

Sodium hydroxide solution: 1.0 mol dm⁻³ sodium hydroxide stock solution was prepared by dissolving the approximate weight of the solid compound into optimum volume of carbon dioxide-free bidistilled water. Then, the stock solution was standardized of exactly known molarity according to the usual methods.

Potassium chloride solution: 1.0 mol dm⁻³ stock solution of potassium chloride was prepared by dissolving the requisite amount in the appropriate volume of deionized water.

Universal buffer solutions: Modified universal buffer series H₃PO₄, CH₃COOH, H₃BO₄ and NaOH of pH values 1.70–11.90 were prepared in aqueous media containing 40 wt% methanol, according to Britton [15]. The pH values of solutions, at 20°C, were checked with a practionic MV-87 digital pH-meter accurate to ± 0.05 pH-unit.

Due to the presence of methanol in the aqueous media of different pH, the acidity, basicity, dielectric constant and ion activities of these partially aqueous solutions are altered compared to those of the pure aqueous ones. The measured pH values of the former solution must be corrected by applying the equation [16]: pH* = pH (R) – δ, where pH* is the corrected reading and pH(R) is the meter reading obtained in a partially aqueous medium, the pH-meter being standardized with standard aqueous buffer solutions. The value of δ for aqueous buffer solutions containing 40 wt% methanol is 0.09 [16].

Kinetic procedure for hydrolysis measurements: Each of the reactant solution was introduced into a glass-stoppered tube in appropriate amount. These tubes were then placed in an ultrathermostat. After temperature equilibrium was attained, a known volume of the reactants was mixed rapidly in a 25 ml measuring flask and made up with the same solvent used as for the reagents. The mixing time was taken as the zero reaction time. The hydrolysis rate of Schiff base was observed and recorded spectrophotometrically by measuring the absorbance at the characteristic wavelength (λ_{max}) of the Schiff base, at different time intervals, when the hydrolysis products did not absorb at this wave-length. The amounts of Schiff base hydrolysed at different time intervals were calculated by Beer's law. The reaction rate constants were evaluated from the slopes of the first-order rate plots.

Physical measurements: The kinetic runs were achieved spectrophotometrically by means of a Shimadzu UV-Visible Recording Spectrophotometer UV-240 using 1.0 cm matched fused silica cells. Infrared spectra were recorded in the region 4000–400 cm⁻¹ on a Pye Unicam SP 1100 Infrared Recording Spectrophotometer, by the KBr-disc technique. ¹H NMR spectra (chloroform) were recorded on a Gemini 200 Varian Spectrometer (200 MHz) and the spectra extended from 0 to 15 ppm.

RESULTS AND DISCUSSION

Base hydrolysis mechanism: The partial order of the base hydrolysis reaction with respect to both the Schiff base and sodium hydroxide used in the reaction medium was determined making use of the initial rate as a function of the initial concentration method [17]:

$$b = \frac{\log\left(\frac{d_k}{d\theta}\right)_1 - \log\left(\frac{d_k}{d\theta}\right)_2}{\log b_1 - \log b_2}$$

where b is the partial order with respect to Schiff base, $(d_k/d\theta)_1$ and $(d_k/d\theta)_2$ are hydrolysis reaction rates at Schiff base initial concentrations b_1 and b_2 , respectively. The hydrolysis data of Schiff base in the presence of sodium hydroxide in hydrolysis medium refer to the partial hydrolysis rate of Schiff base strictly following second-order kinetics. In other words, the base hydrolysis reaction is first-order with respect to each of the Schiff base and of sodium hydroxide. Good convincing evidence for the

