



KINETICS OF OXIDATION OF 3'-CHLORO-2-HYDROXY-1-NAPHTHALIDENEANIL BY POTASSIUM BROMATE IN ACIDIC MEDIUM

U. N. Pol

Department of Chemistry, Willingdon College, Sangli (M.S.) India

ABSTRACT

Potassium bromate and sodium bromate are stable and easily stored oxidants. Potassium bromate easily oxidize Schiff base in aqueous acetic acid medium. The kinetics of oxidation of 3'-chloro-2-hydroxy-1-naphthalideneanil has been studied. The study is carried out at five different temperatures and the thermodynamic parameters such as ΔE , ΔH , ΔS , ΔG and frequency factor (A) are determined. A suitable mechanism suggested on the basis of kinetic results.

Keywords : Bromate, Anils, Schiff base, Kinetic study, Oxidation, Thermodynamics parameter.

INTRODUCTION :

Potassium bromate are commercially available stable solid which can handle easily than liquid bromine and hydrobromous acid solutions. Potassium bromate has been widely used in the oxidation of many organic compounds in acidic medium.^[1-8] The reaction conditions, particularly the strength and nature of acid used is crucial and determines which direction the reaction is proceeds. Kalyan et al.^[9] describes the kinetics of the oxidation of some aldose and amino sugars by potassium bromate in hydrochloric acid medium. The kinetics of the oxidation of D -(+)-glucose^[10] by potassium bromate in acidic medium was also studied. The present communication deals with the kinetic study of oxidation of 3'-chloro-2-hydroxy-1-naphthalideneanil by potassium bromate in acid medium.

EXPERIMENTAL :

All the reagents used were of A. R. grade Triple distilled water was used throughout the experiments and absolute alcohol used as a solvent and required chemicals was prepared by standard methods. The Schiff base 3'-chloro-2-hydroxy-1-naphthalideneanil was prepared by refluxing 2 hydroxy-1-naphthaldehyde with meta chloro aniline in ethanol. A drop of pyridine was added as catalytic agent. This mixture was refluxed for 3 hours and purified by recrystallization.^[11] The concentration of Schiff base is 5×10^{-3} M. The concentration of HClO_4 was 5×10^{-2} M. The concentration of KBrO_3 was 5×10^{-2} M. The concentration of $\text{Na}_2\text{S}_2\text{O}_3$ is 1.5×10^{-3} M. The stock solution of KBrO_3 is 50% V/V in acetic acid-water mixture. At different time intervals 5 ml reaction mixture were pipetted out and titrated against 0.0015 N sodium thiosulphate solution by adding excess KI solution. The unused bromate reacts with KI in acid solution in accordance with the equation.



EFFECT OF VARIOUS CONCENTRATION OF OXIDANT- To determine the order of reaction with respect to oxidant, the reaction was carried out at different concentrations of

oxidant, keeping other parameters constant. Concentration of substrate, perchloric acid, ionic strength of solution and temperature of reaction were kept unchanged. Velocity constant k_1 values are given in table No. 1. From results reaction is independent of potassium bromate concentration and reaction is of first order with respect to the change in oxidant concentration.

Table No. 1

Effect of change in concentration of oxidant on the reaction rate

[Schiff base] = 5×10^{-3} M, $\mu = 0.05$, Solvent = 50% HOAc V/A,
 [HClO₄] = 5×10^{-2} M.

[Oxidant] x 10 ⁻⁴ M	3	5	7	9	11
k_1 x 10 ⁻² min ⁻¹	1.563	1.230	1.179	1.310	1.309

EFFECT OF VARIOUS CONCENTRATION OF SUBSTRATES (SCHIFF BASE) :

The concentration of substrate (Schiff base) varied between 0.003 M to 0.008 M. Concentration of oxidant was kept constant. All other parameters were kept constant. The average value of velocity constant are determined and tabulated in table No. 2. The graph of $\frac{1}{K_1}$ Vs $\frac{1}{[\text{Schiff base}]}$ are linear and are not passing through origin which indicate the formation of a complex as shown in Fig. 1.

