Asian Journal of Chemistry Vol. 9, No. 1 (1997), 58–62

Kinetics and Mechanism of Acid Bromate Oxidation of 2-Hydroxy-1-Naphthalideneanil

UMESH N. POL, RAMESH S. YAMGAR and S.S. DODWAD*
Physical Chemistry Division, The Institute of Science
15, Madam Cama Road, Mumbai-400 032, India

The kinetics of oxidation of the Schiff base, 2-hydroxy-1-naphthalideneanil by potassium bromate in aquo-acetic acid medium has been studied. The reaction is found to obey the first order rate equation. The study is carried out at five different temperatures. The study is also undertaken by change in the concentration of oxidant, change in the concentration of $HClO_4$ and change in 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.

INTRODUCTION

Potassium bromate has been widely used as an oxidant in the oxidation of many organic compounds in acid medium[1–6]. The present communication deals with the kinetic study of acid bromate oxidation of 2-hydroxy-1-naphthalideneanil.

EXPERIMENTAL

All the materials used were of AR grade. The Schiff base was prepared by refluxing 2-hydroxy-1-naphthaldehyde and aniline in ethanol for 2–3 h and purified by recrystallization[7]. The stock solutions of $KBrO_3$ in 50% v/v in acetic acid-water mixture and sodium thiosulphate were prepared and standardised by known methods.

The reaction was followed by removing aliquots of reaction mixture at known intervals of time and quenching the reaction by adding excess of KI solution. The unused bromate reacts with KI in acid solution in accordance with the equation

$$BrO_3^- + 6I^- + 6H^+ \rightleftarrows Br^- + 3I_2 + 3H_2O$$

The liberated iodine was estimated by titrating against standard thiosulphate solution using starch as an indicator. The end product or oxidised product of the reaction is analysed on the basis of qualitative tests and its IR spectra.

Dependence of the reaction on oxidant and substrate (Schiff base)

In order to determine the order of reaction with respect to the oxidant, the reaction was carried out at different initial concentrations of oxidant and at fixed concentration of other reactants. The ionic strength of the reaction is kept constant by the addition of potassium chloride. The K_1 values (average) are given in Table-1 and it is seen that the reaction is independent of potassium bromate concentration. This clearly shows that the reaction is of first order with respect to the change in concentration of oxidant.

TABLE-1
EFFECT OF CHANGE IN CONCENTRATION OF OXIDANT ON THE REACTION RATE

Solvent = HOAc (50%), [Schiff base] = 5×10^{-3} M, [$HClO_4$] = 0.5×10^{-1} M, $\mu = 0.05$

[Oxidant] $\times 10^{-4}$ M	3.0	5.0	7.0	9.0	11.0
$K_1 \times 10^{-2}$ min^{-1}	0.9307	0.8868	0.9504	1.0611	1.0412

To study the reaction of various concentrations of Schiff base, it is carried out at six different concentrations of Schiff base by keeping all other parameters constant. The average K_1 values are determined and tabulated in Table-2. Plot of $1/K_1$ *vs.* 1/[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. 1.

TABLE-2
EFFECT OF CHANGE IN CONCENTRATION OF SCHIFF BASE ON THE REACTION RATE

Solvent = HOAc (50%), [Oxidant] = 5×10^{-3} M, [$HClO_4$] = 0.5×10^{-1} M, $\mu = 0.05$

[Schiff base] $\times 10^{-3}$ M	3.0	4.0	5.0	6.0	7.0	8.0
$K_1 \times 10^{-2}$ min^{-1}	0.4893	0.6936	0.8868	1.1987	1.5793	2.0239

