



## KINETIC STUDY AND MECHANISM OF HYDROLYSIS OF N-SALICYLIDENE-m-CHLOROANILINE

ANIL S. KIRDANT<sup>a</sup>, S. G. SHANKARWAR and T. K. CHONDHEKAR\*

Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University  
AURANGABAD (M.S.) INDIA

<sup>a</sup>Vasnat Mahavidyalaya, KAIJ Dist.: Beed (M.S.) INDIA

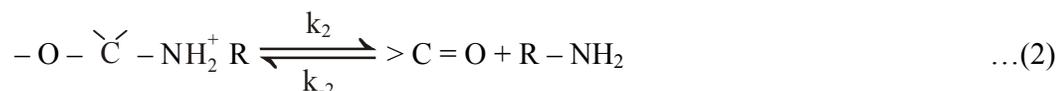
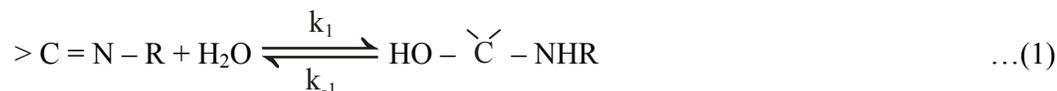
### ABSTRACT

The hydrolysis of Schiff base is an important reaction of biochemical interest. Kinetics of hydrolysis reaction of the Schiff base, N-salicylidene-m-chloro aniline (HL) has been studied in the pH range 2.86-12.30 at temperature 303 K. A rate profile diagram of pH v/s rate constant shows that the rate minimum in the pH range 5.21-10.22 and then increases reaching a plateau at pH > 11.42. Suitable reaction mechanism has been suggested for the hydrolysis of the Schiff base in acidic, neutral and basic media. From the effect of temperature on the rate, various thermodynamic parameters have been evaluated.

**Key words:** Schiff base, Hydrolysis, Kinetics.

### INTRODUCTION

The hydrolysis of Schiff base is an important reaction with biochemical interests<sup>1-3</sup>. The hydrolysis of number of Schiff base oximes, semicarbazones, and related compounds has been shown to proceed through eq.-(1) and (2) with step 1 as rate determining at neutral and alkaline pH values and step (2) as rate determining at acidic pH values<sup>4</sup>. The catalytic effect of hydrogen, hydroxyl and metal ions on the formation and hydrolysis of imines have been studied by several workers<sup>5-7</sup>. In the present work, we have presented here a systematic study of the hydrolysis of Schiff base, N-salicylidene-m-chloroaniline at different pH values.



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\* Author for correspondence

## EXPERIMENTAL

The chemicals used such as salicylaldehyde, m-chloroaniline,  $\text{CaCl}_2$ , ethanol etc. were of AR grade. The Schiff base was prepared by condensation reaction of salicylaldehyde and m-chloroaniline in ethanolic medium for about one hour. Resulting yellow coloured crystals were cooled and recrystallized from ethanol. It was characterized by physical methods such as m.p., TLC, elemental analysis and IR spectra.

### Kinetic measurements

The rate of hydrolysis of Schiff base was followed spectrophotometrically at 440 nm using UV/VIS 1601 Shimadzu spectrophotometer. Universal buffer solutions were prepared according to the reported methods<sup>8</sup>. The pH was determined by using an Elico LI-120 pH meter. The temperature was varied between 293 – 308 K. The concentration of imine was kept at  $1.0 \times 10^{-4}$  mol.  $\text{dm}^{-3}$ . The ionic strength of the reaction mixture was maintained at  $\mu = 0.1$  mol.  $\text{dm}^{-3}$  by using KCl (E. Merck). All other chemicals used were of A. R. grade (E. Merck). In a typical kinetic run, the solutions containing appropriate amounts of Schiff base and buffer solution were prepared at room temperature and allowed to equilibrate in previously adjusted thermostat. The quartz cuvettes were also allowed to equilibrate at the same temperature in the thermostatic cell block. After mixing, the reaction mixture was immediately transferred to a quartz cell and the decrease in absorbance of Schiff base with time was followed against the reagent blank kept in another quartz cell. The decrease of absorbance with time was followed at  $\lambda = 440$  nm using spectrophotometer within 20 s of mixing the Schiff base.

