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# Effect of Transition Metal Ions on the Hydrolysis of the Methyl Derivatives of Salicylanil

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The catalytic effect of Ni(II), Zn(II) and Cu(II) ions on the hydrolysis of the methyl derivatives of salicylanil has been studied at pH-4.58 at 35°C. The hydrolysis follows the sequence *meta* > *para* > *ortho* in the absence and presence of metal ions. The presence of metal ions accelerates the hydrolysis rate according to the sequence Ni(II) > Zn(II) > Cu(II) which is in accordance with the Irving and Williams order of stability constants of metal chelates involving nitrogen and oxygen donor ligands. The initial retardation of rate of hydrolysis observed at lower Cu(II) concentrations has been explained as due to Jahn-Teller distortion of the metal complex to achieve stability. A suitable reaction mechanism has been suggested for the metal ion-catalysed hydrolysis of the imines under study.

## INTRODUCTION

The hydrolysis of Schiff bases is an important reaction of biochemical and biological interest.[1–4] The effect of hydrogen ions, hydroxyl ions and metal ions on the hydrolysis[4–10] of some Schiff bases has been studied. In this laboratory the kinetics and reaction mechanism of the hydrolysis of the imine, salicylanil and its methyl derivatives[11–15] has been investigated in detail. In the acidic pH range, the proton catalysed attack of water at the reactive imine linkage of the Schiff base has been suggested as the rate determining step[13] for the hydrolysis reaction. On the basis of steric hindrance, inductive, mesomeric and resonance effects, it has been established that in the acidic range, the rate constants of hydrolysis follow the sequence[13] salicylanil > *meta* > *para* > *ortho*. Further the sequence has been justified on the basis of the proton dissociation constants ($pK_1$) of the imines under study.

In this paper, we are reporting the catalytic effect of Ni(II), Cu(II) and Zn(II) ions on the acidic hydrolysis of the methyl derivatives of salicylanil.

## 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 standard methods available in literature and their structures were confirmed by elemental anlysis, m.p. and IR spectra. Stock solutions of 0.1 M metal perchlorates in 0.2 M perchloric acid were prepared using standard methods. All chemicals used were of A.R. grade (E. Merck).

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## Kinetic Measurements

The hydrolysis was studied spectrophotometrically in 40% ethanol-water (v/w) medium at 35°C at pH *ca.* 4.58 obtained from acetate buffer. The pH value of the acetate buffer was determined using an "ELICO LI-120" digital pH meter. The concentration of the Schiff base was kept at $4 \times 10^{-3}$ mol dm$^{-3}$. The metal ion concentrations used were in the range $1–4 \times 10^{-3}$ mol dm$^{-3}$. The ionic strength of the reaction mixture was maintained at 0-0.1 mol dm$^{-3}$ using 1 M sodium perchlorate.

A solution of sodium perchlorate, acetate buffer, metal ion solution and ethanol in required amounts were allowed to equilibrate in a previously adjusted thermostat (accuracy ±0.1°C). The reaction was initiated by adding a known amount of the Schiff base in ethanol which was also maintained at the same temperature. The progress of the 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 excellent straight lines and the pseudo first order rate constants were calculated from the slopes of these plots.

## RESULTS AND DISCUSSION

The first order rate constants for the hydrolysis of the Schiff base A, B and C, in the absence and presence of Ni(II), Zn(II) and Cu(II) ions in 40% ethanol-water (v/v) medium at pH = 4.58 and $\mu$ = 0.1 mol dm$^{-3}$ at 35°C are tabulated in Table-1.