Table No. 2

Effect of change in concentration of Schiff base on the reaction rate

Solvent = HOAc (50%), [Oxidant] = 5×10^{-4} M,
 [HClO₄] = 5×10^{-2} M, $\mu = 0.05$

[Schiff base] x 10 ⁻³ M	3	4	5	6	7	8
k_1 x 10 ⁻² min ⁻¹	0.763	0.994	1.230	1.530	1.944	2.513
1/ k_1	130.92	100.52	81.2611	63.3594	51.4165	39.7851
1/Substrate	333.33	250.00	200	166.66	142.85	125.00

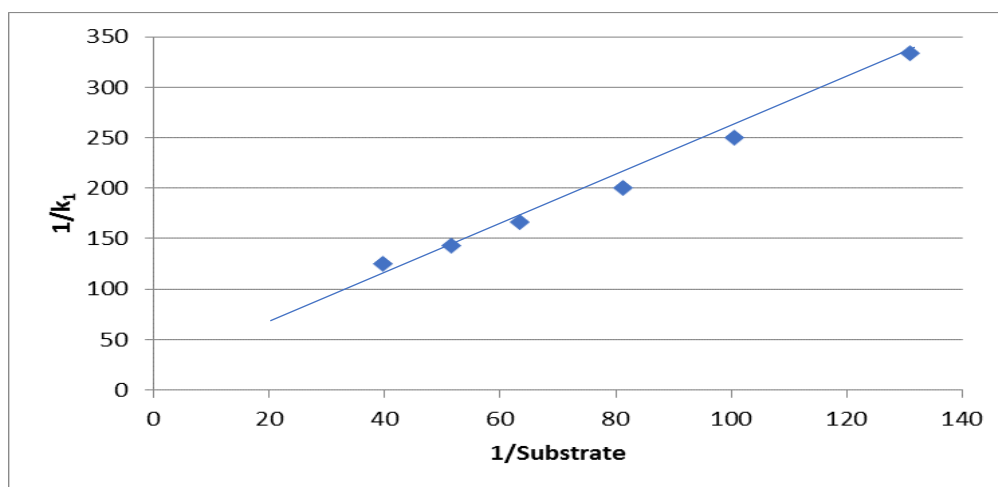


Fig. 1 : Plot of 1/ k_1 Vs 1/Schiff base

Effect of $[\text{HClO}_4]$:

The reaction was studied at five different concentrations of perchloric acid keeping other factors constant. The average rate constant k_1 were calculated and reported in table 3.

The graph of $\log k_1$ Vs $\log [\text{HClO}_4]$ is shown in Fig. 2.