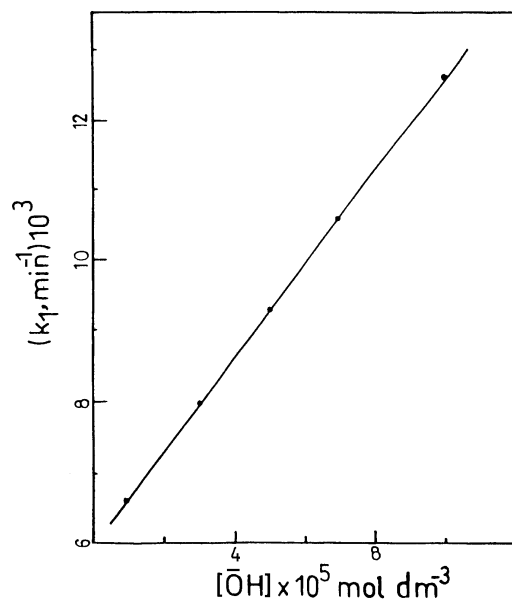
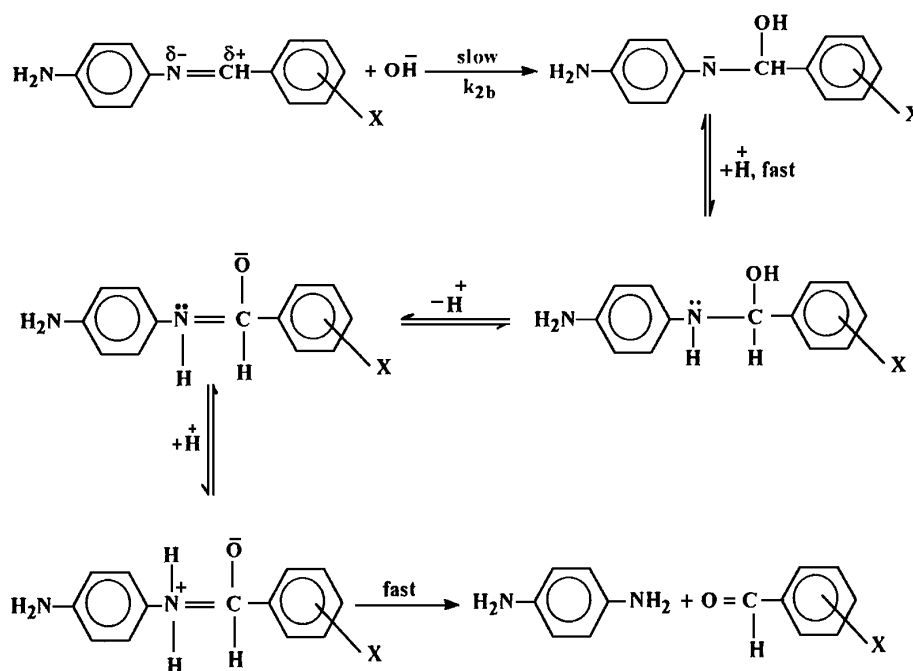


Figure 1. First-order rate constant as function of sodium hydroxide concentration for the base hydrolysis of 5×10^{-5} mol dm $^{-3}$ solution of Schiff base I, in aqueous medium containing 40 wt% methanol, at 35°C and μ 0.1 mol dm $^{-3}$.

first-order dependence of the hydrolysis reaction with respect to sodium hydroxide was achieved from the satisfactory straight line obtained on plotting the reaction rate constant values (k_{1b}) against $[\text{NaOH}]$, as shown in Figure 1. On the other hand, it was observed that the hydrolysis reaction rate of the Schiff base increases with increasing sodium hydroxide concentration in the hydrolysis medium. This indicates that the hydrolysis reaction of these compounds is dependent of sodium hydroxide and catalyzed by hydroxide ions. This behaviour can be illustrated on the basis that, under such basic media studied, the Schiff base is expected to be partially polarized. Therefore, the rate-determining step is suggested to be a hydroxide ion attack on the free Schiff base forming a carbinolamine anion intermediate [10,12]. This carbinolamine intermediate undergoes at least one proton transfer before it can break-down to products, such proton transfer is expected to be fast [18]. Generally, the base hydrolysis mechanism of the Schiff bases studied is suggested to be as in Scheme 1.

Following the above suggested mechanism, we can say that the rate of the base hydrolysis follows the kinetic equation: Hydrolysis rate = k_{2b} [Schiff base][hydroxide ion], where k_{2b} is the second-order rate constant. k_{2b} can be readily derived making use of the following relation: $k_{2b} = k_{1b}/a$, where a is the molar concentration of hydroxide ion, k_{1b} is the observed first-order rate constant (k_{obs}), which is practically determined from the slope of the first-order rate plots of the base hydrolysis reaction of Schiff base.