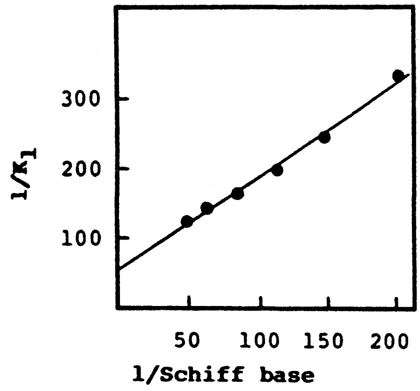


Fig. 1 Plot of $1/k_1$ vs. 1/substrate

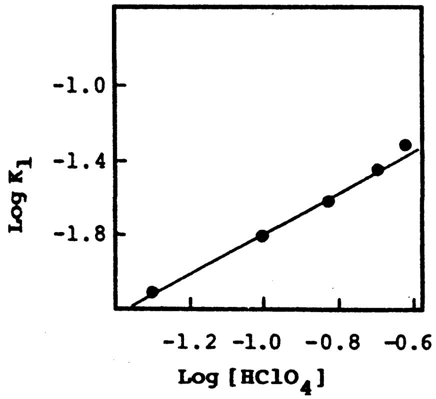


Fig. 2 Plot of log k_1 vs. log [$HClO_4$]

Effect of [$HClO_4$]

The reaction was studied at four different concentration 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 [$HClO_4$] is shown in Fig. 2.

TABLE-3

EFFECT OF VARYING [$HClO_4$] ON THE REACTION RATES

Solvent = HOAc (50%), [Schiff base] = 5×10^{-3} M, [Oxidant] = 0.5×10^{-1} M, $\mu = 0.05$

[$HClO_4$] × 10^{-1} M	0.5	1.0	1.5	2.0	2.5
$K_1 \times 10^{-2}$ min^{-1}	0.8868	1.5848	2.4644	3.5790	4.9987

The straight line with slope = 1.05 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 increase with the increasing concentration of perchloric acid. Therefore it seems that H^+ ion is playing the role of catalyst in the reaction.

Effect of Ionic Strengths

In order to study the effect of ionic strength on the reaction rate, the reaction was carried out at four different ionic strengths. The ionic strength of the reaction mixture is maintained by the addition of requisite quantities of KCl while the concentration of other reactants kept unchanged. The results are tabulated in Table-4 and it indicates that K_1 values decrease with the increase in ionic strength. Thus the retarding effect is observed on addition of KCl salt. A plot of log K_1 against $\sqrt{\mu}$ is shown in Fig 3. The plot obtained is a straight line with negative slope of 0.50 which indicates that 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%), [Schiff base] = 5×10^{-3} M,
[Oxidant] = 5×10^{-1} M, [$HClO_4$] = 0.5×10^{-1} M

μ	0.01	0.02	0.03	0.04
$K_1 \times 10^{-2}$ min^{-1}	2.2918	1.8533	1.4874	1.1766

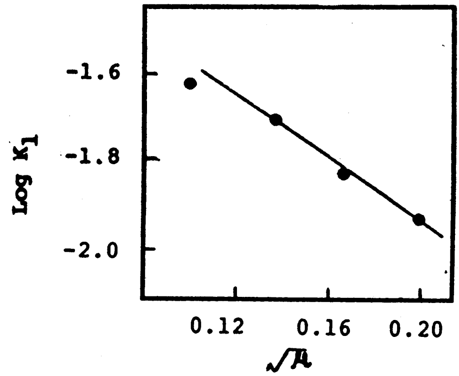


Fig. 3 Plot of log K_1 vs. $\sqrt{\mu}$

Influence of temperature on reaction rate

The rate measurements have been made at five different temperatures and thermodynamic parameters *viz.* ΔE^*, ΔH^* and ΔS^* are calculated. The frequency factor (A) has also been determined 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 the reaction. This is confirmed by recording IR spectra of oxidised product and the qualitative tests[8].

