

## Effect of Metal Ions on the Hydrolysis of the Schiff Bases Derived from 5-Chloro-4,6-Dimethyl-2-Hydroxy Benzaldehyde

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The catalytic effect of Ni(II), Ce(III) and Zr(IV) ions on the hydrolysis of substituted derivatives of 5-chloro-4,6-dimethyl-2-hydroxy benzaldehyde has been studied spectrophotometrically at  $298 \pm 1$  K. The rate of hydrolysis by the different metal ions follows the sequence  $Zr(IV) > Ni(II) > Ce(III)$  which is higher than the rate of hydrolysis in the absence of metal ions. A suitable reaction mechanism has been suggested for the metal ion catalyzed hydrolysis of the imines under study.

**Key Words:** Hydrolysis, 5-Chloro-4,6-dimethyl-2-hydroxy benzaldehyde, Spectrophotometric study.

### INTRODUCTION

The catalytic effect of metal ions has been recognized in a wide variety of reactions involving organic substrates<sup>1,2</sup>. One important reaction of biological interest is the effect of metal ions on the hydrolysis of imines. Dash and Nanda<sup>3</sup> made a detailed kinetic study of the hydrolysis of N-salicylideneaniline in the presence and absence of Co(II), Ni(II), Cu(II) and Zn(II) ions using 10% ethanol-water as solvent. The reactivity of the chelates towards hydrolysis was found to follow the reverse sequence of their stability constant, the most thermodynamically stable complexes undergoing the slowest rate of hydrolysis<sup>4</sup>. Imines capable of forming bicyclic chelate rings are known to be stabilized towards hydrolysis under mildly acidic conditions<sup>5,6</sup>. However, imines which can form monocyclic chelates such as N-salicylideneaniline are rapidly hydrolyzed in presence of metal ions.

The ability of forming metal ion complex depends upon the ratio of ionic charge to ionic radius. Higher the ratio, greater is the complexing ability of the metal ion. The present paper discusses the ability of different metal ions to catalyze the hydrolysis of the Schiff bases derived from 5-chloro-4,6-dimethyl-2-hydroxy benzaldehyde. It would be expected that high metal to ligand ratio would form 1 : 1 complexes that would be susceptible to nucleophilic attack by water or hydroxide ion. Rate measurement for the Ni(II), Ce(III) and Zr(IV) induced hydrolysis of the different imines derived from 5-chloro-4,6-dimethyl-2-hydroxy benzaldehyde were made spectrophotometrically using 75 : 25 dioxane:water as solvent in order to examine (a) effect of metal ions on the rate of hydrolysis of the coordinated imines; (b) effect of substituents on the kinetic lability of the metal complexes; (c) effect of metal ion concentration on the rate of hydrolysis.

## EXPERIMENTAL

### Synthesis of the ligands:

- (A) N-[5-chloro-4,6-dimethyl-2-hydroxy benzylidene] aniline,  
 (B) N-[5-chloro-4,6-dimethyl-2-hydroxy benzylidene]-4-chloroaniline  
 (C) N-[5-chloro-4,6-dimethyl-2-hydroxy benzylidene]-4-methoxyaniline

were prepared as follows:

5-Chloro-4,6-dimethyl-2-hydroxy benzaldehyde and the respective amine was added to ethanol in 1 : 1 ratio and the mixture was heated under reflux for 4 h. The ethanol was removed in vacuum. The resulting Schiff bases were purified by repeated recrystallization from ethanol and dried over calcium chloride. The structure and purity of the compound was confirmed by m.p., TLC and IR spectra.

TABLE-1  
 PHYSICO-CHEMICAL AND SPECTRAL DATA OF SCHIFF BASES

SR	m.f.	m.w.	Colour and nature	m.p. (°C)	IR $\nu(\text{C}=\text{N})$ ( $\text{cm}^{-1}$ )	$\lambda_{\text{max}}$ (nm)
A	$\text{C}_{15}\text{H}_{14}\text{ClNO}$	259.58	Yellow crystalline	85	1613.0	367 nm
B	$\text{C}_{15}\text{H}_{13}\text{Cl}_2\text{NO}$	293.9	Yellow crystalline	122	1611.3	366 nm
C	$\text{C}_{16}\text{H}_{16}\text{ClNO}_2$	289.6	Yellow crystalline	132	1613.8	375 nm

### Kinetic Measurements

Kinetic measurements were carried out at  $298 \pm 1$  K. The concentration of metal was varied between  $1 \times 10^{-4}$  mol  $\text{dm}^{-3}$  to  $5 \times 10^{-4}$  mol  $\text{dm}^{-3}$  using 75 : 25 dioxane : water as solvent.