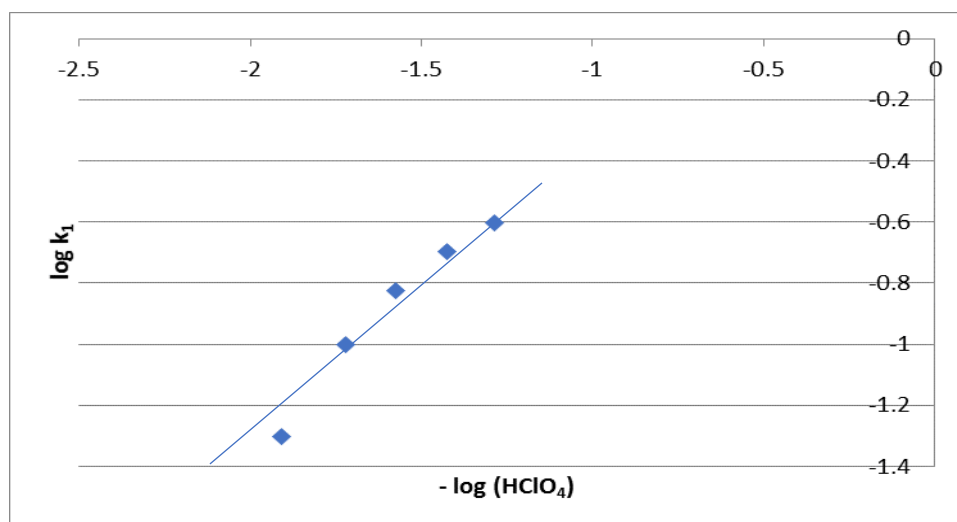
Table No. 3

Effect of varying $[\text{HClO}_4]$ on the reaction rates

Solvent = HOAc (50%), [Schiff base] = 5×10^{-3} M, [Oxidant] = 5×10^{-4} M

$\mu = 0.05$

$[\text{HClO}_4] \times 10^{-2}$ M	5	10	15	20	25
$k_1 \times 10^{-2} \text{ min}^{-1}$	1.230	1.893	2.651	3.749	5.178
$\log k_1$	-1.9098	-1.7226	-1.5765	-1.4260	-1.2857
$\log [\text{HClO}_4]$	-1.3010	-1.000	-0.8239	-0.6989	-0.6020



Plot of $\log K_1$ Vs $\log [\text{HClO}_4]$

Graph shows a straight line with slope 1.00 is obtained. This indicates that the reaction is of 1st order. From the values of k_1 it is clearly seen that k_1 values increases with increase in concentration of perchloric acid. Therefore it seems that H^+ ion is playing the role of catalyst in the reaction.

Effect of Ionic Strengths :

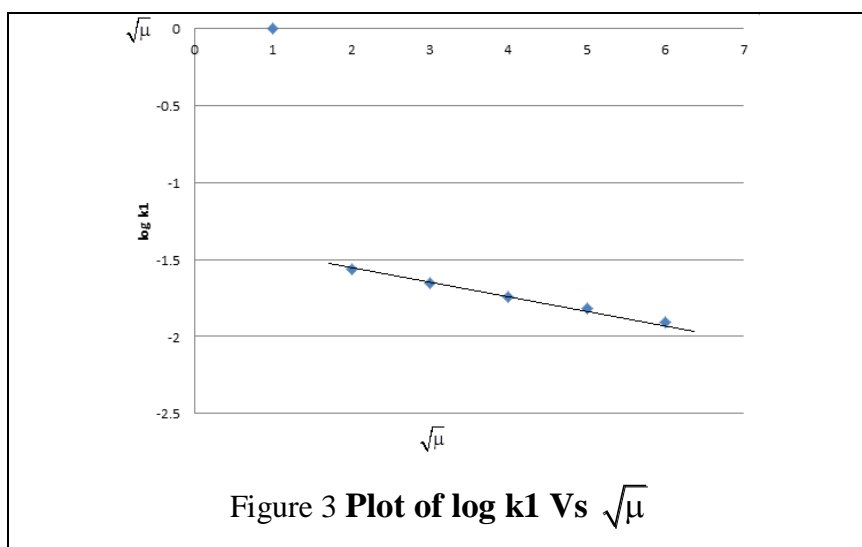
To study the effect of ionic strength on the reaction rate, the reaction was carried out at five different ionic strengths and this is maintained by the addition of requisite quantities of KCl while the concentration of other reactants are kept unchanged. Obtained results were tabulated in table no. 4 and it indicates that k_1 values decreases with the increase in ionic strength. Thus the retarding effect is observed on addition of KCl salt. A graph of $\log k_1$ against $\sqrt{\mu}$ is shown in Fig. 3. The plot obtained is a straight line with a negative slope which is the value of $Z_A Z_B$. It seems that the rate determining step of reaction probably involves univalent ions with opposite charges.