Scheme 1



Effect of Schiff base molecular structure on the base hydrolysis rate: The general features of the kinetics for hydrolysis of $5 \times 10^{-5} \text{ mol dm}^{-3}$ solutions of Schiff bases I–VI have been examined in aqueous media containing 40 wt% methanol and in the presence of $7 \times 10^{-5} \text{ mol dm}^{-3}$ sodium hydroxide, at 35°C , and ionic strength $\mu 0.1 \text{ mol dm}^{-3}$. This is done to clarify the role of polar substituents (X and Y) on the rate of hydrolysis and also to collect more information confirming validity of the suggested mechanism in alkaline media. In all cases studied, typical first-order rate constants (k_{1b}) were determined from the slopes of the $\log(a-x) \quad . \quad t$ relationship as depicted in Figure 2, and the values are listed in Table 2. The second-order rate constant values (k_{2b}) were also derived and registered in Table 2. Examination of the results, shown in Table 2, indicate that the rate of hydrolysis of the mono-functional Schiff bases studied, being dependent largely on the nature and position of the polar substituents (X) attached to the aromatic aldehydic moiety. It is evident that the first-order rate constants for hydroxide ion attack on the free bases increases with increasing electron-donating power of the substituent (X), according to the following order: ***o*-OH (compound I) > *p*-OH (compound II) > *p*-NO₂ (compound III)**. This behaviour may be attributed to increasing of positive charge on aldimine carbon atom with increasing the electron-donating power of substituent. This will result in an increase in the electrophilic character of the aldimine carbon atom rendering it highly susceptible to nucleophilic attack by hydroxide ion. This behaviour is in accordance with the proposed mechanism.

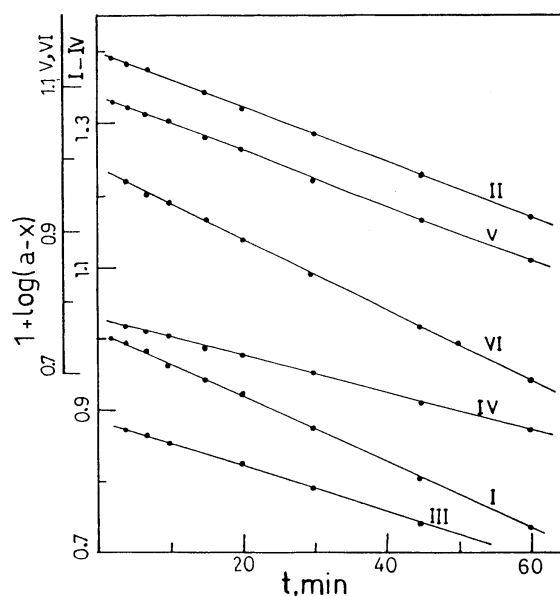


Figure 2. First-order rate plots for the base hydrolysis of $5 \times 10^{-5} \text{ mol dm}^{-3}$ solutions of Schiff bases I–VI, in aqueous medium containing 40 wt% methanol, in the presence of $7 \times 10^{-5} \text{ mol dm}^{-3}$ NaOH, at 35°C and $\mu 0.1 \text{ mol dm}^{-3}$.

Table 2. Observed first-order rate constant values (k_{1b}) and calculated second-order rate constant values (k_{2b}) for the base hydrolysis of $5 \times 10^{-5} \text{ mol dm}^{-3}$ solutions of Schiff bases I–VI in aqueous medium containing 40 wt% methanol, in the presence of $7 \times 10^{-5} \text{ mol dm}^{-3}$ sodium hydroxide, at 35°C and $\mu 0.1 \text{ mol dm}^{-3}$.

Schiff base	λ_{max} , nm	Observed first-order rate constant values (k_{obs} , min^{-1}) $\times 10^3$	$[\text{OH}^-] \times 10^5 \text{ mol dm}^{-3}$	Calculated second-order rate constant values (k_{2b} , $\text{min}^{-1} (\text{mol dm}^{-3})^{-1}$)
I	367	9.5 ± 0.22	7.0	135.7 ± 0.24
II	350	9.12 ± 0.17	7.0	130.3 ± 0.18
III	411	6.91 ± 0.01	7.0	98.7 ± 0.01
IV	365.5	6.04 ± 0.34	7.0	86.3 ± 0.30
V	368	10.8 ± 0.40	7.0	154.3 ± 0.38
VI	368.5	11.5 ± 0.60	7.0	164.3 ± 0.63

The precision of the k_{1b} values was treated by the linear least-squares method.

