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A Comparative Study of the Kinetics of Hydrolysis of the Methyl Derivatives of Salicylanil

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A comparative study of the hydrolysis of the methyl derivatives of salicylanil has been done in the pH range 3.57–12.65 at 35°C. The reaction mechanisms in acidic, neutral and basic media have been discussed on the basis of steric hindrance, inductive, mesomeric and resonance effects. The rates of hydrolysis of the Schiff bases have been correlated with their proton dissociation constants.

INTRODUCTION

The kinetics of hydrolysis of the Schiff base, salicylanil has been studied in great detail in this laboratory. As a continuation of this work, the kinetic study of the hydrolysis of the methyl derivatives of salicylanil was undertaken. The present paper discusses their comparative rates of hydrolysis on the basis of steric hindrance, inductive, mesomeric and resonance effects. An attempt has been made to correlate the rates of hydrolysis of the Schiff bases with their proton dissociation constants.

EXPERIMENTAL

The Schiff bases, N-salicylidene-*o*-methyl aniline (A), N-salicylidene-*m*-methyl aniline (B) and N-salicylidene-*p*-methyl aniline (C) were prepared using methods available in literature. Their structures were confirmed by IR spectra, elemental analysis and m.p. 40°C (A), 48°C (B) and 99°C (C). The hydrolysis was studied spectrophotometrically in a series of universal buffer solutions in the pH range 3.57–12.65 in 40% ethanol-water (v/v) medium at 35°C. The pH values of the buffers were determined using an "ELICO-LI-120" digital pH meter. The concentration of the Schiff base was kept at 4×10^{-4} mol dm^{-3}. The ionic strength was maintained at $\mu = 0.1$ mol dm^{-3} using 1 M sodium perchlorate (E. Merck).

A solution of sodium perchlorate, buffer and ethanol in requisite amounts was allowed to equilibrate in a previously adjusted thermostat (accuracy ± 0.1°C). The reaction was initiated by adding a known volume of the Schiff base in ethanol which was also maintained at the same temperature. The progress of the

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hydrolysis was monitored by measuring the decrease of absorbance of the Schiff base with time at $\lambda = 390$ nm (a), $\lambda = 400$ nm (B) and $\lambda = 421$ nm (C) using an ELICO ULTRA Spec Model CL-54 spectrophotometer. The plots of log $(A_t - A_\alpha)$ against time were found to be straight lines and from the slopes of these plots, the pseudo first order rate constants were calculated.

The equilibria involving the Schiff base (HL) may be represented as

$$H_2L^+ \overset{K_1}{\rightleftarrows} HL + H^+ \tag{1}$$

$$HL \overset{K_2}{\rightleftarrows} L^- + H^+ \tag{2}$$

where H_2L^+, HL and L^- represent the protonated, neutral and anionic (due to the deprotonation of the phenolic group) forms respectively.

pK_1 values were determined by a potentiometric titration of 4×10^{-4} M Schiff base against 0.01 M HCl using a digital pH meter. The pK_1 values of the Schiff bases in 40% ethanol-water (v/v) medium and $\mu = 0.1$ mol dm^{-3} were determined as 4.320 for salicylanil, 4.357 (A), 4.498 (B) and 4.731 (C).

The Schiff base anion (L^-) shows absorption maxima at $\lambda = 420$ nm (salicylanil)[1], $\lambda = 390$ nm (A), $\lambda = 400$ nm (B) and $\lambda = 421$ nm (C). pK_2 values were calculated spectrophotometrically in 40% ethanol-water (v/v) medium and $\mu = 0.1$ mol dm^{-3} as 10.490 (salicylanil), 9.709 (A), 9.712 (B) and 10.400 (C).

RESULTS AND DISCUSSION

Discussion of pK_1 values: The pK_1 values indicate the dissociation of proton from the protonated nitrogen atom in the Schiff base and can even be considered as the proton affinity towards the electronegative nitrogen atom of the azomethine linkage. The pK_1 values were determined as 4.320 for salicylanil[1], 4.357 for (A), 4.498 for (B) and 4.731 for (C). In (C), the strong positive inductive effect of the methyl group in the *para* position comes in full force along with the resonance effect of the benzene ring. As a result, the electron density is directly released to the nitrogen atom making it highly basic. The resulting proton affinity for the nitrogen atom is reflected in the pK_1 values of (C) which is the highest among the pK_1 values of salicylanil and its methyl substituted derivatives, (A), (B) and (C).

