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FORMATION OF N-SALICYLIDENE-p-CHLOROANILINE: A KINETIC STUDY

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ABSTRACT

The second order reaction rate constant for the reaction of salicyaldehyde with p-Chloro aniline have been reported in ethanol at temperature range 303 to 318 k. The rate of reaction is first order with respect to salicyaldehyde and p-chloro aniline. The rate of reaction increases with increases in temperature. The thermodynamic parameters are used to explain the nature of reaction. Suitable reaction mechanism has been suggested for the formation of the Schiff base. From the effect of temperature on the rate of reaction various thermodynamic parameter have been evaluated.

Key words: Schiff base, N-Salicylidene-p-chloroaniline, Kinetics.

INTRODUCTION

The Schiff bases are condensations products of amines with active carbonyl compounds. The Schiff bases are also called as imines[1], anilis and azomithines. They contain azomethines (> C=N-) group and hence can acts as effective lignads. The kinetic studies of Schiff base formation as well as other carbonyl addition reaction have been interested chemists for some time. The imines derived from anilines and its derivative with aromatic aldehydes has a wide variety of applications in biological[2,3] and analytical[4] chemistry. Schiff bases are known to be neoplasm inhibitors[5,6], antiviral[7], anticonvulsants[8], antimicrobial[9], anticancer[10], plant growth regulator[11] and antituburecular[12], agents. 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[13-17]. Schiff bases formation involves a two step reaction between the carbonyl compound and the amino compound. First, addition takes place to form a carbinolamine, which then undergoes dehydration[18]. Both step are reversible and subject to general acid-base catalyst[19].

Literature survey reveals that there is enormous growth of the study of metal complexes of Schiff bases. The catalytic effect of hydrogen, hydroxyl and metal ions on the formation and hydrolysis of imines have been studied by several workers[16,17,20-23]. In the present work, we reported here kinetic study and mechanism of the formation of Schiff base, N-Salicylidene-p-Chloroaniline in ethanol medium spectrophotometrically.

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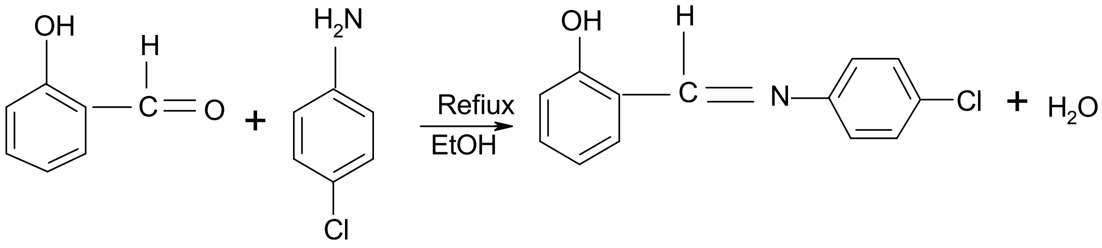
EXPERIMENTAL

Schiff base were prepared by refluxing equimolar mixture of purified salicyaldehyde and p-Chloro aniline in ethanol medium for about three hours. The resulting mixture was cooled and filtered to obtain solid Schiff base. The Schiff base obtained was recrystallised from ethanol. The purity was checked by melting point (100°C) and TLC.



Salicylaldehyde p-Chloro aniline Schiff base

Kinetic measurements

The rate of formation of Schiff base was followed by spectrophotometer at λ_{max}. By using UV-VIS, 1601 Shimuadzu Spectrophotometer. The basis of the spectrophtometry is Beer's law. This relates the absorbancy of a solution to the concentration of the species present. The prerequisite of the spectrophtometry is the validity of the Beer's law. It is possible to ascertain the concentration of a given species in solution, if it absorbs radiation of a particular wavelength and obeys Beer's law. True variation of this law can arise when moderately concentrated solutions are used. The law is obeyed only in dilute solutions.