On the other hand, the high hydrolysis rate observed in the case of Schiff base I ($X = \text{F-OH}$), relative to the others, can be interpreted on the principle of the possible existence of F-OH compound in a tautomeric equilibrium of the type ketoamine \rightleftharpoons enolimine form [19,20]. Thus, in alkaline solutions this compound exists mainly in the ketoamine tautomer (ionized-form), which is expected to breaking-down fast. This is owing to the high mesomeric interaction of the $-\text{OH}$ group belonging to this

compound in alkaline media, which leads to increase the charge density on the ketoamine tautomer [20].

The observed fast base hydrolysis of Schiff base II (X = -OH), as compared to that of compound III (X = -NO₂), can be attributed to the expected ionization of phenolic -OH group substituent in such alkaline media employed. This will result in stabilization of the positive charge on the carbon azomethine group and facilitate the attack of hydroxide ion on the ionized Schiff base. Accordingly, relatively fast hydrolysis rate is observed in the case of compound II. The slowness showed in the hydrolysis rate of Schiff base III is attributed also to the high electron-withdrawing character of the -NO₂ group. This will result in delocalization of charge within the Schiff base molecule, where -NO₂ group behaves as acceptor center [21]. This behaviour increases the planarity of the Schiff base molecule [22]. Thus, stability of >C=N group is increased, *i.e.*, slow hydrolysis is observed. This behaviour can be considered as a further evidence for the suggestion that the rate-determining step in such alkaline media is the attack of hydroxide ion on the free Schiff base. On the other hand, it was observed that the double Schiff bases (V and VI) were more rapidly hydrolyzed than the mono-functional Schiff bases (I-III). This is mainly due to the high geometric flexibility and non-planarity of the double Schiff bases [23,24] and thus to the presence of some steric factors. All these facts indicate that the basic character of the azomethine group is increased and thus nucleophilic attack by hydroxide ion becomes more pronounced (rate-determining step). Furthermore, it is reasonable to expect that both the acceptor character of >C=N group and donor behaviour of -NH₂ group of the mono-functional Schiff bases may in different way increase the stabilization of imine bond against hydrolysis. This property is not available in the case of the double Schiff bases.

Effect of solutions of different pH's on rate of hydrolysis: The hydrolysis rates for 7×10^{-5} mol dm⁻³ solutions of mono-, bi-functional and double Schiff bases (I-VI) have been studied in a series of buffer solutions having pH ranging from 1.68 to 11.85, in aqueous media containing 40 wt% methanol, at an ionic strength of 0.1 mol dm⁻³ adjusted with 1.0 mol dm⁻³ KCl, at 30°C. For each compound, the determined first-order hydrolysis rate constants (k_1) are plotted against pH, as in Figure 3. A rate profile diagram of pH *vs* rate constant (Fig. 3) shows that the rate is minimal at alkaline region (pH > 8.95), and too rapid at strongly acidic media (pH < 3.53). The observed complex variation of the hydrolysis rate with pH can be interpreted satisfactory in terms of the suitable acid and base hydrolysis mechanisms.

Rate-limiting pathways: In the pH range 1.68-11.85, the hydroxy Schiff bases under investigation were found to undergo hydrolysis by various rate-determining pathways as follows: (i) A path involving the attack of hydroxide ion on the imine anion, L⁻(k_1). (ii) A pure hydrolysis including the addition of water molecule to the aldimine linkage of the neutral imine, HL(k_2). (iii) A hydrolysis process involving the reaction of water with the protonated substrate, H₂L⁺(k_3). (iv) The decomposition of fully protonated Schiff base, H₃L²⁺, in an acid catalyzed path (k_4). Thus, the overall rate of hydrolysis will be: Hydrolysis rate = $k_1[L^-] + k_2[HL] + k_3[H_2L^+] + k_4[H_3L^{2+}]$.