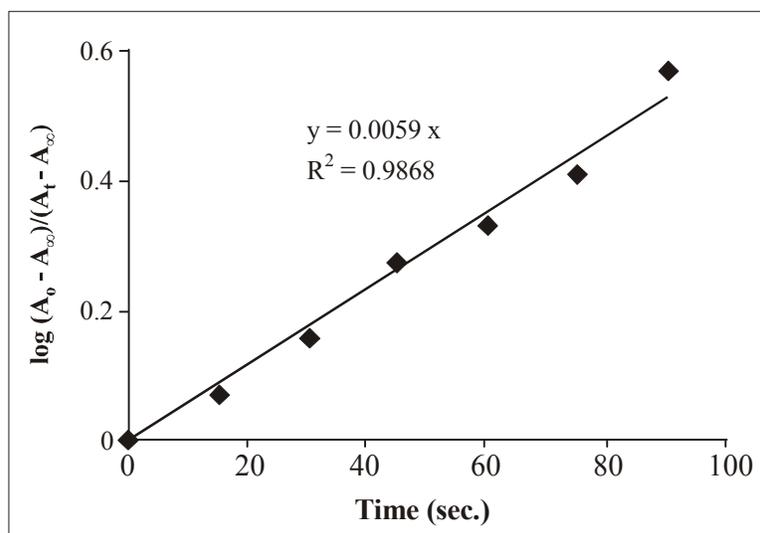
The plots of  $\log (A_t - A_\infty)$  vs time were found to be straight lines and pseudo first order rate constants were calculated from the slopes. From the effect of temperature on the reaction rate, energy of activation  $E_a$  and other thermodynamic parameters were evaluated.

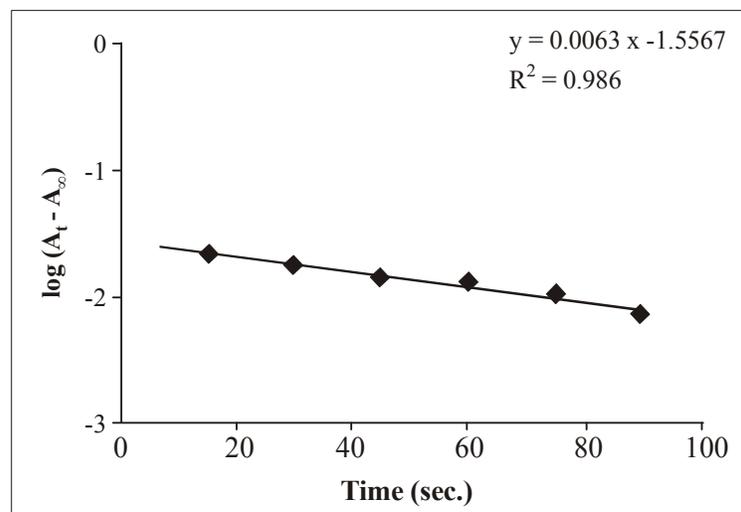
## RESULTS AND DISCUSSION

The order of reaction was calculated by integration method (Table 1) and graphical method. The calculated rate constants and order of reaction were confirmed by plotting a graph of  $\log (A_0 - A_\infty / A_t - A_\infty)$  vs time. It was obtained as a straight line passing through origin (Fig. 1) and plot of  $\log (A_t - A_\infty)$  vs time was a straight line with a negative slope (Fig. 2). It indicates that the reaction follows pseudo- first order.

**Table 1: First order rate constant for N-salicylidene-m-chloroaniline**

Medium (Ethanol – Water) [SB] = A <sub>4</sub>		Temp. = 30°C pH = 3.16			Buffer-Acetate μ = 0.1 M
Time	O. D.	A <sub>0</sub> - A <sub>∞</sub>	A <sub>t</sub> - A <sub>∞</sub>	Log (A <sub>0</sub> - A <sub>∞</sub> / A <sub>t</sub> - A <sub>∞</sub> )	k x 10 <sup>2</sup> s <sup>-1</sup>
0	0.123				
15	0.119	0.026	0.022	0.0725	1.114
30	0.115	0.026	0.018	0.1597	1.226
45	0.111	0.026	0.014	0.2688	1.376
60	0.109	0.026	0.012	0.3358	1.289
75	0.107	0.026	0.010	0.4149	1.274
90	0.104	0.026	0.007	0.5699	1.458
∞	0.097				
				k <sub>mean</sub>	1.26
				k <sub>Graph</sub>	1.36