In (B), the positive inductive effect of the methyl group in the *meta* position is relatively less. As a result the nitrogen atom is less basic in (C). The resulting decrease in proton affinity for the nitrogen atom is reflected in the pK_1 value of (B) which is less than that of (C) but greater than the pK_1 value of salicylanil.

In (A), the bulky methyl group of the *ortho* position offers steric hindrance leading to the rotation of the tolyl ring out-of-plane of the non-bonding electrons of the nitrogen atom. Further the planarity of the imine molecule is disturbed due to the interaction of the methyl group with the hydroxyl group of the salicyl part of the molecule. As in (B) and (C), the positive inductive effect of the methyl group leads to the release of electron density to the nitrogen atom. But due to steric hindrance offered by the methyl group, the mesomeric effect due to resonance is almost negligible. Consequently the nitrogen atom becomes much less basic and the protonation of the nitrogen atom is greatly hindered. Thus the pK_1 value of (A) is less than that of (B) and (C). Due to the positive inductive effect of the methyl group in the *ortho* position, the pK_1 value of (A) is slightly greater than that of salicylanil.

Comparative rates of hydrolysis of Schiff bases

The rate constants in the pH range 3.57–12.65 at 35°C are listed in Table-1. In this pH range, the imines (HL) may be assumed to undergo hydrolysis by four rate-determining pathways[3]:

(1) an acid-catalysed addition of water to the imine linkage of the protonated imine, H_2L^+ (k_1);
(2) a spontaneous addition of the water of the imine linkage of neutral imine, HL (k_2);
(3) the addition of water to the imine anion, L^- (k_3);
(4) the addition of hydroxyl ion to the imine anion, L^- (k_4).

TABLE-1
RATE CONSTANT DATA FOR THE HYDROLYSIS OF METHYL-SUBSTITUTED SALICYLANILS

Ethanol-water = 40% (v/v), Temp. = 35°C, $\mu = 0.1$ mol dm^{-3}

pH	$k \times 10^3\ s^{-1}$		
	A	B	C
3.57	20.70	71.61	40.30
4.36	6.30	21.13	14.13
4.58	3.00	10.10	7.30
5.06	1.10	3.72	3.70
5.42	0.60	1.41	1.10
6.30	0.23	0.69	0.90
7.04	0.30	0.93	0.86
7.95	—	—	0.69
8.34	—	—	—
8.82	—	—	—
9.95	—	—	3.98
10.76	—	7.16	11.00
11.75	—	8.41	11.90
12.39	3.55	10.23	15.40
12.65	3.98	10.12	18.10

The last pathway in which the hydroxyl ion predominates may be eliminated as the rate constants were found to be almost independent of the hydroxyl ion concentration (Table-1).

Hence the overall rate of hydrolysis will be

$$\text{Rate} = k_1(HL^+) + k_2(HL) + k_3(L^-) \qquad (3)$$

Hydrolysis of Schiff bases in acidic pH range

The rate constants were found to vary linearly with hydrogen ion concentration in the acidic pH range (Table-1). In this acidic range, equation 3 reduces to

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

$$k = \frac{k_1}{K_1}(H^+) + k_2 \qquad (4)$$

For all the Schiff bases, the plots of k vs. (H^+) were found to be straight lines with zero intercepts. From the slope of the plot, $\frac{k_1}{K_1}$, the rate constant for the addition of water to the protonated imine (k_1) was calculated. As the intercept of the plot was zero, k_2 was taken as zero.