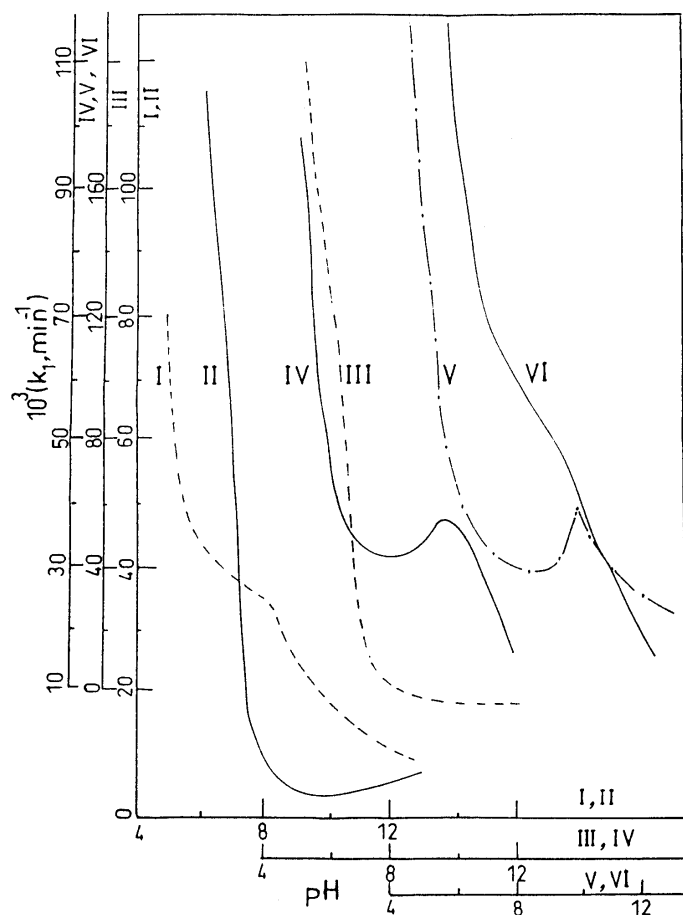
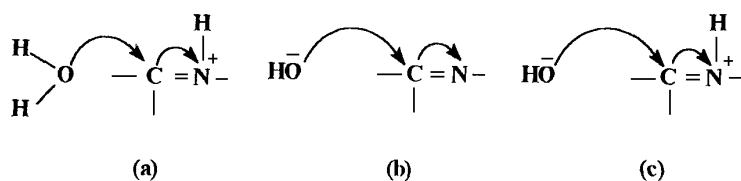


Figure 3. First-order hydrolysis rate constants k_1 vs. pH for $7 \times 10^{-5} \text{ mol dm}^{-3}$ solutions of Schiff bases I–VI, in aqueous media containing 40 wt% methanol, at 30°C and $\mu 0.1 \text{ mol dm}^{-3}$.

Furthermore, under basic, neutral and acidic conditions, the following remarks have been noticed:

(i) In alkaline region ($\text{pH} > 8.95$), the hydrolysis rate of the Schiff base II ($-\text{OH}$) increases slightly as the pH of the medium is increased. This indicates that the hydrolysis reaction of this compound is pH-dependent in the pH range 8.95–11.85 and catalyzed by hydroxide ions. In such basic media, the Schiff base II is expected to occur in anionic form (L^-), due to the neutralization of the phenolic proton of the hydroxy group by the hydroxide ions of alkali [21]. The observations above lead to the assumption that the complex formed may be an "Arrhenius complex". In the presence of an excess catalyst, an "Arrhenius complex" leads to specific hydroxide ion catalysis [25,26]. All these points indicate that the rate-determining step is the reaction of the Schiff base anion (L^-) with hydroxide ion (Scheme 1). On the other hand, above pH 8.95 for compounds I and VI, and $\text{pH} > 9.75$ for compounds IV and V, the hydrolysis

rates of these compounds decrease with increasing the pH of the medium. This may be accounted for the corresponding decrease in the concentration of the polarized Schiff base as the pH of the medium is increased. This will probably lead to make the attack of hydroxide ion on the pre-equilibrium polarized Schiff base more difficult. Therefore, slow hydrolysis rate is observed. In other words, the hydrolysis mechanism of the Schiff bases studied under basic conditions can be illustrated on the principle that, for Schiff bases derived from basic amines, the hydrolysis rate-determining step may correspond to addition of water to the protonated imine (a), the addition of hydroxide ion on the free substrate (b), and the attack of hydroxide ion on the protonated Schiff base (c).