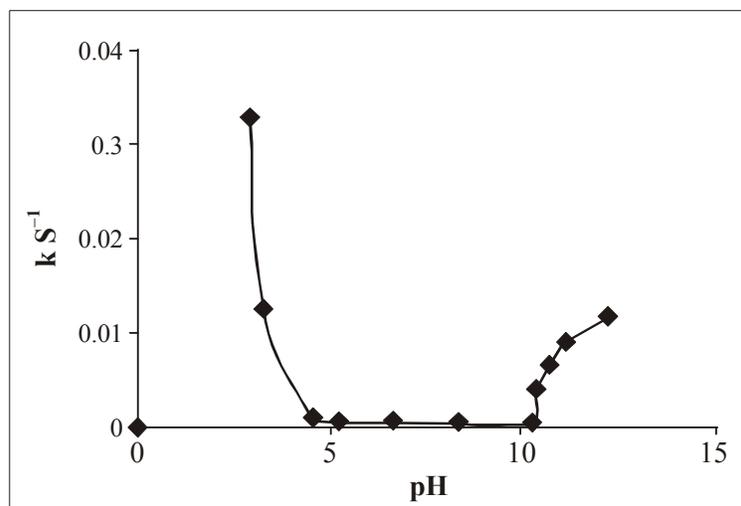
**Fig. 1: Plot of  $\log (A_0 - A_\infty / A_t - A_\infty)$  versus time at 30°C for hydrolysis of N-salicylidene-m-chloro aniline at pH = 3.16**



**Fig. 2:** Plot of  $(A_t - A_\infty)$  versus time log at 30°C for hydrolysis of N-salicylidene-m-chloroaniline at pH = 3.16

### Effect of pH on hydrolysis of N-salicylidene-m-chloroaniline

The rate constant values in the pH range 2.86-12.30 at 293 K are listed in Table 1. A rate profile diagram of pH v/s rate constant at 293.16 K, and ionic strength  $\mu = 0.1 \text{ mol. dm}^{-3}$  shows that the rate is minimum in the range  $5.21 < \text{pH} < 10.22$  (Fig. 3).



**Fig. 3:** Plot of  $k$  against pH at 303 K for the hydrolysis of N-salicylidene-m-chloroaniline at  $\mu = 0.1 \text{ mol. dm}^{-3}$

### Rate – limiting pathways

In the pH range 2.86-12.30, the Schiff base (HL) may be assumed to undergo hydrolysis by four rate determining pathways<sup>5</sup> -

- (i) The acid catalysed addition of water to the imine linkage of protonated Schiff base,  $H_2L^+$  ( $k_1$ ),
- (ii) A spontaneous path involving the addition of water to the imine linkage of the neutral imine, HL ( $k_2$ ),
- (iii) The addition of water to the imine anion,  $L^-$  ( $k_3$ ), and
- (iv) The addition of hydroxyl ion to the imine anion,  $L^-$  ( $k_4$ ).

The last step in which the hydroxyl ion predominates may be eliminated as the rate constant was found to be almost independent of the hydroxyl ion concentration at  $pH > 10.73$  (Table 2). Thus, the overall rate of hydrolysis will be -

$$\text{Rate} = k_1 (H_2L^+) + k_2 (HL) + k_3 L^- \quad \dots(1)$$

The deprotonation and protonation equilibria of the imine (HL) may be represented as -