Standard curve

The solution of Schiff base of various concentrations (0.0001 M to 0.002 M) was prepared using ethanol solvent. Using 0.002 M solution, λ_{max} was determined. The absorbance of each coloured solution was then measured, at this λ_{max} 385 nm. The readings are recorded in Table 1. The plot of absorbance (optical density) versus concentration of the Schiff bases has been obtained as a straight line (Fig. 1). The plot was used as standard curve for the determination of concentration of Schiff bases for the kinetic measurements.

Table 1: Optical density at λ_{max} 385 nm

Conc. of SB	O.D
0.000	0.000
0.0002	0.340
0.0004	0.593
0.0006	0.877
0.0008	1.158
0.0010	1.514

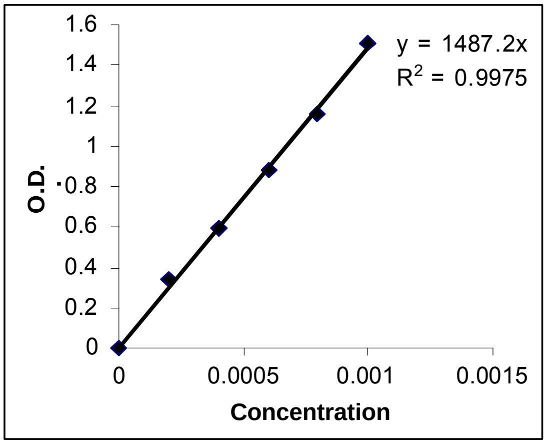


Fig: 1: Standard Curve O.D. Vs Concentration

Experimental procedure for kinetic measurements

Salicylaldehyde solution (25 mL) of desired molarity was taken into 50 mL flask. In another 50 mL flask p-Chloro aniline solution (25 mL) of desired molarity were taken. Both the flasks were then allowed to stand in thermostatic water bath to attain the required temperature. Then content of the flask having p-Chloro aniline solution transferred to the flask containing salicylaldehyde. Thus obtained reaction mixture was thoroughly shaken and kept in thermostatic water bath at desired temperature. After mixing, the reaction mixture was transferred to a quartz cell and the increase of absorbance due to Schiff base formation with time was followed against the blank kept in another quartz cell at λ_{max}. At different time intervals solution was employed to determine optical density. From this optical density, concentration (x) of Schiff base present at particular time was determined with the help of the standard curve. It was observed that this method gave reproducible and quantitative result.

Methods of calculations of the rate constant

For the equimolar quantities of reactants, value of second order rate constant were calculated using relation -

$$k = \frac{1}{at}\frac{x}{(a-x)}$$

If concentrations of reactants are different, the values of second order rate constants have been calculated by using relation

$$k = \frac{2.303}{(a-b)t}\log\frac{b(a-x)}{a(b-x)}$$

Where, t = time in second.

a = initial concentration of Salicylaldehyde.

b = initial concentration of aniline.

x = amount of Schiff base formed in time t.

Graphical k values were obtained from the slope of the linear plot of 1/(a-x) versus time (t) for equal concentration and plot of log [(a-x) /(b-x)] versus time (t) for unequal concentrations.

Order of reaction with respect to Salicylaldehyde

To determine the order of reaction with respect to salicylaldehyde, the reaction has been carried out at different concentrations of salicylaldehyde by keeping the concentration of p- methyl aniline constant at a particular temperature. Van't Hoff's differential method[24] was applied to determine the order with respect to salicylaldehyde by equation[25,26].

$$n = \frac{\log\left[\frac{dc}{dt}\right]I - \log\left[\frac{dc}{dt}\right]II}{\log c\,I - \log c\,II}$$

The amount of product formed (x) was plotted against the time in minutes. From the curve, the values of dc/dt have been calculated.

Order of reaction with respect to p-Chloro aniline

The order of reaction with respect to p-Chloro aniline was determined by varying concentration of p-Chloro aniline by keeping the concentration of salicylaldehyde constant at a particular temperature. The order with respect to p-Chloro aniline was determined by applying van't Hoff's differential method. The values of dc/dt were evaluated by plotting amount of product formed (x) against time (t) in minutes. From the effect of temperature on the reaction rate the energy of activation E_a, enthalpy of activation (ΔH^*), entropy of activation (ΔS^*), free energy (ΔG^*) and frequency factor (A) were calculated.

