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ORIGINAL ARTICLE

The hydrolysis of pyridilmonoimines in acidic aqueous media

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Acetate buffer

Abstract The rates of hydrolysis of some pyridilmonoimines have been investigated in aqueous methanol medium of acetate buffer. The hydrolysis of the studied bases found to be slower than that of benzylideneaniline. It is evident from the dependent of the rate constants upon the buffer concentration that the rate equation has the form of special and general acid catalysis. From the results it is suggested that the rate-determining step appears to be the protonation of the nitrogen atom of the imino group of the monoamines at the employed pH.

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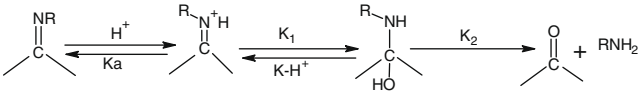
1. Introduction

The intermediacy of Schiff bases in the catalytic action of several enzymes has generated a great deal of interest in the mechanism of formation and hydrolysis of these compounds (Kayse and Pollack, 1977; Metzler et al., 1980; Sanchez-Ruiz et al., 1982; Spaganitcz and Martell, 1984; Garcia del Vado et al., 1987; Vazquiz et al., 1989).

The formation and hydrolysis of a number of Schiff bases, oximes, semicarbazones and related compounds have been shown to proceed through the intermediate formation of carbinolimine which subsequently breaks down, with the formation of carbinolamine (k_1) as a rate-determining step at high pH and the break down to products (k_2) as a rate-determining step at lower pH (Kayse and Pollack, 1977; Cordes and Jencks, 1963).



It has been established (Kayse and Pollack, 1977; Rosenberg et al., 1974; Sayer and Colon, 1980; Katzhendler and Goldbum, 1985) that the general behavior of the hydrolysis depends on the pH range. Under basic conditions (pH > 7) the rate-determining step is the attack of hydroxide ion on the substrate. When the pH reaches more acidic values (pH < 5), in which all the bases exist predominantly as the conjugate acids, the rate constants reflects the rate of attack of water on the fully protonated substrates. Under still more acidic conditions the decomposition of the tetrahedral carbonolamine is the rate-determining step. Carbinolamine itself may break down through the following Scheme (Rosenberg et al., 1974; Sayer and Colon, 1980; Katzhendler and Goldbum, 1985).

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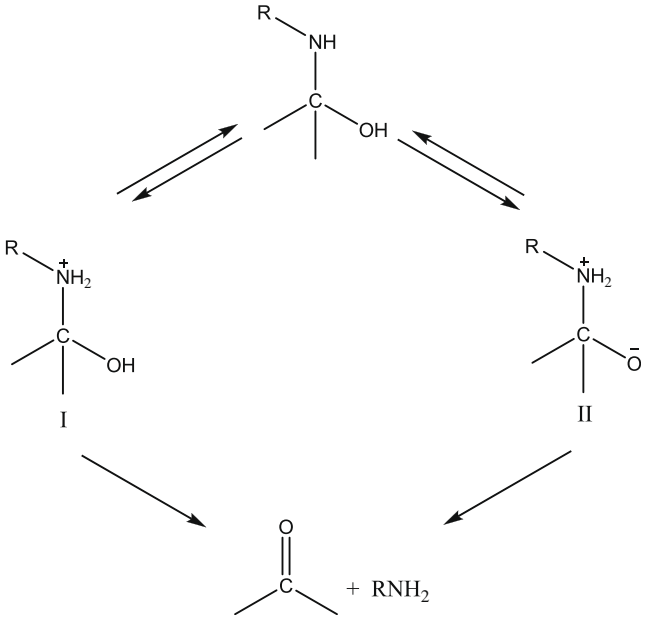


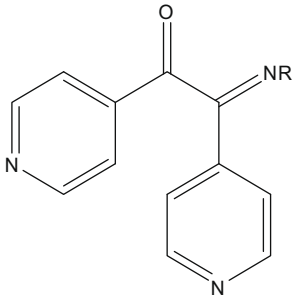
The intermediate may decompose through either a positively charged species (I) or a Zwitter ion (II). At very high acidity (pH < 2) product formation proceeds via intermediate (I) (Fischer et al., 1980; Jones and Wolfenden, 1986).

Furthermore these species are interconvertable through a complex series of reaction. This Scheme is self-explanatory for the change in the rate-determining step of the decomposition of the carbinolamine as the buffer concentration varies, illustrating the sensitivity of the hydrolysis reaction to specific and general acid catalysis (Billobono and Favini, 1969; Archilla et al., 1971).

