

# KINETICS & MECHANISM OF 2'-CHLORO-2-HYDROXY-1-NAPHTHALIDENEANIL BY POTASSIUM BROMATE

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## ABSTRACT

*The kinetics of oxidation of the Schiff base, 2'-chloro-2-hydroxy-1-naphthalideneanil has been studied by potassium bromate in aqueous medium. The reaction is found to obey the first order rate equation. The kinetic study is carried out at five different temperatures. The study has been undertaken by change in the concentration of oxidant, change in the concentration of HClO<sub>4</sub> and change in the ionic strength. These changes also show first order behaviour. The thermodynamic parameters ΔE, ΔH, ΔG and ΔS have been calculated and reported. The frequency factor (A) is also computed. Ionic strength effects show a negative effect on rate constant.*

**Keywords :** Bromate, kinetic study, thermodynamic parameter, oxidation.

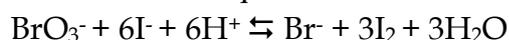
## INTRODUCTION

Potassium bromate is commercially available, stable solid which can be handled more easily than liquid bromine & hydrobromous acid solution. The potassium bromate has been widely used in the oxidation of any organic compounds in the acidic medium<sup>1-5</sup>. This oxidation is recognized as friendly to environment compared to the oxidation carried out by transition metal containing reagents such as bromate, permanganate, cerium and ruthenium salts etc. In spite of much work which has been performed on the oxidation of organic compounds with bromate, organic synthesis using bromate salts is still less. The over oxidation & bromination, oxidative bromination generally interfere with clean reactions & new products may be obtained. The reaction condition and strength of the acids used is very important which determines the direction of the reaction. The present communication deals with the kinetic study of acid bromate oxidation of 2'-chloro-2-hydroxy-1-naphthalideneanil.

## EXPERIMENTAL

All the materials used were AR grade. The Schiff base 2'-chloro-2-hydroxy-1-naphthalideneanil was prepared by refluxing 2-hydroxyl-1-naphthaldehyde with ortho chloro aniline in ethanol. A drop of pyridine was added as a catalytic agent. This mixture was refluxed for 3 hours and purified by recrystallisation<sup>6</sup>. The stock solutions of KBrO<sub>3</sub> in 50% V/V in acetic acid-water mixture and sodium thiosulphate were prepared and standardized by known methods.

The reaction followed by removing aliquots of reaction mixture at known intervals of time & quenching the reaction by adding excess of KI solution. The unused bromate reacts with KI in acid solution in accordance with the equation<sup>7</sup>.



Using starch as an indicator the liberated iodine was estimated by titrating against standard solution of sodium thiosulphate. The oxidized product is confirmed by the qualitative analysis and infrared spectra.

**Dependence of the rate of reaction on oxidant & substrate (Schiff base)**

By using different initial concentration of the oxidant with fixed concentration of the reactants the order of the reaction was determined.

Potassium chloride was used to keep the ionic strength of the reaction to be constant. The velocity constant i.e.  $k_1$  values are given in table No.1. It is seen that the reaction is independent of potassium bromate concentration. From the table it is clearly understood that the reaction is of pseudo first order with respect to the change in oxidant concentration.

**TABLE-1**

**Effect of concentration of oxidant on the rate constant.**

Solvent = HOAc (50%), [Schiff base] =  $5 \times 10^{-3}$  M

[HClO<sub>4</sub>]= $0.5 \times 10^{-2}$  M,  $\mu=0.05$

[oxidant] x 10 <sup>-4</sup> M	3.0	5.0	7.0	9.0	11.0
$k_1 \times 10^{-2} \text{min}^{-1}$	2.62	1.902	1.667	1.673	1.538

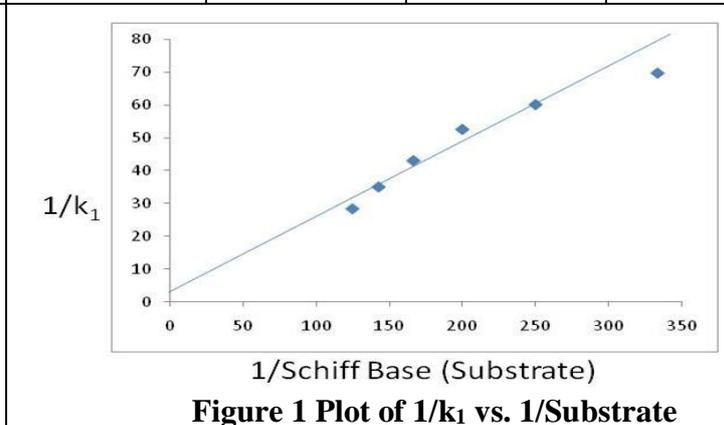
Six different concentration of Schiff base were used to study reaction of various concentrations of substrate (Schiff base). The other parameters were kept constant. The average value of velocity constant are determined & tabulated in Table No.2. The graph of  $1/k_1$  vs  $1/(\text{Schiff base})$  is a straight line with the intercept on  $1/k_1$  axis indicating the formation of complex between the Schiff base and oxidant as shown in fig.no.1