### Hydrolysis of Schiff base in acidic and neutral pH range

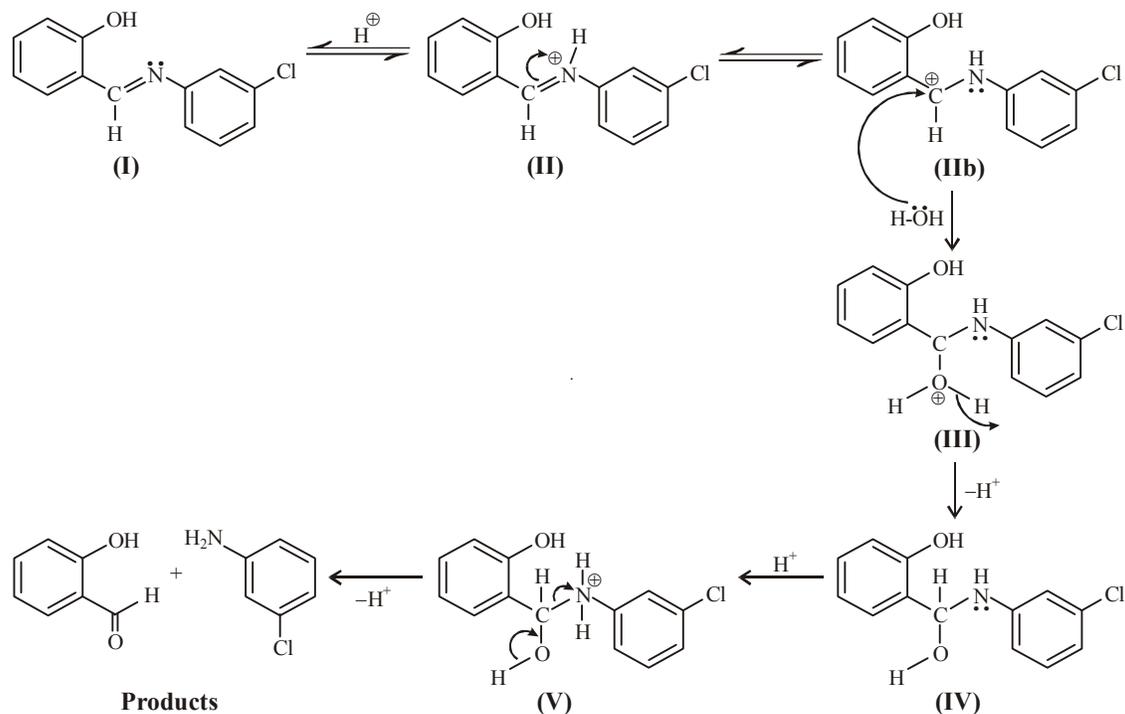
The rate constant varies linearly with hydrogen ion concentration in the pH range 4.51-6.61 (Table 2). In this pH range, equation (1) reduces to (5) as -

$$\text{Rate} = k_1 (H_2L^+) + k_2 (HL) \quad \dots(4)$$

$$K = (k_1/K_1) [H^+] + k_2 \quad \dots(5)$$

A plot of  $k$  vs  $[H^+]$  was found to be a straight line with slope  $k_1/K_1$  from which  $k_1$  was calculated to  $8.13 \times 10^{-3} \text{ sec}^{-1}$  at 303 K. Since the intercept of the plot is zero,  $k_2$  is taken as zero. In the acidic pH range, the proton catalysed attack of water on the reactive imine linkage of (HL) is suggested to be the rate- limiting step for the hydrolysis (Scheme 1). The

extremely low rates in the neutral pH range are due to negligible protonation of (HL). Consequently, the attack of water on the protonated imine is very slow. The addition of water to the neutral imine is therefore suggested to be rate – limiting step. The mechanism of hydrolysis N-salicylidene-m-chloroaniline shows path<sup>9</sup> (**Scheme 1**).



**Scheme 1**

### Hydrolysis of Schiff base in basic medium

In the basic range,  $\text{pH} > 10.42$ , the rate constant initially increases with increase in  $\text{pH}$  and is nearly independent of hydroxyl ion concentration at  $\text{pH} > 11.15$  (Table 2). In this  $\text{pH}$  range, the Schiff base may be assumed to be exclusively in the anionic form  $\text{L}^-$  due to the neutralization of the phenolic proton of the ortho- hydroxyl group by the  $\text{OH}^-$  ion of alkali<sup>5</sup>.

The above observations lead to the assumption that the complex formed may be Arrhenius complex. In the presence of excess catalyst, Arrhenius complex leads to specific hydroxyl ion catalysis at low hydroxyl concentration and the rate reaches a limiting value at

higher hydroxyl ion concentration<sup>7</sup>. In the present study, the rate increases with the hydroxyl ion concentration at low hydroxyl ion concentrations.

Further, the rate reaches a limiting value at higher hydroxyl ion concentrations. All these facts indicate that the rate-limiting step is the slow reaction of Schiff base anion L<sup>-</sup> water ( $k_4$ )<sup>5,10</sup>. The average value of the rate constants at pH > 11.15 is taken as  $k_4 = 11.74 \times 10^{-3} \text{ sec}^{-1}$  at 303 K. It is observed that initially the rate is maximum at low pH and then it sharply decreases with increasing pH up to 5. Above pH 5, the rate remains constant up to pH 10 and again increases with increasing pH and attains limiting value. It is represented by plotting pH v/s k (Fig. 3).

