Kinetic study of hydrolysis of N-salicylidene-m-methyl aniline spectrophotomerically

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ABSTRACT

Kinetics of hydrolysis reaction of the Schiff base, N- salicylidene-m- methyl aniline (HL) have been studied in the pH range 2.86-12.30 in the temperature range 293-308 K. A rate profile diagram of pH v/s rate constant shows the rate minimum in the pH range 5.21-10.22 and reaches a plateau at pH > 10.73. Suitable reaction mechanism has been suggested for the hydrolysis of the Schiff base in acidic, neutral and basic medium. From the effect of temperature on the rate, various thermodynamic parameters have been evaluated.

Keywords: Schiff base, hydrolysis, kinetics.

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INTRODUCTION

The study of kinetics of formation and hydrolysis of Schiff bases has received a considerable attention due to its relevance to the transformation (conversion) of $>C=0$ to $>C=N$ and vice versa in biochemical processes **[1-4].** Literature survey reveals that a great deal of work has been reported on the complexation of metal ions with Schiff bases for the study of structure and stability of the complexes. The catalytic effect of hydrogen, hydroxyl and metal ions on the formation and hydrolysis of imines have been studied by several workers **[5-8].** In the present work we represented here systematic study of the hydrolysis of Schiff base, N-salicylidene -m-methyl aniline at different pH values.

EXPERIMENTAL SECTION

The imine was prepared by refluxing calculated amounts of salicylaldehyde and m-methyl aniline in ethanol medium for about one hour. On cooling, the resulting yellow coloured crystals were recrystalised from ethanol, melting point = 40 ^{0}C. The purity was checked by TLC.

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Kinetic measurements

The rate of hydrolysis of was Schiff base was followed spectrophotometrically at 405 nm by using uv/vis, 1601, Shimadzu spectrophotometer. Universal buffer solutions were prepared according to the reported methods **[9-10].** 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 1×10^{-4} mol dm^{-3}. The ionic strength of the reaction mixture was maintained at $\mu = 0.1$ mol 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 bases and buffer solutions 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 of 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 λ = 405 nm. Using spectrophotometer within 20 s of mixing the Schiff base.

The plot of log (A_t-A_∞) 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 Ea and other thermodynamic parameters were evaluated.

RESULTS AND DISCUSSION

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

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[3].

- The acid catalysed addition of water to the imine linkage of protonated Schiff base, H_2L^+ (k_1).
- A spontaneous path involving the addition of water to the imine likage of the neutral imine, HL (k_2).
- The addition of water to the imine anion, L$^-$ (k_3).
- 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 1). Thus the overall rate of hydrolysis will be,