TABLE-1
RATE CONSTANT DATA FOR THE HYDROLYSIS OF METHYL DERIVATIVES OF SALICYLANIL

Ethanol-water = 40% (v/v), $\mu$ = 0.1 mol dm$^{-3}$, pH = 4.58, Temp. = 35°C

| Schiff Base | $(M^{2-}) \times 10^3$ mol. dm$^{-3}$ | First order rate constant $k \times 10^3$ s$^{-1}$ | | |
|---|---|---|---|---|
| | | Ni(II) | Cu(II) | Zn(II) |
| N-Salicylidene-<br>*o*-methyl aniline<br>(A) | 0 | 3.00 | 3.00 | 3.00 |
| | 1 | 5.20 | 2.00 | 4.20 |
| | 2 | 6.53 | 2.70 | 5.90 |
| | 3 | 9.50 | 4.30 | 8.41 |
| | 4 | 13.50 | 8.10 | 11.10 |
| N-Salicylidene-<br>*m*-methyl aniline<br>(B) | 0 | 10.10 | 10.10 | 10..10 |
| | 1 | 16.80 | 6.00 | 15.14 |
| | 2 | 19.95 | 6.60 | 17.18 |
| | 3 | 37.90 | 10.00 | 31.00 |
| | 4 | 52.48 | 14.90 | 47.50 |
| N-Salicylidene-<br>*p*-methyl aniline<br>(C) | 0 | 7.30 | 7.30 | 7.30 |
| | 1 | 10.94 | 6.00 | 10.80 |
| | 2 | 15.30 | 6.38 | 14.29 |
| | 3 | 17.90 | 9.10 | 17.60 |
| | 4 | 35.90 | 14.30 | 31.60 |

The data in Table-1 reveals that the hydrolysis follows the sequence *meta* > *para* > *ortho* in the absence[13] and presence of the metal ions under investigation. The presence of metal ions accelerates the hydrolysis rate according to the sequence Ni(II) > Zn(II) > Cu(II). The variation of rate constant with ($M^{2+}$) for Schiff base A is shown in Fig. 1. Similar graphs were obtained for Schiff bases B and C.

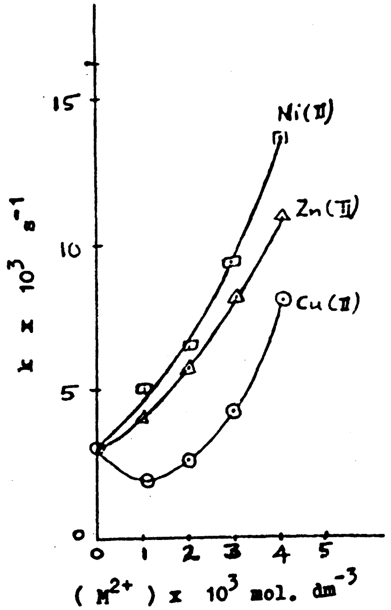
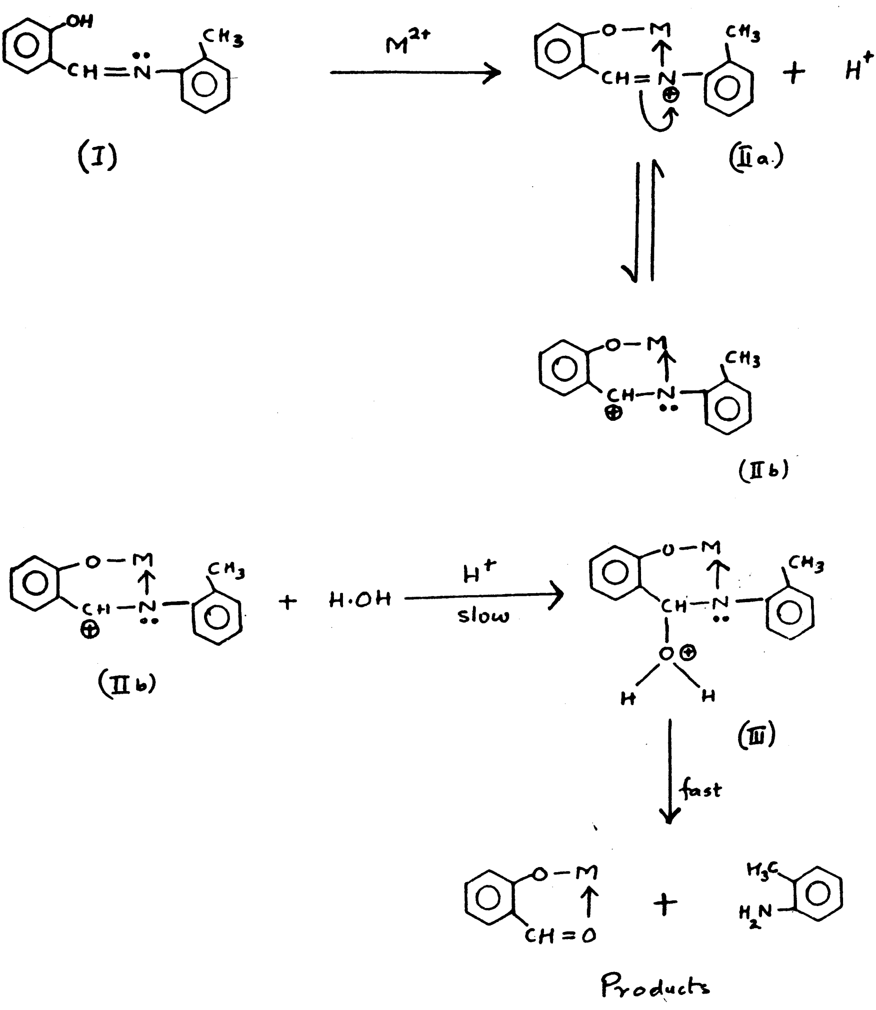