Chart I outlines the reaction mechanism of the hydrolysis of one of the Schiff bases (A) in the acidic range. The nitrogen atom first gets protonated at a fast rate and this protonation is facilitated by the intensification of the electron density on the nitrogen atom by an adjacent group. Subsequently the nitrogen atom withdraws the electron density on the carbon atom of the C=N bond through the double bond. This renders the carbon atom of the imine linkage electropositive and hence vulnerable to the nucleophilic attack of water. The proton-catalysed attack of water at the reactive imine linkage of HL, k_1 is therefore suggested as the rate-determining step. In the acidic pH range, the rate constants follow the sequence, salicylanil[1] > *meta* > *para* > *ortho*. This sequence can be explained on the basis of pK_1 values. In (A), due to the steric hindrance offered by the methyl group in the *ortho* position, the nitrogen atom is weakly basic. As a result its protonation and the subsequent withdrawal of electron density from the carbon atom of the imine linkage are hindered. Hence the nucleophilic attack of water on the less electropositive carbon atom is very slow. This explains the low rate of hydrolysis of (A). In (B), the nitrogen atom is relatively more basic. This facilitates the withdrawal of electron-density from the carbon atom of the imine linkage leading to a faster nucleophilic attack of water on the electropositive carbon atom. In (C), the nitrogen atom is highly basic, hence the withdrawal of electron density from the carbon atom of the imine linkage is less than in the case of (B). Consequently the nucleophilic attack of water of the electropositive carbon atom is less than in the case of (B). As the pK_1 value of salicylanil is the least, its nitrogen atom is least basic. This greatly facilitates the electron withdrawal of electro density from the carbon atom of the imine linkage and the subsequent nucleophilic attack of water on the electropositive carbon atom. Thus the rate of hydrolysis of salicylanil is highest among the four Schiff bases under study.

Hydrolysis of Schiff bases in neutral pH range

In the neutral pH range, the rates are minimum and almost constant. These negligible rates are attributed to very low catalytic activity of proton due to which the protonation of the imine is negligible. Consequently the attack of water on

CHART-I

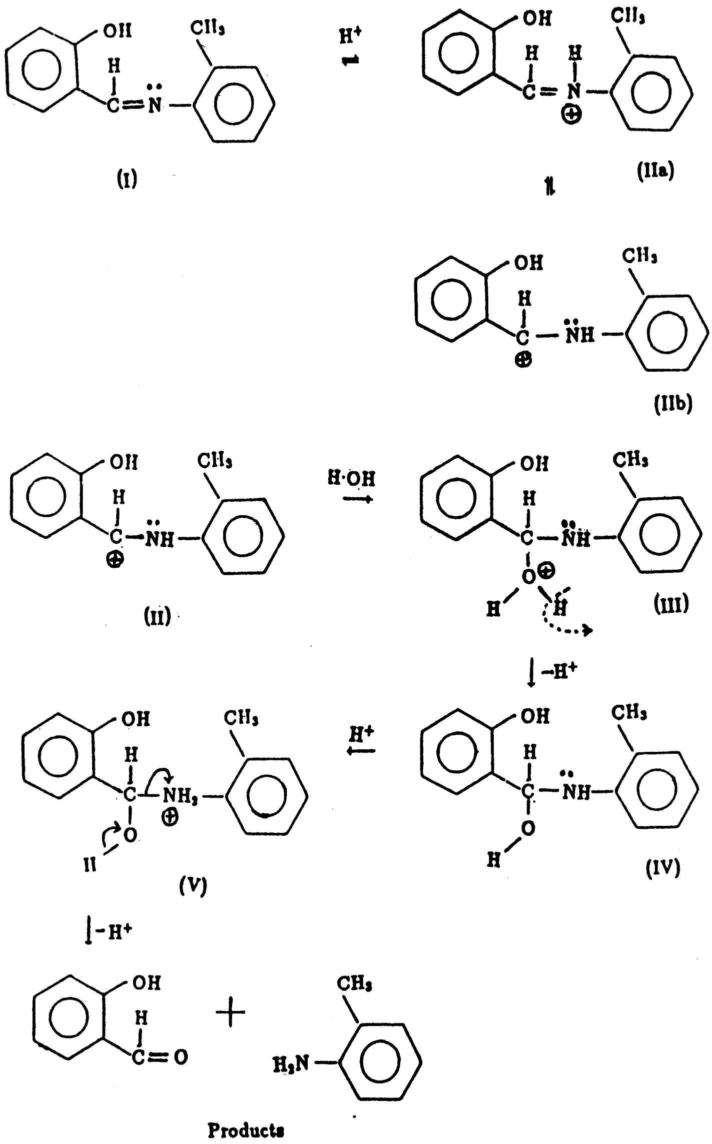
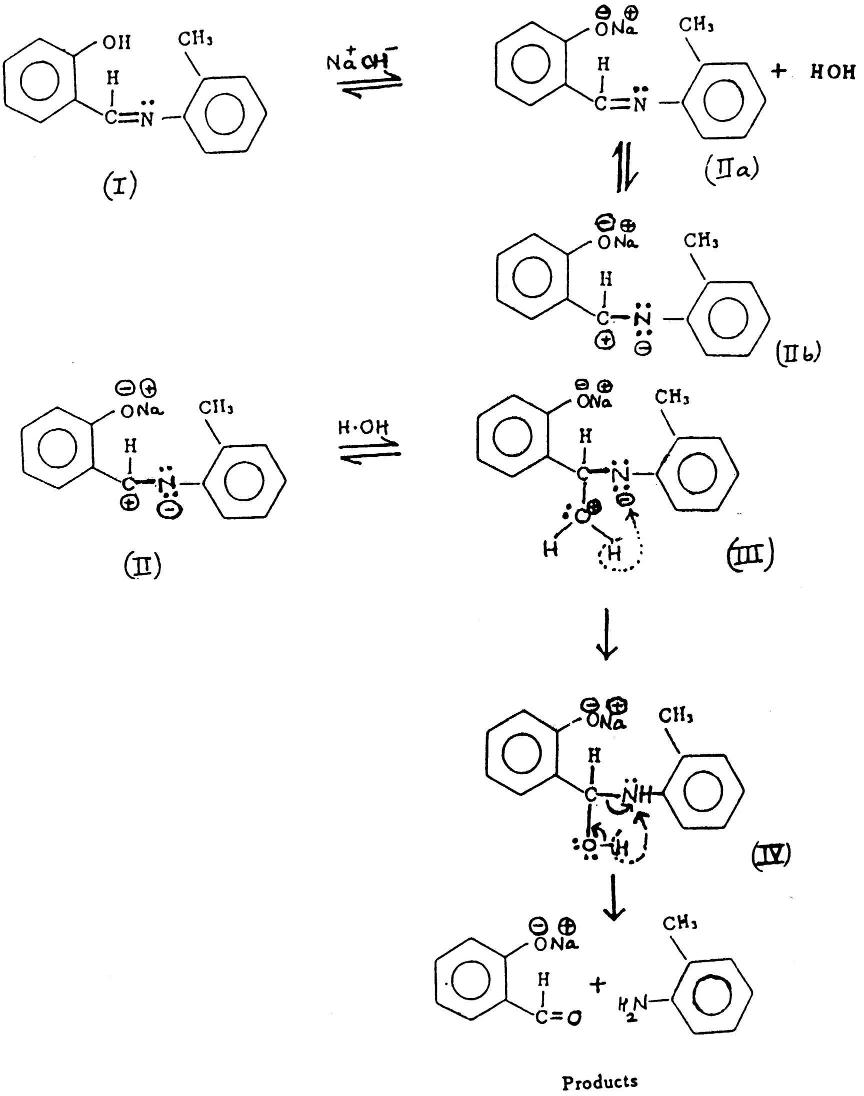