TABLE-5
EFFECT OF TEMPERATURE ON RATE CONSTANT

Solvent = HOAc (50%), [Schiff base] = 5×10^{-3} M,
[Oxidant] = 5×10^{-4} M, $\mu = 0.05$, [$HClO_4$] = 0.5×10^{-1} M

Temp K	$K_1 \times 10^{-2}$ min^{-1}	ΔE kcal mol^{-1}	ΔH kcal	ΔG kcal	ΔS e.u.	A sec
308	0.5384			23.7432	-21.4109	7.594×10^8
313	0.8868			23.8500	-21.3410	7.775×10^8
318	1.4152	18.2169	17.1602	23.9567	-21.3049	7.829×10^8
323	2.1774			24.0638	-21.3148	7.710×10^8
328	3.0346			24.1700	-21.4954	6.970×10^8

The overall rate equation obtained is

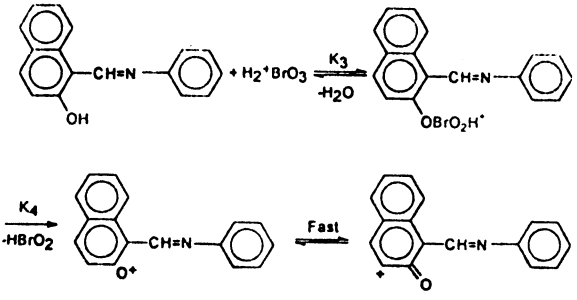
$$\frac{-d[BrO_3^-]}{dt} = \frac{K_1K_2K_3[H^+][BrO_3^-][\text{Schiff base}]}{1 + K_2\,(\text{Schiff base}]}$$

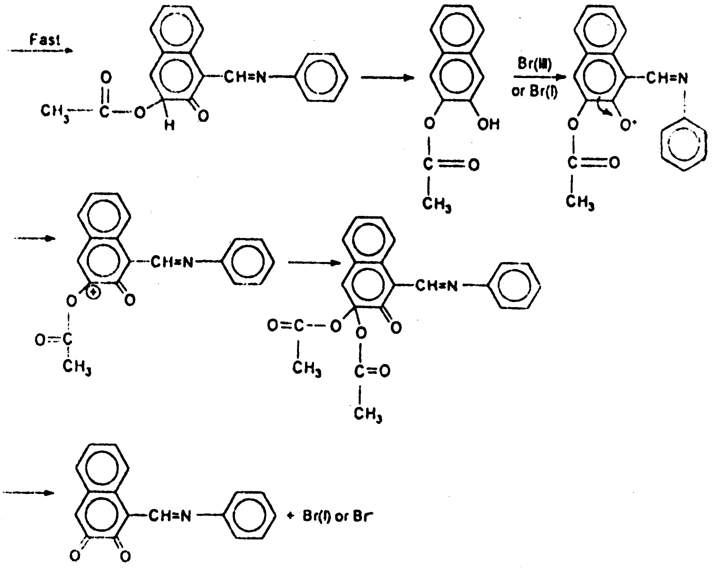
Mechanism

Based on the above data, a possible mechanism[4] shown below has been proposed for the oxidation of Schiff base by $KBrO_3$..

$$H^+ + BrO_3^- \xrightarrow{K_1} HBrO_3$$

$$HBrO_3 + H^+ \xrightarrow{K_2} H_2 + BrO_3^-$$





REFERENCES

1. D.N. Sharma, *Indian J. Chem.*, **11**, 756 (1973).
2. R. Natarajan and N. Venkatasubramanian, *Indian J. Chem.*, **17A**, 257 (1979).
3. Vijayalaxmi and E.V. Sundaram., *J. Indian Chem. Soc.*, **55**, 567 (1978).
4. ________, *Indian J. Chem.*, **15A**, 612 (1977).
5. R. Natarajan and N. Venkatasubramanian, *Tetrahedron Lett.*, **57**, 5021 (1969).
6. N. Krishnamurthy, C.H. Sanjeeva Reddy and E.V. Sundaram, *Indian J. Chem.*, **28A**, 288 (1989).
7. P.S. Prabhu, Ph.D. Thesis, University of Bombay (1986).
8. 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).

(*Received*: 8 May 1996; *Accepted*: 29 August 1996) AJC-1153