Table No. 4
Effect of ionic strength on the reaction rate

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

 [Oxidant] = 5×10^{-4} M, [HClO₄] = 5×10^{-2} M

μ	0.01	0.02	0.03	0.04	0.05
$k_1 \times 10^{-2} \text{ min}^{-1}$	2.748	2.214	1.820	1.516	1.230
$\log k_1$	-1.5608	-1.6548	-1.7399	-1.8193	-1.9098
$\sqrt{\mu}$	0.100	0.1414	0.1732	0.200	0.2236


Effect of Temperature on Constant Rate :

The reaction was carried out at five different temperatures over a range of 308-328 K. The frequency factor (A) and other thermodynamic parameters ΔE , ΔH , ΔG , ΔS have been calculated and reported in table 5. The negative ΔS values indicate formation of more rigid activated complex. The end product analysis shows that a quinone is formed at the end of reaction. This is confirmed by recording IR spectra of oxidized product and the qualitative tests.^[12]

Table No. 5
Effect of temperature on rate constant

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

 [Oxidant] = 5×10^{-4} M, $\mu = 0.05$, [HClO₄] = 0.5×10^{-2} M

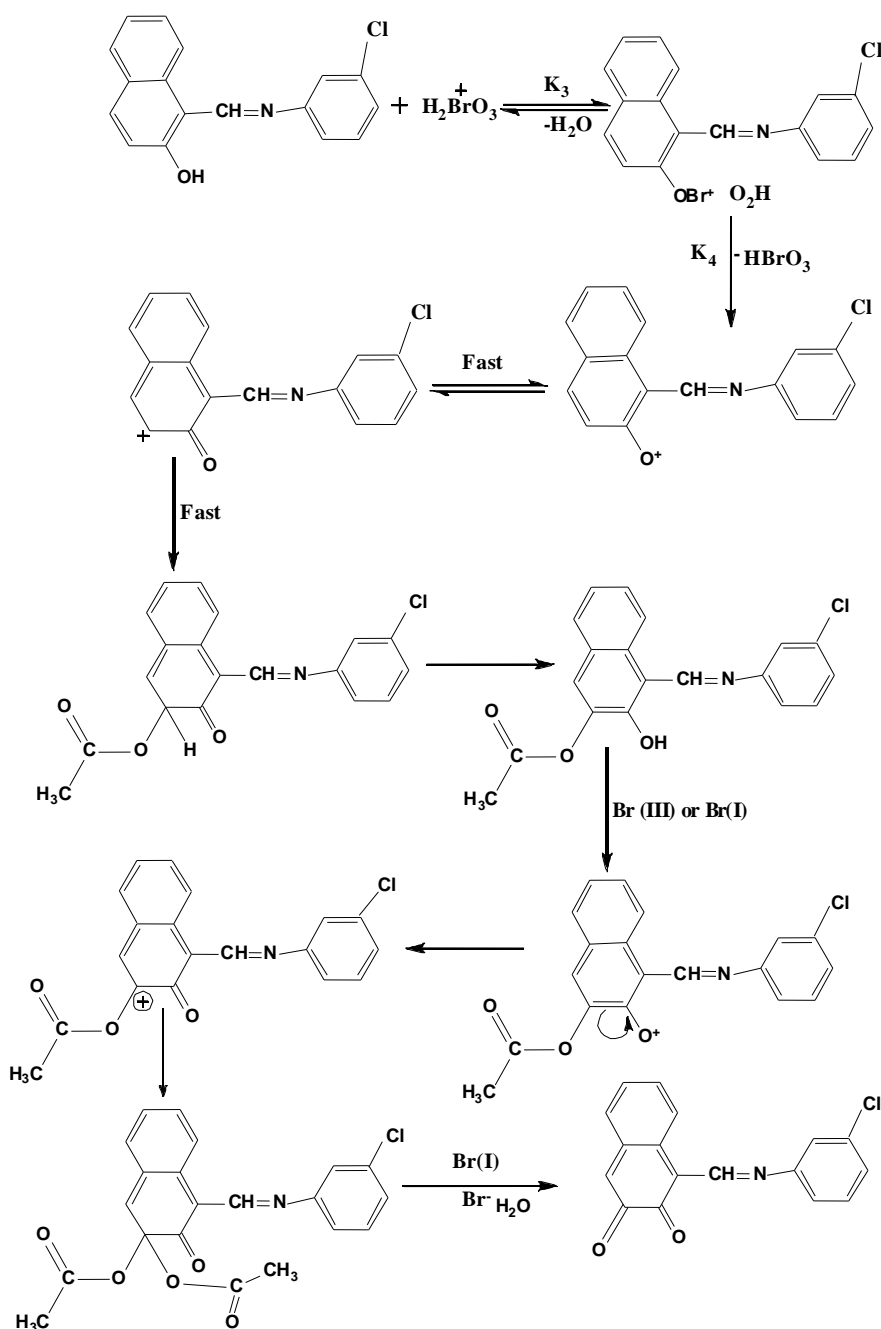
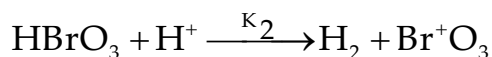
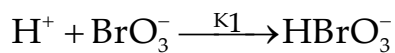
Temperature K	$k_1 \times 10^{-2}$ min^{-1}	ΔE kcal /mol ⁻¹	ΔH kcal	ΔG kcal/mol	ΔS e.u.	A $\text{sec}^{-1} \times 10^5$
308	0.8794			23.467	-33.064	8.0960
313	1.2306			23.633	-33.116	7.914
318	1.7229	13.7281	13.2705	23.798	-33.107	7.8342
323	2.4706			23.964	-33.106	8.0223
328	3.4433			24.129	-33.103	8.0723

