

# Physical Kinetic Study of Some Substituted Alcohols with N -Bromophthalimide in Aqueous Acetic Acid Medium

Reeta Patel<sup>1</sup>, Dr. P.K.Singh<sup>2</sup>, S. S. Saket<sup>3</sup>

<sup>1,2</sup>Department of Chemistry, S.G.S. Govt. P.G. (Autonomous) College, Sidhi (M.P)

<sup>3</sup>Department of Chemistry, Govt. Girls P. G. College, Satna(M.P.)

## ABSTRACT

Kinetic study of some substituted alcohols with N-bromophthalimide (NBP) in aqueous acetic acid medium .The oxidation kinetics of alcohols with NBP shows a first order dependence on NBP and fractional order on substituted alcohols. The variation of ionic strength,  $H^+$  and phthalimide (reaction product) have no significant effect on reaction rate. Effect of varying dielectric constant of medium on the rate has been studied. Activation parameters for the reaction have been evaluated from Arrhenius plot by studying the reaction at different temperature.

**Keywords:** Kinetics, Substituted Alcohol, N-Bromophthalimide. Parameter

## INTRODUCTION

The kinetics of oxidation of substituted benzyl alcohols by organic halo chromates such as Quinolinium dichromate[1], Imidazolium Dichromate[2], Benzyl triethylammonium Chlorochromate[3], Quinoxalinium bromochromate[4], Benzimidazolium Fluorochromate[5], Pyridinium bromochromate[6], Tetrabutyl ammonium tribromide[7], etc. have been studied earlier. A number of reports on kinetic studies of oxidation of benzyl alcohols with variety of N-halo compounds such as N-bromosuccinimide[8], N-bromosaccharin[9], N-bromoacetamide[10] and Chloramine-T[11] as oxidants have been reported. N-bromophthalimide (NBP) is a potential oxidizing agent[12-14] and it seems that there are no reports about the kinetics of oxidation of benzyl alcohols by NBP. The present work reports kinetics and mechanism of oxidation of benzyl alcohols by N-bromophthalimide in 50% acetic acid.

## EXPERIMENTAL SECTION

### Materials:

The oxidant NBP (Aldrich sample) was used. Acetic acid (A.R.grade) was purified by the literature procedure. The standard solutions of substituted benzyl alcohols were prepared in acetic acid.

Double distilled water was employed in all kinetic runs. To prevent photochemical effect, the freshly prepared solution of NBP was stored in an amber colored bottle and its strength was checked iodometrically[using 1% solution of freshly prepared starch as an indicator.

### Preparation of substrate solution

Three substrate viz.,  $\alpha$  phenyl propyl alcohol,  $\beta$  phenyl methanol,  $\alpha$  phenyl ethanol [some substituted alcohols] of analytical grade have been used as such obtained after distillation. The solution was prepared of desired concentration by calculating their molecular weight and specific gravity.

### Preparation of $CuSO_4$ , $K_2Cr_2O_7$ and $COOH$

The standard solution of  $CuSO_4 \cdot 5H_2O$  (B.D.H) sample by dissolving its required amount of in distilled water followed by addition of 2-3 drops of glacial acetic acid. The standard solution of  $K_2Cr_2O_7$  was prepared by dissolving its weighted quantity in distilled water as standard solution.

The standard solution of oxalic acid  $(COOH)_2 \cdot 2H_2O$  AR sample was prepared by dissolving its definite amount in distilled water.

**Preparation of H<sub>2</sub>SO<sub>4</sub> solution**

Stock solution of H<sub>2</sub>SO<sub>4</sub> of appropriate strength was prepared by diluting the calculated volume (from specific gravity) of acid with distilled water and finally its concentration was determined by titrating it against standard solution hydroxide solution using phenolphthalein as an indicator.

**Kinetic Measurements:**

All kinetic measurements were made under pseudo first order conditions, by keeping large excess of benzyl alcohols over oxidant NBP. Mixture containing requisite amounts of solutions of benzyl alcohol, Hg(OAc)<sub>2</sub> in 50% acetic acid were equilibrated at 303K. To this mixture was added a measured amount of pre-equilibrated (303K) standard solution of NBP.

To maintain the desired temperature (within + 0.1o C) the reaction mixture was kept in a thermostated water bath and the progress of the reaction was monitored spectrophotometrically by withdrawing aliquots of the reaction mixture at regular time of intervals. The reaction rate was monitored at λ<sub>max</sub> of NBP by measuring the absorbance of the unreacted NBP at the respective time. All reactions were carried out in flask blackened outside to prevent any photochemical reaction.