Studies that are concerned with the activation parameters of hydrolysis (Chaturvedi and Cordes, 1967; Weinstein and McIninch, 1960) indicate the complexity of the effects of structural alternation on the reactivity.

The studied bases are similar to the well know and thoroughly studied benzylideneanilines, however the pyridoyl group may introduce some effects that make their hydrolysis different from that of benzylideneanilines.

This work is devoted to investigating the hydrolysis of some pyridilmonoimines in acidic aqueous media at different temperatures in order to shed some light on the mechanism, catalysis, and activation parameters of the hydrolysis of these compounds. The studied compounds have the following structures:



Where R is:

1. CH_3; 2-(methylimino)-1,2-di(pyridine-4-yl)ethanone.
2. C_6H_6; 2-(phenylimino)-1,2-di(pyridine-4-yl)ethanone.
3. 4-Chlorophenyl: 2-(4chlorophenylimino)-1,2-dipyridin-4-yl)-ethanone.
4. 4-Toly; 2-(4-methylphenylimino)-1,2-di(pyridi-4-yl)eth anone.
5. 4-Methylphenyl; 2-(methoxyphenylimino)-1,2-di(pyridine-4-yl)ethanone.

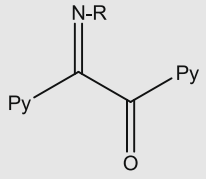
2. Experimental

Due to low solubility of the bases in water, 50/50 v/v methanol/water mixtures used as solvents. Reactions were followed spectrophotometrically employing LKB ULTROSPEC II 4050 UV/VIS spectrophotometer equipped with a thermostatic cell holder. Temperature was maintained with the aid LAUDA K_4R thermostated bath using PHILLIP HARRIS precession thermometer. The reactions were carried out at an ionic strength of 0.1, maintained through the addition of KCl, and followed to 90% completion.

The measurements of the hydrolyses rates were typically done as follows; the appropriate volume of the imine solution was rapidly diluted with buffer to attain a concentration of 1×10^{-4} M. The solution then rapidly transferred to a quartz cell of path length of 1 cm. The hydrolyses then monitored spectroscopically at 340 nm which represents the wave length of the imino group absorption.

The average values of the rate constants were reproducible to less than 1% for five determinations. The spectra of the hydrolyzed bases were found to be similar to those of pyridil

Table 1 Rate constants and thermodynamic parameters of the hydrolysis of the studied bases in acetate buffer (pH 4) at constant ionic strength.



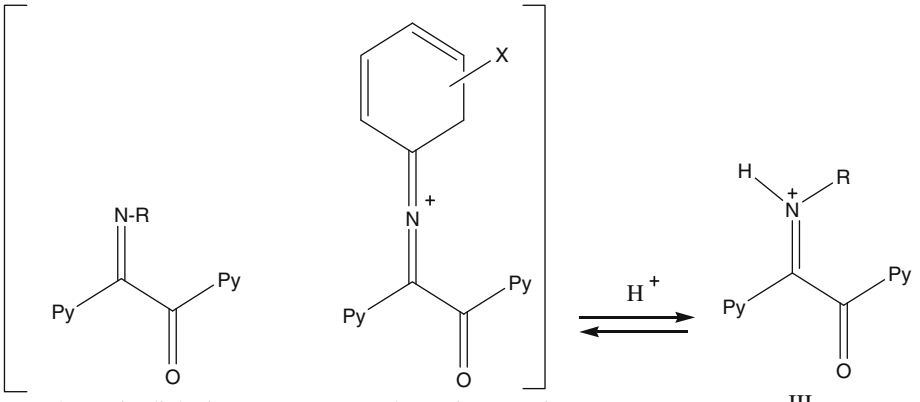
R	$k \times 10^3$ (s^{-1})		E_a (kJ mol^{-1})	$-H$ (kJ mol^{-1})
CH_3	303	7.42	80.0	77.5
	308	12.62		
	313	21.67		
C_6H_6	303	0.03	100.5	98.0
	308	2.70		
	313	4.12		
4-ClC_6H_4	303	0.93	136.3	133.8
	308	1.85		
	313	3.80		
4-MeC_6H_4	303	2.02	103.4	100.9
	308	3.86		
	313	5.65		
4-$MeOC_6H_4$	303	2.38	107.6	105.1
	308	4.80		
	313	4.40		

and the amine. Rate constants were determined as the slopes of the lines obtained from plotting the logarithm of the absorbance ($-\ln A$) against the time (s).