$$\text{Rate} = k_1\,(H_2L^+) + k_2\,(HL) + k_3\,(L^-) \hspace{3cm} (1)$$

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

$$H_2L \;\overset{K_1}{\rightleftharpoons}\; HL + H^+$$

$$HL \rightleftharpoons L^- + H^+$$ K_2
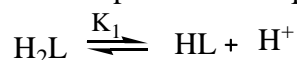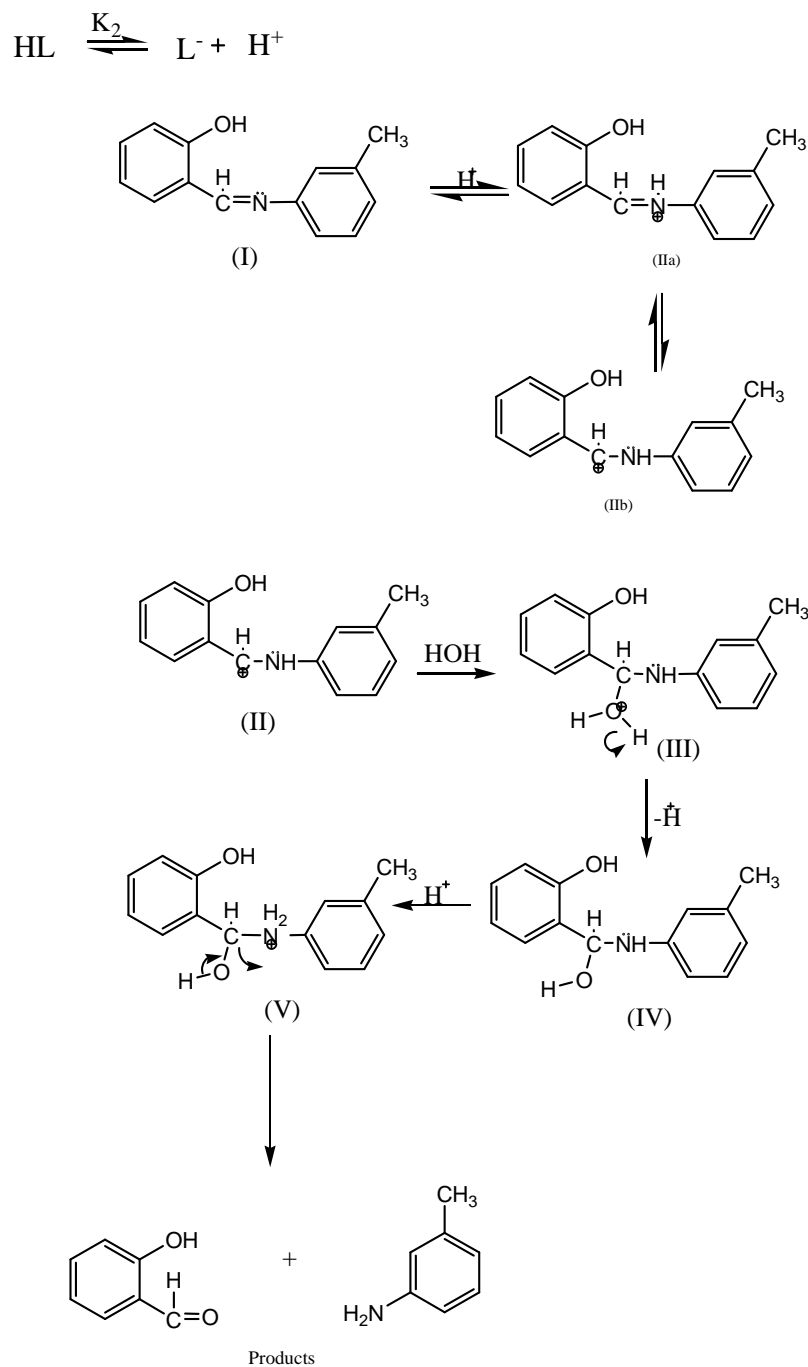
Scheme 1

Hydrolysis of Schiff base in acidic and neutral range of pH

The rate constant varies linearly with hydrogen ion concentration in the pH range 4.51-6.61 (Table1). In this pH range, equation (1) reduces to (2),

Rate = k_1 (H_2L^+) + k_2 (HL)

$K = (k_1/K_1) [H^+] + k_2$ (2)

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 x10^{-3} at 303K. 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.

Hydrolysis of Schiff base in basic medium

In the basic range, pH >10.42, the rate constant initially increases with increase in pH and is nearly independent of hydroxyl ion concentration at pH > 10.73 (Table 1). In this pH range, the Schiff base may be assumed to be exclusively in the anionic form L^- due to the neutralization of the phenolic proton of the ortho- hydroxy group by the OH^- ion of alkali [3].

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 high hydroxyl ion concentration **[5].** In the present study, the rate increases with the hydroxyl ion concentration at low hydroxyl ion concentrations.

Table: 1 Rate constant data for hydrolysis of N- salicylidene –m- methyl aniline.

Ethanol – water = 40 % (v/v), Temp. = 293K, μ = 0.1 mol dm-3.