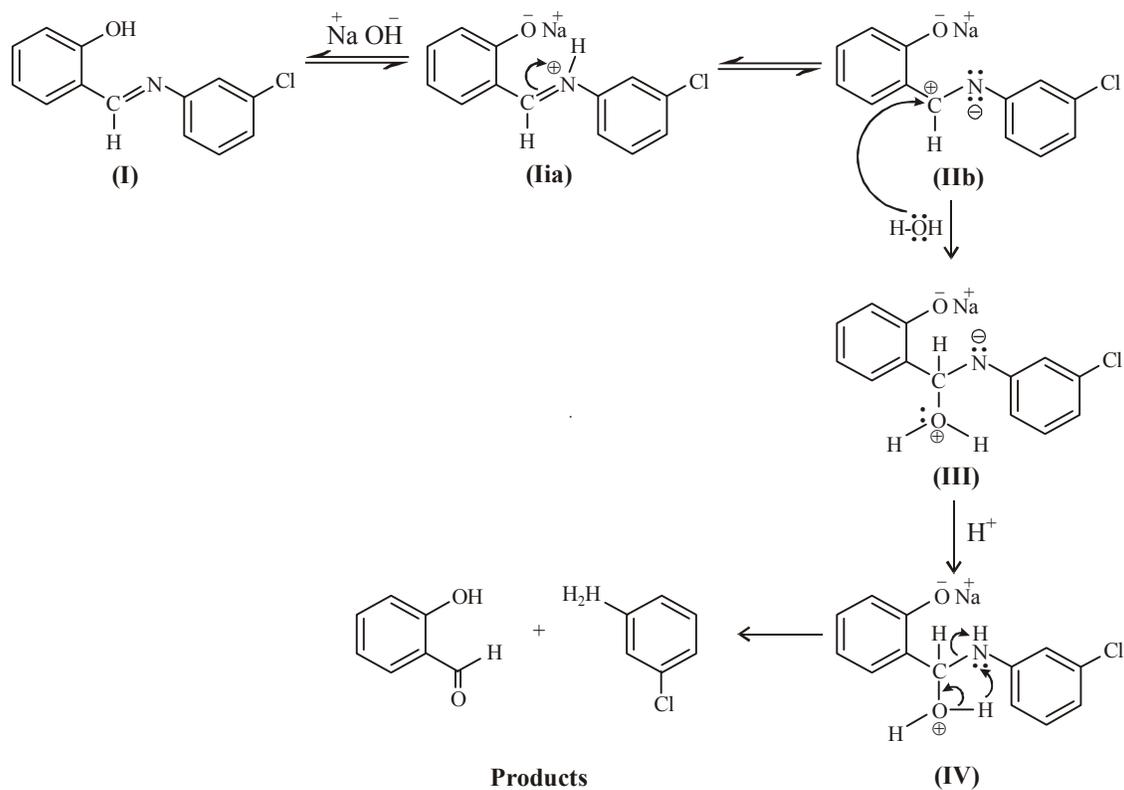
**Table 2: Rate constants for hydrolysis of N-salicylidene-m-chloroaniline at different pH**

Ethanol-water = 40% (v/v)		Temp. = 303 K	$\mu = 0.1 \text{ mol.dm}^{-3}$
pH	$[\text{H}^+] \times 10^6 \text{ mol. dm}^{-3}$	$[\text{OH}^-] \times 10^6 \text{ mol. dm}^{-3}$	$k \times 10^3 \text{ s}^{-1}$
2.86	13800.00		32.814
4.51	2630.00		0.942
5.21	61.66		0.427
6.61	1.95		0.399
8.40		2.53	0.372
10.22		1660.00	0.301
10.42		2630.00	4.100
10.73		5370.00	6.300
11.15		14130.00	8.892
12.30		19250.00	11.450

### Variation of reaction rate with temperature

In order to examine the effect of temperature on reaction rate, the reaction was carried out at different temperatures, 293, 298, 303 and 308 K. The activation parameters  $E_a$ ,