The ligand concentration was maintained at  $1 \times 10^{-4}$  M in all the cases. The reaction was monitored by observing the decrease in absorbance at respective maxima. The ionic strength was maintained constant at 0.05 mol  $\text{dm}^{-3}$  using  $\text{NaClO}_4$ .

A solution containing requisite quantities of metal ion solution was initiated by adding a known amount of Schiff base in dioxane, which was also maintained at the same temperature. The progress of the hydrolysis was monitored at respective wavelength using Shimadzu UV 160-A spectrophotometer. The plots of  $\log(A_t - A_\infty)$  against time were found to be 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 Schiff base A, B and C in the presence of Ni(II), Ce(III) and Zr(IV) ions in 75 : 25 dioxane : water (v/v) medium at constant ionic strength of  $\mu = 0.05$  M at  $298 \pm 1$  K are tabulated in Table-2.

TABLE-2  
RATE CONSTANTS OF VARIOUS COMPOUNDS

## (A) N-[5-chloro-4,6-dimethyl-2-hydroxy benzylidene]aniline

Metal ion concentration	Zr	Ni	Ce
$1 \times 10^{-4}$ M	$3.92 \times 10^{-3}$	$3.0 \times 10^{-3}$	$2.41 \times 10^{-3}$
$2 \times 10^{-4}$ M	$6.0 \times 10^{-3}$	$5.4 \times 10^{-3}$	$4.94 \times 10^{-3}$
$3 \times 10^{-4}$ M	$7.2 \times 10^{-3}$	$6.8 \times 10^{-3}$	$6.3 \times 10^{-3}$
$4 \times 10^{-4}$ M	$8.7 \times 10^{-3}$	$8.4 \times 10^{-3}$	$7.8 \times 10^{-3}$
$5 \times 10^{-4}$ M	$9.3 \times 10^{-3}$	$9.2 \times 10^{-3}$	$8.7 \times 10^{-3}$

## (B) N-[5-chloro-4,6-dimethyl-2-hydroxy benzylidene]-4-chloro aniline

Metal ion concentration	Zr	Ni	Ce
$1 \times 10^{-4}$ M	$2.087 \times 10^{-3}$	$1.752 \times 10^{-3}$	$1.66 \times 10^{-3}$
$2 \times 10^{-4}$ M	$3.58 \times 10^{-3}$	$3.321 \times 10^{-3}$	$2.858 \times 10^{-3}$
$3 \times 10^{-4}$ M	$4.798 \times 10^{-3}$	$4.287 \times 10^{-3}$	$3.92 \times 10^{-3}$
$4 \times 10^{-4}$ M	$5.78 \times 10^{-3}$	$5.18 \times 10^{-3}$	$4.58 \times 10^{-3}$
$5 \times 10^{-4}$ M	$7.386 \times 10^{-3}$	$6.63 \times 10^{-3}$	$5.56 \times 10^{-3}$

## (C) N-[5-chloro-4,6-dimethyl-2-hydroxy benzylidene]-4-methoxyaniline

Metal ion concentration	Zr	Ni	Ce
$1 \times 10^{-4}$ M	$0.815 \times 10^{-3}$	$0.807 \times 10^{-3}$	$0.739 \times 10^{-3}$
$2 \times 10^{-4}$ M	$2.263 \times 10^{-3}$	$2.09 \times 10^{-3}$	$1.828 \times 10^{-3}$
$3 \times 10^{-4}$ M	$2.947 \times 10^{-3}$	$2.748 \times 10^{-3}$	$2.477 \times 10^{-3}$
$4 \times 10^{-4}$ M	$3.507 \times 10^{-3}$	$3.23 \times 10^{-3}$	$3.154 \times 10^{-3}$
$5 \times 10^{-4}$ M	$3.844 \times 10^{-3}$	$3.553 \times 10^{-3}$	$3.352 \times 10^{-3}$

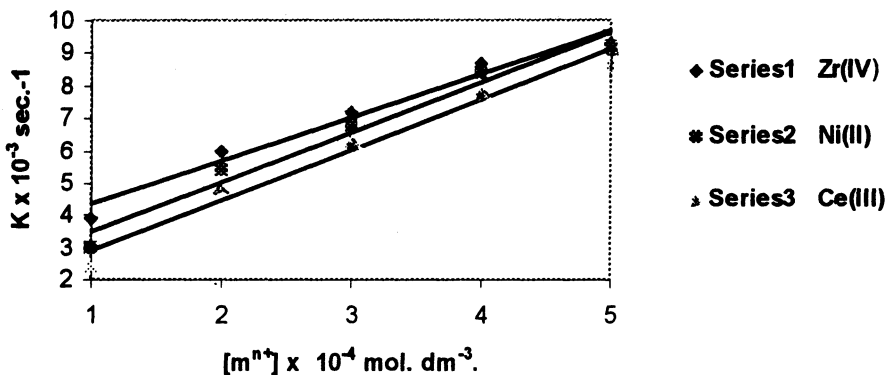
## (1) The effect of metal ion on the rate of hydrolysis of Schiff base (Fig. 1)