The overall rate equation obtained is,

$$\frac{-d[\text{BrO}_3^-]}{dt} = \frac{k_1 k_2 k_3 [\text{H}^+][\text{BrO}_3^-][\text{Schiff base}]}{1 + k_2 [\text{Schiff base}]}$$

Mechanism :

Based on the above data, a possible mechanism^[13,14] shown below has been proposed for the oxidation of Schiff base by KBrO₃.



**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 ΔE , ΔH , ΔS , ΔG and frequency factor (A) were determined by the study of temperature effect on the rate constant. Oxidized product is Quinone, it is stable in nature and the confirmation of compound is obtained by TLC.

REFERENCES :

1. Vogel A.I. Textbook of Practical Organic Chemistry, 4th Edn. London : ELBS / Longman Singapore Publisher Group Pvt. Ltd., 1978; 69 p.
2. Vogel A.I. Textbook of Quantitative Inorganic Analysis 3rd Edn. ELBS/Longman Green and Co. Ltd., 1961; 349 p.
3. Natarajan R., Subramanian Venkata N. Indian J. Chemistry, 1979; 17(A) : 257 p.
4. Shrivastava S. and Singh B.J., Indian Chem. Soc. 69, 335 (1992).
5. Srivastava S., Singh B. React Kinet Catal Lett. 1989, 39 : 243 p.
6. Srivastava S., Singh B.J., Indian Chem. Soc. 1988; 65 : 844 p.
7. Srivastava S., Singh B. Oxid. Communication. 1989; 12 : 140 p.
8. Srivastava S., Singh B. Transition Met Chem. 1991; 16 : 466 p.
9. Sukla S.N. and Bajpai C.D., J. Indian Chem. Soc. 57, 952-954 (1980).
10. Margalili B.F., Zolfigol M.A., Bamoniro A. H., Zaghaghi Z. and Hazar A., Acta. Chem. Slov., 50, 563-568 (2003).
11. Prabhu P.S., Ph.D. Thesis, University of Bombay (1986).
12. W. Flaig Cited in H.H. Perkampus, J. Sandemxiah and C. J. Timmous (Eds). U. V. Atlas of Organic Compounds, Vol. 5, Butterworth Publication, London, B 8127 (1971).
13. Natarajan R. and Venkatasubramanian N., Tetrahedron Letters, 57, 5021 (1969).
14. Pol Umesh N., Yamgar R.S. and Dodwad S.S., Asian J. Chem. 9(2), 195-199(1997).