**TABLE-2**

**Effect of Schiff base concentration on the rate constant.**

Solvent = HOAc(50%), [HClO<sub>4</sub>]= $0.5 \times 10^{-2}$  M,  $\mu=0.05$  [oxidant] $\times 10^{-4}$  M

Schiff base x 10 <sup>-3</sup> M	3.0	4.0	5.0	6.0	7.0	8.0
$k_1 \times 10^{-2} \text{min}^{-1}$	1.432	1.662	1.902	2.326	2.863	3.540



**Effect of [HClO<sub>4</sub>]**

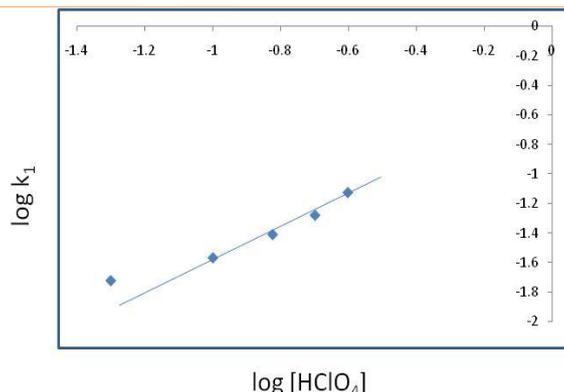
The five different concentration of perchloric acid were prepared & kinetic study was carried out and other factors were kept constant. The rate constant Values ( $k_1$ ) were calculated which are placed in table No. 3 and the graph of  $\log k_1$  Vs  $\log [\text{HClO}_4]$  is shown in fig. 2.

**TABLE-3**

**Effect of varying [HClO<sub>4</sub>] on the rate constant**

Solvent = HOAc (50%), [Schiff base] =  $5 \times 10^{-3}$  M, [oxidant] =  $5 \times 10^{-4}$  M,  $\mu = 0.05$

[HClO <sub>4</sub> ] x 10 <sup>-2</sup> M	5	10	15	20	25
$k_1 \times 10^{-2} \text{min}^{-1}$	1.902	2.714	3.905	5.271	7.513



**Figure 2 Plot of  $\log k_1$  vs.  $\log[\text{HClO}_4]$**

The straight line with slope 1.08 is obtained. The first order rate constant values were calculated. From the values it is seen that  $k_1$  values increases with increase in concentration of perchloric acid. The overall conclusion is that  $\text{H}^+$  ion is playing the role of catalyst in the reaction.

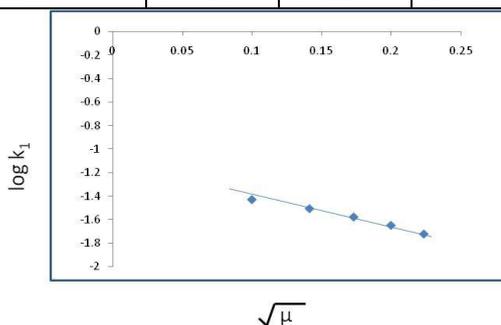
**Effect of ionic strengths**

The effect of ionic strength on the reaction rate was studied. Five different ionic strengths of the reaction were carried out. The ionic strength of the reaction mixture is maintained by the addition of required quantity of KCl keeping the concentration of the other reactants unaltered. The results are shown in table no. 4. It is seen from the table that  $k_1$  values decreases with increase in ionic strength. Thus the retarding effect is observed on addition of KCl salt. A plot of  $\log k_1$  against  $\text{sq.root}(\mu)$  is shown in fig. 3. The plot obtained is a straight line with negative slope which indicates the rate determining reaction probably involves the univalent ions with the opposite charges.

**TABLE-4 : Effect of ionic strength on the reaction rate**

Solvent = HOAc (50%),  $[\text{HClO}_4] = 5 \times 10^{-2}\text{M}$ ,  $[\text{Schiff base}] = 5 \times 10^{-3}\text{M}$ ,  $[\text{Oxidant}] = 5 \times 10^{-4}\text{M}$

$\mu$ (Ionic strength)	0.01	0.02	0.03	0.04	0.05
$k_1 \times 10^{-2} \text{min}^{-1}$	3.728	3.123	2.653	2.254	1.902



**Figure 3 Plot of  $\log k_1$  vs.  $\sqrt{\mu}$**

**Effect of Temperature on rate constant**

The five different temperatures were selected to measure the rates and the different thermodynamic parameters are calculated like  $\Delta E^*$ ,  $\Delta H^*$ , and  $\Delta S^*$ . The frequency factor A has been determined and placed in table No.5. The negative  $\Delta S$  value indicates the formation of rigid activated complex. The end product analysis shows the formation of Quinone at the end of the reaction. This was confirmed by IR spectra of the oxidized product & qualitative test<sup>8</sup>.