3. Results and discussion

The experimental results are gathered in Table 1.

The hydrolysis of the studied bases (compounds **1**–**5**) is considerably slower than those of benzylideneaniline. The rate constant of benzylideneaniline is $1.5 \times 10^{-3}\ s^{-1}$ at pH 7 (Billobono and Favini, 1969) while molecule 1 of the studied compounds show no hydrolysis at this pH. This is explained in terms of the presence of the pyridoyl group instead of the phenyl group as it is the only difference between the two molecules. This group introduces two factors operating in opposite sense, inductive and steric factors. Since electron-withdrawing factors known to increase the hydrolysis therefore the steric factor seems to be predominating but are not the only factors.



I, when R is aliphatic II, when R is aromatic III

The effect of buffer concentration at constant ionic strength on the rate constant of molecule 1 is reported graphically in Figs. 1 and 2. It is clear that the slope of the curve is determined by the increase of [HAc]. Thus it is evident that the rate equation has the form of special and general acid catalysis (Weinstein and McIninch, 1960)

$$K_{obs} = K_H^+ [H^+] + K_{HAc}[HAc]$$

In contrast to the linear buffer plot obtained at pH 4 (Fig. 1) the plot at lower pH (pH 2) is not linear (Fig. 2). The effect of increasing buffer concentration on K_{obs} at lower pH suggests a change in the rate-determining step.

Table 1 shows that the observed rate constants increase with increasing of the electron donating ability of the substituent R on the nitrogen atom of the imino group. It is clear that the rate constant in the case of the aliphatic substituent is much more larger than the case of the aromatic substituent (McCormick and Fory, 2006).

The same trend is also obvious when the substituent is aromatic since *Para* substituent withdrawing groups seem to reduce the rate of hydrolysis in contrast of *Para* substituent donating groups. This behavior consists in which is the rate-determining step of the mechanism. It may be suggested that the rate-determining step appears to be the protonation of the nitrogen atom of the imino group at the employed pH (pH 4). This will be understandable in the terms of the following mechanism:

Thus when R is aliphatic group, it is not possible for the participation of resonance structure II and the protonation of I yields III efficiently. When R is an aryl group, structure II exists and the result is that the protonation is slower because of the lower basicity of nitrogen atom. In this case when the substituent X is an electron-withdrawing group, the participation of II in the resonance hybrid is higher, the basicity of nitrogen atom is lower and the protonation to give III is slower. When

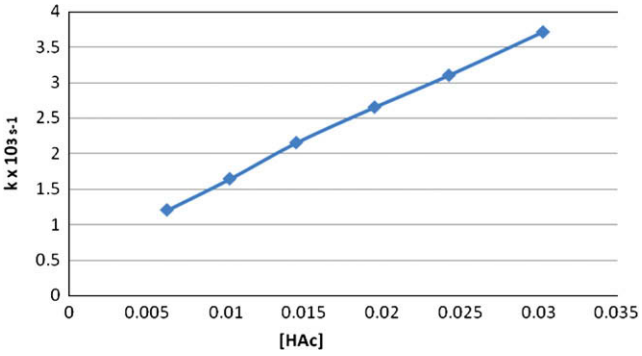


Figure 1 Effect of acid concentration at constant ionic strength (0.1) and pH 4 on the rate of hydrolysis of compound **1** at 30 °C.

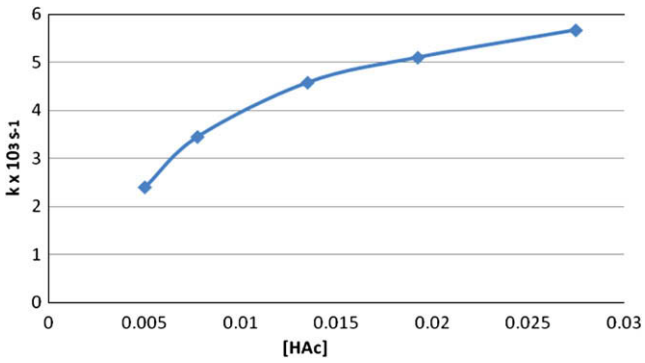


Figure 2 Effect of acid concentration at constant ionic strength (0.1) and pH 2 on the rate of hydrolysis of compound **1** at 30 °C.

X is an electron-donating group, the participation of II in the resonance hybrid is lower, the basicity of nitrogen atom is higher and the protonation to give III is faster.

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