RESULTS AND DISCUSSION

Kinetics of formation of Schiff bases was caried out at equal concentrarion. The second order rate constant was calculated by using equation of second order at equal concentration and graphical k valuses determined from the stiright line plots of 1/(a-x) verses time.

Reaction order

The kinetic study is carried out at different concentration of salicylaldehyde at constant concentration of p-Chloro aniline in ethanol medium at 303 K. The plot of dc/dt against log [S.A.] is liner and slope of plot was found to be nearly one, indicates the order with respect to salicylaldehyde is first order. Similarly the kinetic study is carried out at different concentration of p-Chloro aniline at constant concentration of salicylaldehyde in ethanol medium at 303 K. The plot of dc/dt against log [p-Cl-ANI] is liner and slope of plot was found to be nearly one, indicates the order with respect to aniline is first order.

Effect of temperature on the rate of reaction

Kinetic measurements were carried out at four different temperatures 303, 308, 313 and 318 K at constant concentration of [S.A.] (1×10^{-3} mol dm^{-3}) and p-Chloro aniline (1×10^{-3} mol dm^{-3}) in ethanol. The second order rate constant depends on the reaction temperature[27,28]. The thermodynamic parameters like energy of activation (E_a), enthalpy of activation (ΔH^*), entropy of activation (ΔS^*), free energy (ΔG^*) and frequency factor (A) were calculated (Table 3). From the value of thermodynamic parameter it is observed that $\Delta H^*$and $\Delta S^*$are the important parameter in controlling the rate of reactions. The negative value of entropy of activation indicates that activated complex is less probable and rate is slower. The negative values of entropy of activation show that the intermediate transition state is rigid. The relatively small values of ΔH^* and the negative ΔS^* values are consistent with the reactions which generally proceeds through highly organized transitions stats[29]. If both the reactants are likely charged, the charge density on the surface in the transitions state will be more and hence there can be increase in solvation leading again to a negative ΔS^*[30].

Table 2: Effect of temperature

Temp. (K)	k × 10^3 (dm^3 mol^{-1} s^{-1})
303	10.346
308	15.161
313	21.809
318	32.660

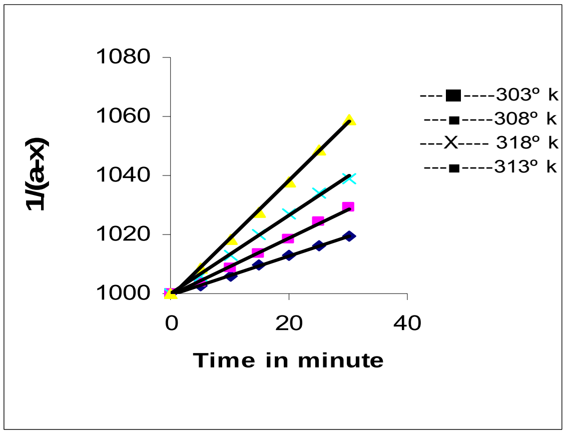


Fig. 2: Plot of 1/ (a-x) versus t

The rate constant values of Schiff base formation at different temperature are listed in the Table 2. The rate of formation of Schiff bases increases with increasing temperature. The plot of log k versus 1/T is straight line (Fig. 3).

Table 3: Thermodynamic parameters

E_a	59.011 KJ
A	1.54 x 10^8
ΔH*	56.491 KJ
ΔS*	-88.343 JK^{-1} mol^{-1}
ΔG*	83.260 KJ mol^{-1}