Fig. 1. Effect of ($M^{2+}$) on the hydrolysis rate of N-salicylidene-*o*-methyl aniline at pH = 4.58 and 35°C.

The Schiff bases under study form monocyclic chelates[5] which are hydrolysed in the presence of metal ions. However Schiff bases which form bicyclic chelates[6] are stable towards hydrolysis in the presence of metal ions in mild acidic conditions. The reaction mechanism of the metal-catalysed hydrolysis of Schiff base A is outlined in Chart I.

The Schiff bases under study have a high tendency to coordinate to metal ions as a bidentate ligand through the imine nitrogen and phenolic oxygen atoms.[16] Hence it is expected that in the presence of metal ions, the substrate exists mainly in the metal-complex form. Accordingly, the azomethine carbon atom is expected to carry a high positive charge relative to that in the absence of metal ion resulting in a higher nucleophilic attack of water on this carbon atom. The proton-catalysed addition of water at the aldimine linkage is therefore suggested as the rate determining step for the hydrolysis of the 1 : 1 metal chelate formed. In the case of Schiff bases forming monocyclic chelates, the metal-nitrogen bond weakens the carbon-nitrogen bond thus rendering it more susceptible to hydrolytic cleavage. Thus there should be some correlation between the strength of the metal-nitrogen bond and the ability of metal ions to catalyse the hydrolysis of the



imines. The decomposition of the carbinolamine intermediate in a metal-complex form is expected to take place faster than in the free form. Further the high tendency of the hydrolysis product, salicylaldehyde to coordinate to metal ion will result in greater hydrolysis of the Schiff bases in the presence of metal ions.

As seen in Fig. 1, the rate constant of hydrolysis of the Schiff base increases with increasing Zn(II) and Ni(II) concentrations. However in the case of Cu(II), at lower metal ion concentrations, an initial retardation in the rate of hydrolysis is observed. This decrease in rate can be explained by the fact that the Cu(II) ion with $d^9$ configuration has unsymmetrical electron distribution in the $d_{x^2-y^2}$ and $d_{z^2}$ orbitals and is subjected to Jahn-Teller distortion. Thus the metal-complex undergoes distortion to achieve stability. Subsequently the increase in Cu(II) concentration has the same effect on the rate constant as has been observed for Zn(II) and Ni(II) *i.e.* the stability of the metal-complex decreases and the rate constant of hydrolysis increases.

The observed greater stability of the Zn(II)-complex[17] with respect to Ni(II)-complex is because the metal-ligand bond in the former is purely electrostatic with little contribution from crystal field stabilisation energy (CFSE). The Zn(II) ion with smaller size will exert more electrostatic attraction.

In the present study, the rates of hydrolysis of the Schiff bases in the presence of transition metal ions follow the sequence Ni(II) > Zn(II) > Cu(II). This sequence can be correlated to the order of stability constants of transition metal chelates valid for most nitrogen and oxygen donor ligands as given by Irving and Williams,[18, 19] *viz.* Cu (II) > Zn(II) > Ni(II). It is thus evident that the rates of hydrolysis of imines are inversely related to the stability constants of their metal complexes.

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