CHART-II



the protonated Schiff base is very slow. The addition of water of the neutral imine[2] HL, (k_2) is therefore suggested as the rate-determining step.

Hydrolysis of Schiff bases in basic pH range

In the basic pH range, the rate constants are found to be nearly independent of hydroxyl ion concentration and to reach a limiting value at higher hydroxyl ion concentrations (Table-1). In this pH range, the imine may be assumed to be in the anionic form, L^- due to the neutralisation of the phenolic proton of the *ortho*-hydroxyl group by the OH^- ion of alkali[3]. Chart II outlines the rate mechanism of the hydrolysis of one of the Schiff bases under study (A). In the basic range, the imine anion L^- is first formed and goes into resonance resulting in the withdrawal of electron density from the carbon atom of the imine linkage by the nitrogen atom. The nucleophilic attack of water takes place at the resulting electropositive carbon atom. The absorption of H^+ from the water molecule neutralises the negative charge on the nitrogen atom. In the basic pH range, the slow reaction of water with the imine anion L^-, (k_3)[3, 4] is therefore suggested as the rate-determining step.

The rates follow the sequence, salicylanil[1] > *para* > *meta* > *ortho*.

The pK_1 values show that the basicity of the nitrogen atom increases in the order *para* > *meta* > *ortho*. Hence the ease of absorption of H^+ from the nucleophilic water molecule also increases in the same order, which explains the above rate sequence.

The pK_1 value of salicylanil indicates that its nitrogen atom is least basic. This greatly facilitates the withdrawal of electron density from the carbon atom of the imine linkage of the imine anion L^-. As a result, the nucleophilic attack of water on the resulting electropositive carbon is fastest. This explains the higher rate of hydrolysis of Schiff bases as compared to that of its methyl derivatives.

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