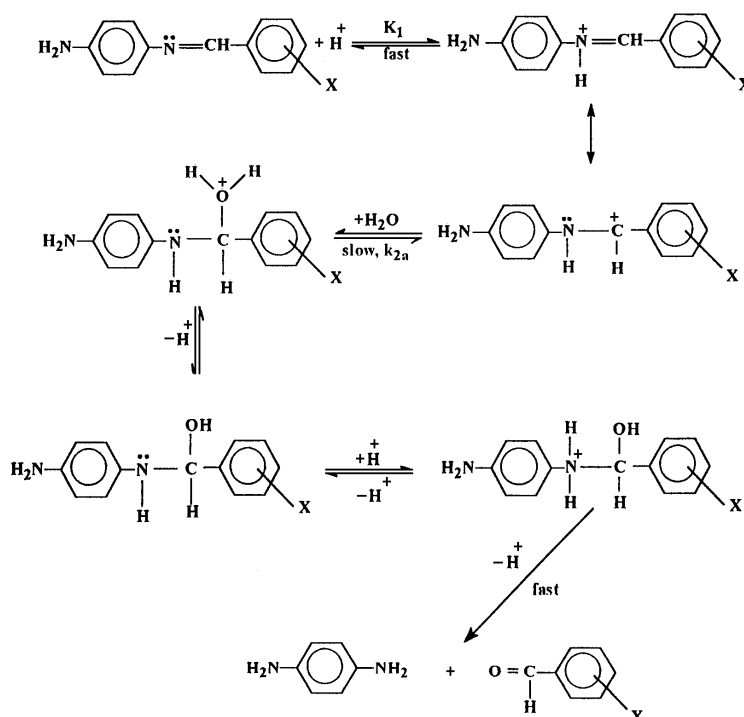


According to the above observations, the hydrolysis reaction of Schiff bases under investigation in alkaline media, involving the rate-determining step, may be the attack of hydroxide ion on the free base or since under these basic conditions only a small fraction of the Schiff base exists as the conjugate acid, in such case, the rate-determining step may be the attack of hydroxide ion on the partially protonated Schiff base. If the attack of hydroxide ion on free base is the rate-determining step, it would be expected that the hydrolysis rates would be accelerated with increasing the pH in the hydrolysis medium. On the other hand, in the case of the attack of hydroxide ion on the partially protonated Schiff base, the effects of polar substituents on the pre-equilibrium protonation reaction will oppose those for the attack of hydroxide ion and consequently, the observed hydrolysis rates show a smaller dependence on the nature of the polar substituents. The observation that, increasing the pH in the hydrolysis medium actually retard the hydrolysis rates, is consistent with the second possibility and strongly suggests that, this reaction involves the attack of hydroxide ion on the protonated Schiff base. On the other hand, above pH 8.15 the hydrolysis rate of compound III ($X = -NO_2$) is little dependent on pH. This behaviour can be explained in terms of the stabilization of the transition state (intermediate carbinolamine, Scheme 1) of this hydrolysis reaction by resonance delocalization of the charge within the Schiff base molecule. This fact can be substantiated by the observed much slower base hydrolysis rate for this compound relative to other ones under similar conditions (the same pH values).

(ii) In the pH range 7.38 – 8.95, the break observed in the pH . hydrolysis rate profile (Fig. 3), for the compounds under investigation, is ascribed to the usual transition from the rate-determining attack of hydroxide ion on the imine anion (L^-) under basic conditions to a reaction involving the addition of water to the protonated substrate (H_2L^+) in slightly acidic media.

(iii) In slightly acidic media ($6.25 > \text{pH} > 4.22$), the rates of hydrolysis for the all compounds studied are pH-dependent, where they increase on lowering the pH of the medium. This is attributed mainly to that the reaction is catalyzed and activated by protons as a result of conversion of the Schiff bases into their conjugate acids ($-\text{CH}=\text{N}^+\text{H}- \leftrightarrow -\text{C}^+\text{H}-\text{NH}-$) in acidic media. In such media, the proton-catalyzed attack of water on the reactive imine linkage of (H_2L^+) becomes the predominant reaction pathway (Scheme 2).