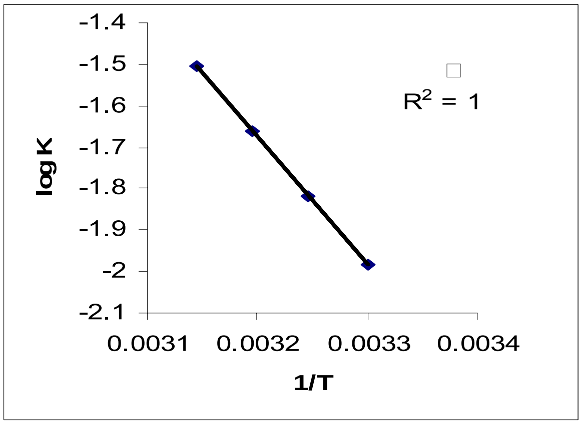
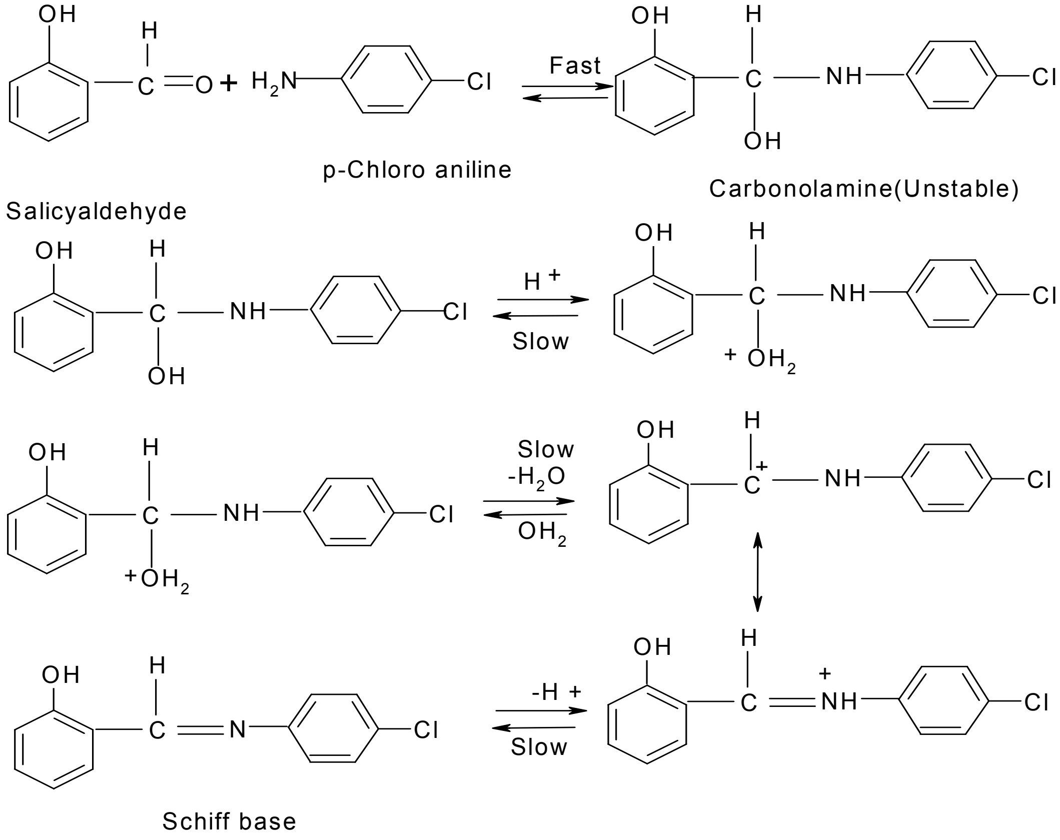


Fig. 3: Plot of log k versus 1/T



Scheme 1

Schiff bases formation involves a two step reaction between the carbonyl compound and the amino compound. First addition takes place to form a carbinolamine which then undergoes dehydration. Both steps exhibit general acid base catalysis[31,32]. It was found that the reaction was first order in the carbonyl compounds and first order in amine. Spectroscopic studies have revealed that, under mild acidic condition there is a fast disappearance of the carbonyl function followed by a slow appearance of the product[33]. Under mild acidic condition, rapid addition of amine to the carbonyl compound followed by the acid-catalysed dehydration of the adduct is the rate-controlling step.

An increase in acidity would promote the reaction because it increases the rate of dehydration step. But with a further increase in acidity the nucleophile (RNH_2) may get protonated (RN^+H_3) and, thus deprived of its lone pair of electrons and is no longer in a position to attack the positive carbonyl carbon .

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