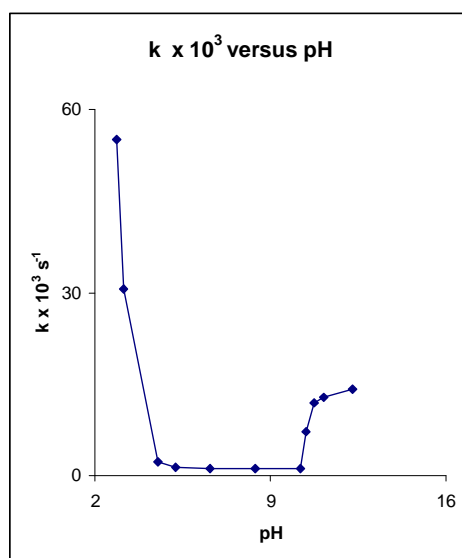| pH	$[H^+] \times 10^6$ mol dm^{-3}	$[OH^-] \times 10^6$ mol dm^{-3}	$k \times 10^3$ S^{-1}
2.86	13800.00		55.10
3.16	6918.00		30.64
4.51	2630.00		2.18
5.21	61.66		1.24
6.61	1.95		1.14
8.40		2.53	1.06
10.22		1660.00	1.05
10.42		2630.00	7.20
10.73		5370.00	11.80
11.15		14130.00	12.72
12.30		19250.00	14.24

Figure: 1 Plot of k against pH at 303K for the hydrolysis of N-salicylidene -m -methyl aniline at μ = 0.1 mol dm^{-3}.

Further the rate reaches a limiting value at higher hydroxyl ion concentrations. All these facts indicate that the rate- limiting step is the slow reactions of Schiff base anion L^- water $(k_4)^3$[6]. The average value of the rate constants at pH > 10.73 is taken as $k_4 = 12.4 \times 10^{-3}$ at 303 K.

Table: 2 Rate constant (order) data of hydrolysis of N-salicylidene-m-methyl aniline

Medium-(ethanol - water) Temp. = 30 ^{0}C   Buffer- Acetate
[SB] = A_2 pH = 3.16   μ = 0.1 M

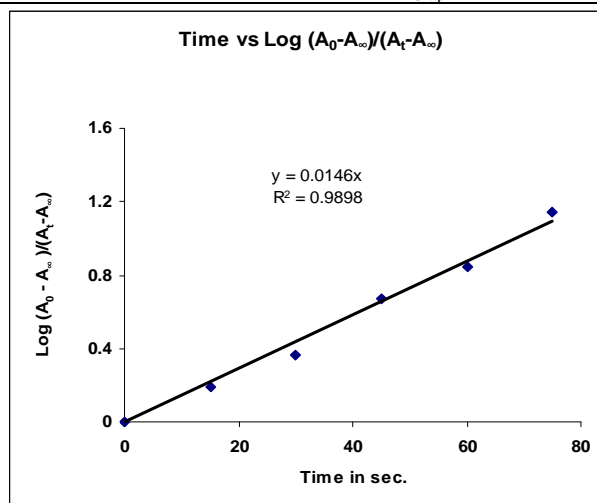| Time	O.D.	A_0-A_∞	A_t-A_∞	Log($A_0-A_\infty/A_t-A_\infty$)	k x 10^2 s^{-1}
0	0.033				
15	0.028	0.014	0.009	0.1919	2.946
30	0.025	0.014	0.006	0.3679	2.825
45	0.023	0.014	0.004	0.5441	2.784
60	0.021	0.014	0.002	0.8451	3.244
75	0.020	0.014	0.001	1.1461	3.519
∞	0.019				
				k_{mean}	3.064
				k $_{Graph}$	3.362