The ability of metal ion to form complex largely depends on the ratio of ionic charge to ionic radius. Higher the charge to radius ratio, greater is the tendency of the metal ion to form complex. This was the reason for selection of various metal ions, like Zr(IV), Ce(III) and Ni(II) for the study of catalytic effect on the rate of hydrolysis of Schiff base. The observations in Table-I reveal that the rate of hydrolysis follows the sequence

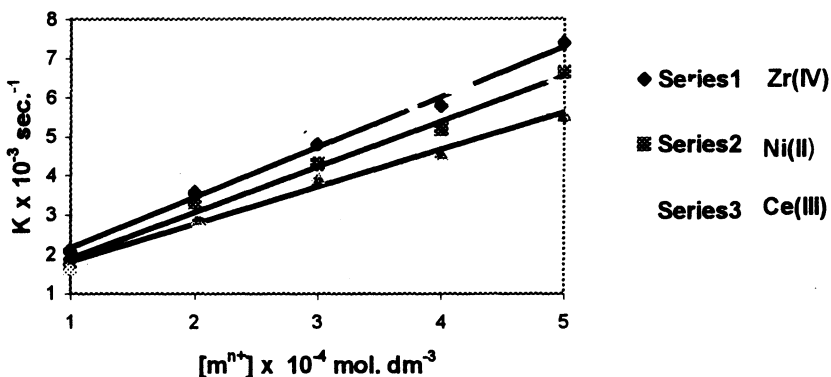


Charge to ionic radius ratio values for the metals Zr(IV), Ni(II) and Ce(III) are  $5.06 \times 10^{10}$ ,  $2.89 \times 10^{10}$  and  $2.8 \times 10^8$  respectively.

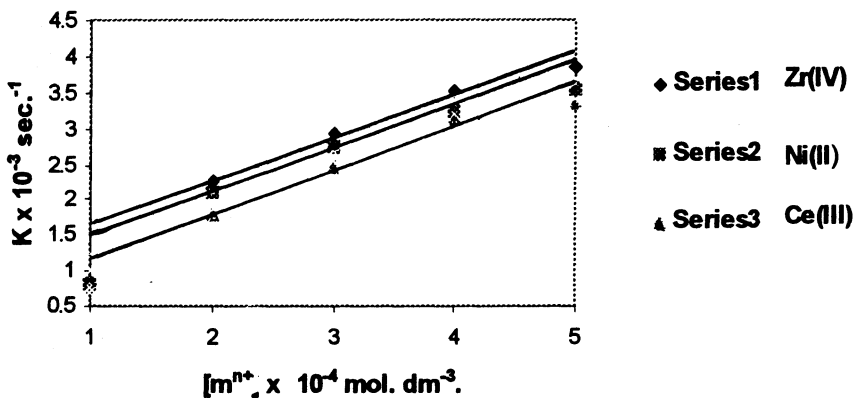
The Schiff bases under study form a coordinate bond with the metal through phenolic oxygen and imine nitrogen. Hence in presence of metal ions the imines mainly exist in the metal complex form, resulting in the withdrawal of electron density from the azomethine carbon atom. Thus the azomethine carbon atom is expected to carry a high positive charge relative to that in the absence of metal ion. This results in a higher nucleophilic attack of water on this carbon atom. Proton catalyzed addition of water at the aldimine linkage ( $-\text{CH}=\text{N}$ ) is therefore suggested as the rate determining step for the hydrolysis. The resulting carbinolamine intermediate decomposes at a faster rate into the product.



N-[5-chloro-4,6-dimethyl-2-hydroxy benzylidene]aniline



N-[5-chloro-4,6-dimethyl-2-hydroxy benzylidene]-4-chloroaniline



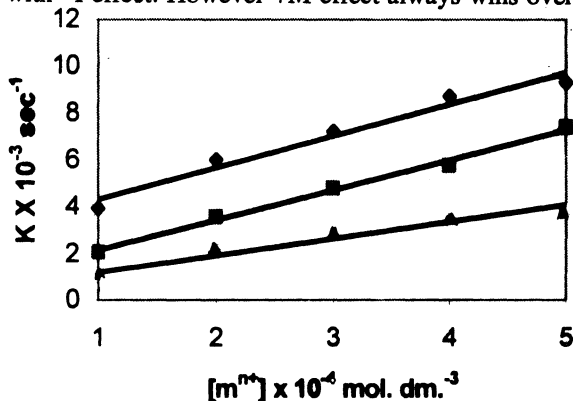
N-[5-chloro-4,6-dimethyl-2-hydroxy benzylidene]methoxyaniline