Scheme 2



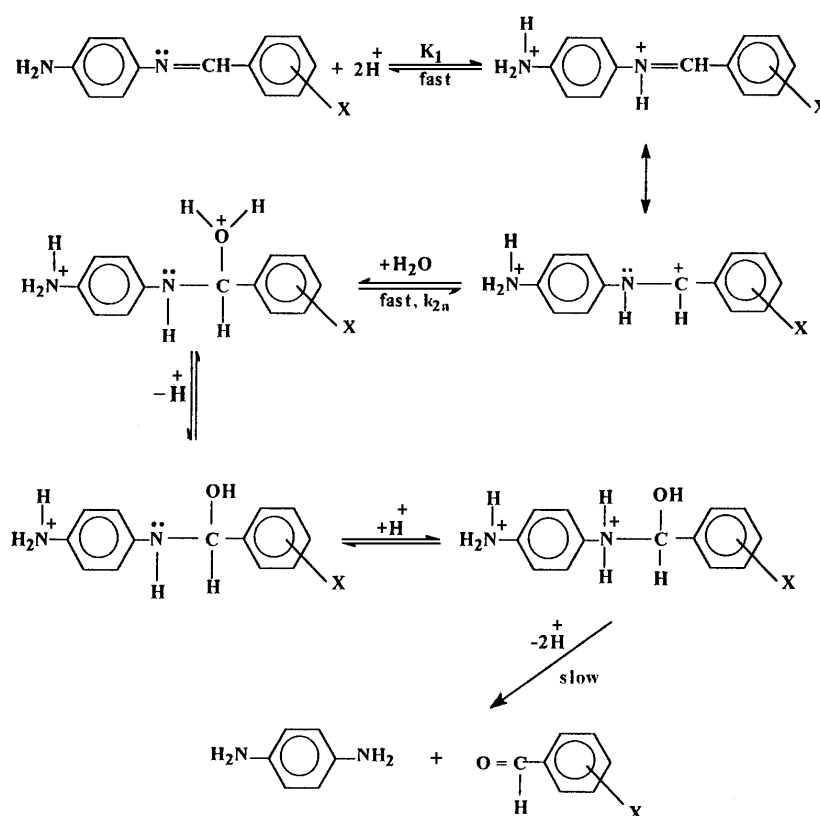
Accordingly, the hydrolysis mechanism involves the conversion of the azomethine group to its conjugate acid in a rapid pre-equilibrium followed by a slow water attack. This suggestion has a reasonable theoretical base, since the anil carbon assumes considerable carbonium-ion character in the conjugate form and this is more susceptible to nucleophilic attack by water [27]. Furthermore, such compounds in their conjugate acid form will result in a more pronounced electrophilic character of the carbonimine group.

It is worth mentioning that the ortho-hydroxy derivatives (I, IV, V and VI) are expected to be more rapidly hydrolyzed relative to the other compounds. This is mainly due to an intermediate compound involving a water molecule positioned with the help of the adjacent bulky hydrophilic $-OH$ group. Despite this, ortho-hydroxy compounds showed relatively low hydrolysis compared to that of the compounds II and

III. This is explained in the principle that the F -OH group of the ortho-hydroxy Schiff bases studied has a tendency to interact with the nitrogen azomethine group through an intramolecular H-bond solvated complex [21]. This will result in stabilization of the imine bond against hydrolysis. Thus, low hydrolysis rate was observed.

(iv) Under more acidic conditions ($\text{pH} < 4.22$), the compounds exhibit hydrolysis that is too rapid to be followed by conventional methods. This can be explained on the basis that, under more acidic conditions, the Schiff bases are expected to be completely converted into their conjugate acids and thus the starting substrates are fully protonated (H_3L^{2+}). Therefore, the rate-determining step is suggested to be the water-catalyzed decomposition of the fully protonated substrate (H_3L^{2+}) rather than the attack of water on the protonated imine (H_2L^+) in moderately acidic media [26,28]. The underlying mechanism can be plausibly suggested as follows:

Scheme 3



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