Figure:2 (a) Plot of Time versus Log ($A_0-A_\infty/A_t-A_\infty$) at 30 ^{0}C for the hydrolysis of N-salicylidene -m -methyl aniline at pH = 3.16
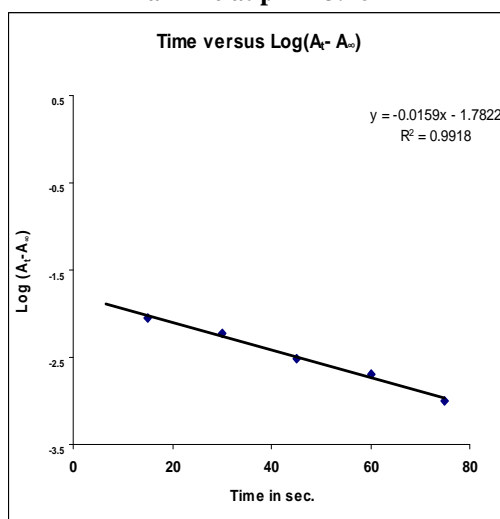

Figure:2 (b) Plot of Time versus Log (A_t-A_∞) at 30 ^{0}C For hydrolysis of N-salicylidene -m -methyl aniline at pH = 3.16

Effect of temperature and thermodynamic parameters

The hydrolysis of Schiff base was carried out at four different temperatures 293,298,303, 308 K. From, the effect of temperature on the reaction rate the various thermodynamic parameters like energy of activation Ea, $\Delta H^{\neq}$, $\Delta G^{\neq}$ and $\Delta S^{\neq}$ were evaluated are given in the table- II. The plot of $(3 + \log k)$ v/s $1/T$ is linear (Fig.-II) for the hydrolysis of N-salicylidene -m -methyl aniline. The negative $\Delta S^{\neq}$ value obtained can perhaps be explained by a model in which water molecules are tightly held to the imine linkage, the nucleus of the hydrolytic reaction **[11-13].** The large negative values observed may an extensive reorientation of solvent molecules as a result of the formation of the activated complex.

Table: 3 Rate constants and activation parameters for N-salicylidene -p -chloro aniline

Temperature	10^3 x k s^{-1}	Ea cal mol^{-1}	$\Delta S^{\neq}$ cal mol^{-1}	$\Delta G^{\neq}$ cal mol^{-1}	$\Delta H^{\neq}$ cal mol^{-1}	Log A
293 K	1.883					
298 K	2.324					
303 K	3.050	9501.28	-40.745	21034.69	8908.836	5.9497
308 K	4.149					

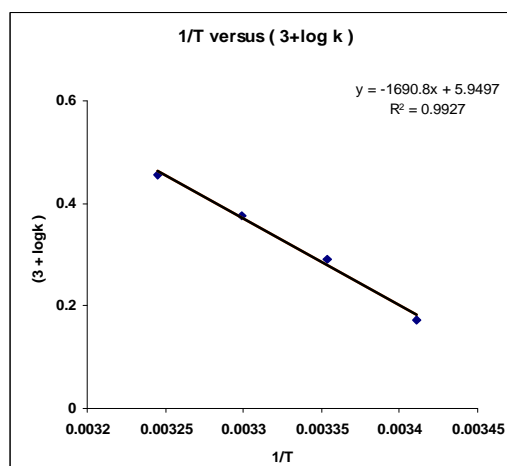**Figure: 3 (a). Plot of (3+ log k) against 1/T for the hydrolysis of N-salicylidene -m -methyl aniline.**
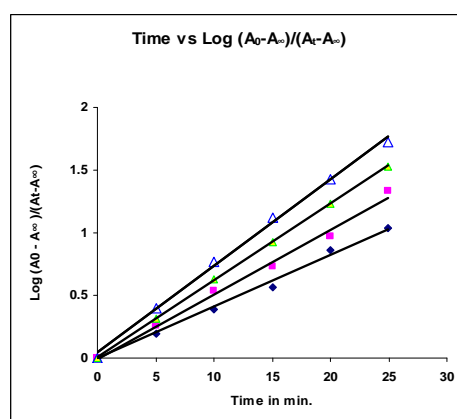

Figure: 3 (b) Plot of log (A_0-A_∞)/ (A_t-A_∞) against Time

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