Fig. 1. Effect of metal ions on the rate of hydrolysis

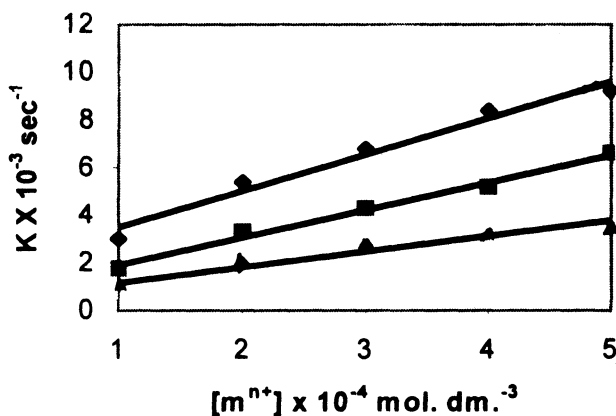
Due to higher charge to ionic radius ratio, Zr(IV) metal forms strongest bond with the imine nitrogen. The metal-nitrogen bond weakens the C—N bond, thus rendering it more susceptible to hydrolytic cleavage. Hence there is a relation between strength of the M—N bond and the ability of metal ion to catalyze the hydrolysis of the imines. Thus Zr(IV) complex shows highest value of rate constant, which indicates that it is highly labile to hydrolysis. Thus Zr(IV) forms less stable complex than Ni(II) and Ce(III), whereas Ce(III) shows lowest value of rate constant as it forms a highly stable complex. This is evident from the lowest charge to radius ratio for Ce(III) ions.

## (2) The effect of substituents (Fig. 2)

The —Cl group is selected to exhibit its +M, —I effect and —OCH<sub>3</sub> group is substituted to exhibit its +M, +I effect on the rate constant as compared to the parent compound (A) with no substitution in the aniline ring. The rate constant for compound (B) was expected to be lower than that of (A) due to the presence of —Cl group with —I effect. However +M effect always wins over —I effect and



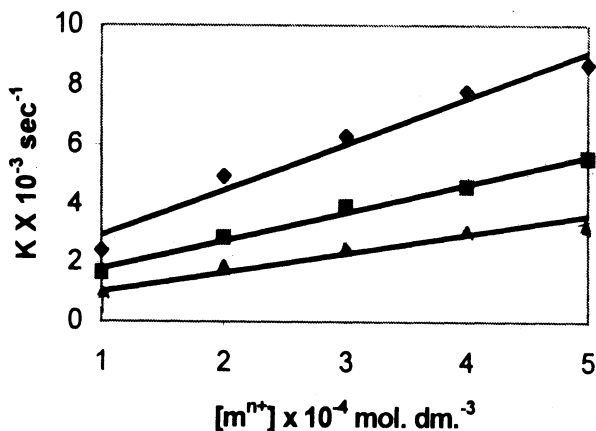
◆ Series 1 Aniline    ■ Series 2 4-chloro aniline    ▲ Series 3 4-methoxy aniline  
(I) Rate constant vs. [Zr]



(II) Rate constant vs. [Ni]

Fig. 2. Effect of substitution on the rate of hydrolysis (Contd.)

◆ Series 1 Aniline    ■ Series 2 4-chloro aniline    ▲ Series 3 4-methoxy aniline



◆ Series 1 Aniline    ■ Series 2 4-chloro aniline    ▲ Series 3 4-methoxy aniline

(III) Rate constant vs. [Ce]

Fig. 2. Effect of substitution on the rate of hydrolysis

the same is observed in case of ligand (B). The substitution by —Cl group has actually stabilized the compound (B). Hence the rate constant for the hydrolysis of compound (B) is lower than that of compound (A). In compound (C) a strong positive mesomeric effect (+M) is expected by oxygen atom with its lone pair of electrons of the methoxy group. This stabilizes the compound (C) by increasing the electron density on the azomethine carbon atom which is therefore not readily attacked by a strong nucleophile like H<sub>2</sub>O. As a result the rate constant for the hydrolysis of (C) is lowest in the series.

### (3) Effect of M<sup>n+</sup> concentrations on the rate of hydrolysis

It is observed from the values of rate constants in Table-2 that the rate constants for compounds A, B and C increase with increase in the concentration of metal ion.

### ACKNOWLEDGEMENT

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