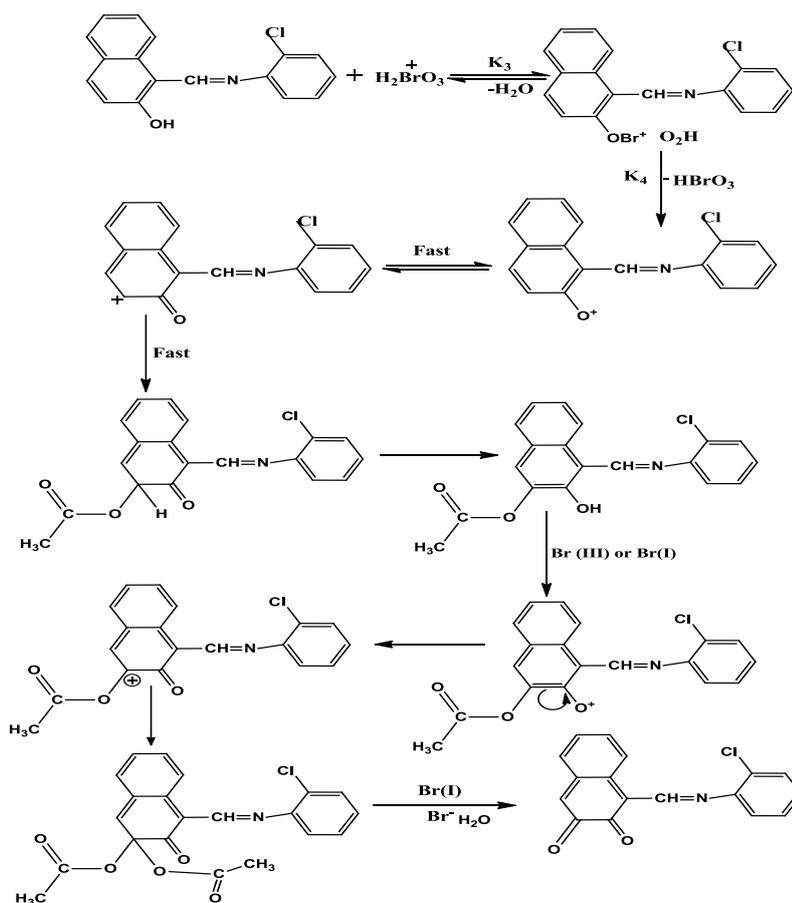
**TABLE-5**
**Effect of temperature on rate constant**

 Solvent = HOAc (50%) [Schiff base] =  $5 \times 10^{-3}M$ , [oxidant] =  $5 \times 10^{-4}M$ 
 $\mu = 0.05$ ,  $[HClO_4] = 5 \times 10^{-2}M$ 

Temp. K	$k_1 \times 10^{-2} \text{ min}^{-1}$	$\Delta E \text{ kcal mol}^{-1}$	$\Delta H \text{ kcal}$	$\Delta G \text{ K cal/mol}$	$\Delta S \text{ (e.u)}$	A $\text{min}^{-1} \times 10^4$
308	1.4978			23.190	-35.7204	3.0697
313	1.9040			23.370	-35.9064	2.8946
318	2.5010	11.3998	12.1265	23.550	-36.0025	2.8536
323	3.4413			23.730	-35.9893	2.9696
228	4.5717			23.910	-36.0280	3.0095

The overall rate equation obtained is

$$-d[BrO_3^-]/dt = k_1 k_2 k_3 [H^+] [BrO_3^-] [\text{Schiff base}] / 1 + k_2 [\text{Schiff base}]$$

**Mechanism** - A possible mechanism 9, 10 shown below has been proposed for the Oxidation of Schiff base by  $KBrO_3$ 

**CONCLUSION:**



The reaction was first order in  $[\text{BrO}_3^-]$ , [substrate] as well as  $[\text{H}^+]$ . A negative kinetic salt effect was observed. Thermodynamic parameters,  $\Delta E$ ,  $\Delta H$ ,  $\Delta S$ ,  $\Delta G$  & frequency factor (A) were determined from the study of temperature effect on the rate constant. The oxidized product is Quinone and found to be stable in nature. The confirmation of compound is obtained by TLC and IR

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