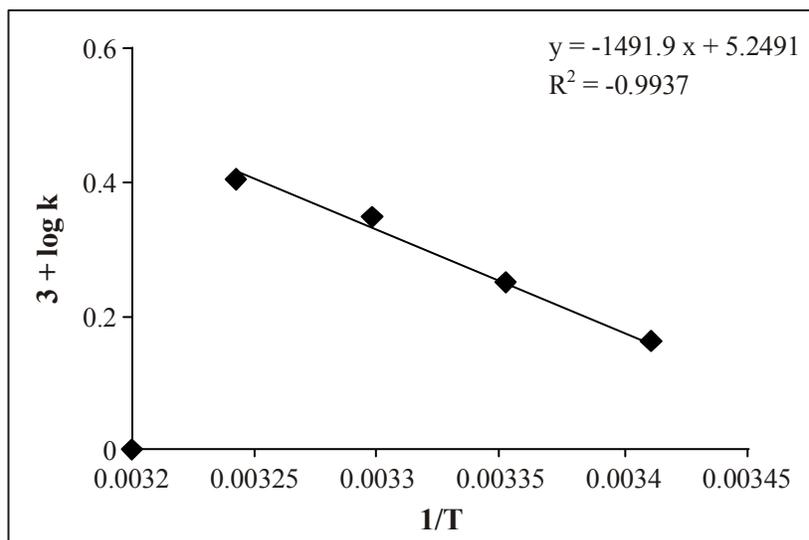
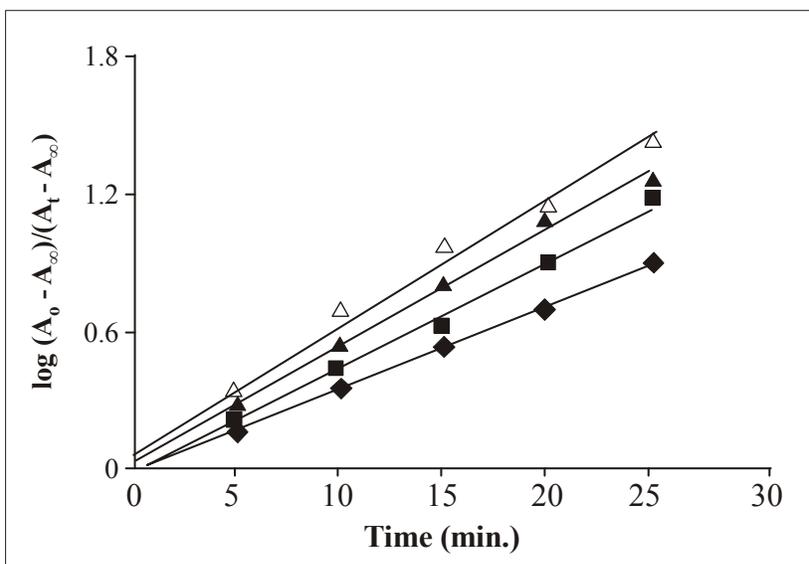
$\Delta H^\ddagger$ ,  $\Delta G^\ddagger$  and  $\Delta S^\ddagger$  were calculated and these are given in the Table 3. The plot of  $\log k$  v/s  $1/T$  was linear (Fig. 4)



**Scheme 2**

**Table 3: Activation parameters**

Temp. (K)	$10^3 \times k$ ( $s^{-1}$ )	$E_a$ calmol $^{-1}$	$\Delta S^\ddagger$ calmol $^{-1}$	$\Delta S^\ddagger$ calmol $^{-1}$	$\Delta S^\ddagger$ calmol $^{-1}$	log A
293	0.1434					
298	0.2468					
303	0.3441	6684.92	-50.668	21209.99	6092.472	5.2491
308	0.4002					

**Arrhenius plot****Fig. 4: Plot of log k against 1/T****Fig. 5: Plot of  $\log (A_0 - A_\infty) / (A_t - A_\infty)$  against time at different temperature**

From the values of thermodynamic parameters, it is observed that  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  are important parameters in controlling the rates of reactions<sup>11</sup>. The negative values of entropy

of activation indicate that activated complex is probable. The high negative value of entropy of activation suggests that the reaction may occur between like charged ions or ions and neutral molecules and may generate rigid intermediate transition state resulting in slow rate of the reaction. The values of frequency factor lies below  $10^{10}$  and hence, present reaction may be taking place between ions of like charges<sup>12</sup>. Activation entropy values are negative. This is because the protonated water molecule is held up at the nitrogen atom of imine linkage. The large negative values of  $\Delta S^\ddagger$  also indicate an extensive reorientation of the solvent molecules as a result of the formation of the activated complex<sup>13,14</sup>.

A negative value of  $\Delta S^\ddagger$  means that the activated complex is more ordered than the reactants. A more negative  $\Delta S^\ddagger$  indicates that frequency factor A will have smaller value and the reaction will be slower. For slower reactions, a higher value of  $\Delta G^\ddagger$  will be observed at given temperature. The rate of hydrolysis was increased with increase in temperature. Relatively constant values of  $\Delta G^\ddagger$  suggest similar mechanism of all the reactions.

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