**Typical kinetic run for the influence of concentration of oxidant, N-bromophthalimide (NBP) on reaction velocity**

[alpha phenyl propyl alcohol] = 2.50 × 10<sup>-2</sup> (mol dm<sup>-3</sup>);  
 [NBP] = 2.50 × 10<sup>-3</sup> (mol dm<sup>-3</sup>);  
 [H<sup>+</sup>] = 1.00 × 10<sup>-3</sup> (mol dm<sup>-3</sup>);  
 HOAc-H<sub>2</sub>O = 30% (v/v);  
 Temp. = 313 K

**Vol. of  $\frac{N}{1000}$  hypo (ml)**

**Table: 1**

S. No.	Time (sec)		10 <sup>4</sup> k <sub>1</sub> (s <sup>-1</sup> )
	0	5.0	-
	600	3.95	3.92
	1200	3.20	3.71
	1800	2.50	3.85
	2400	1.95	3.92
	3000	1.55	3.90
	3600	1.25	3.85
	4200	1.00	3.83

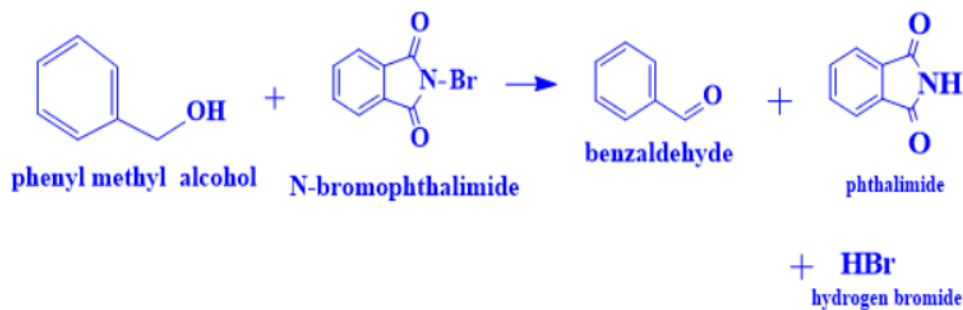
Average k<sub>1</sub> = 3.85 × 10<sup>-4</sup> (s<sup>-1</sup>), Graphical k<sub>1</sub> = 3.83 × 10<sup>-4</sup> (s<sup>-1</sup>)

**Stoichiometry and Product Analysis:**

Stoichiometry of the reaction was ascertained by equilibrating the reaction mixture containing an excess of NBP over benzyl alcohol and mercuric acetate in 50% acetic acid for 24 hrs. at 30o C. The unreacted oxidant (NBP) was determined by iodometrically.

The estimated amount of unreacted NBP showed that one mole of benzyl alcohol consumes one mole of NBP.

The 1:1 Stoichiometry is represented by following equation.



Benzyl alcohol (0.2 Mole) and NBP (0.4 Mole) were mixed together with mercuric acetate (0.5 Mole) in 50 % aqueous acetic acid (total volume 100 ml). The reaction mixture was set aside for about 24 hrs. to ensure completion of the reaction. It was then evaporated and extracted with ether. The layer was separated and dried.

## RESULT AND DISCUSSION

The kinetics of oxidation of benzyl alcohol by NBP in 50% acetic acid was carried at 303 K under pseudo first order conditions. The reactions were carried out under pseudo first order conditions of [Benzyl alcohol]  $\gg$  [NBP]. The Plot of  $\log [NBP]$  Vs time found to be linear indicating first order dependence of the reaction rate and from the slopes of such plots pseudo first order rate evaluated. Plot of  $\log k'$  Vs  $\log [Benzyl\ alcohol]$  was linear with slope less than unity for all the benzyl alcohols indicating a fractional order dependence on rate of benzyl alcohol.

### Effect of Hydrogen Ion:

When the dependence of the reaction rate on hydrogen ion concentration was carried at different initial concentrations of  $H_2SO_4$ , no significant change in rate constant was observed. There was marginal change in rate constant with variation of hydrogen ion concentration. Protonated NBP is not involved in reaction mechanism which may be attributed to the negligible effect of variation of  $H_2SO_4$  on the reaction rate.

### Effect of Ionic Strength:

The ionic strength of the reaction was varied by the addition of the influence of ionic strength on the reaction rate was studied. It was found that the ionic strength of the reaction medium has negligible effect on the reaction rate.

### Mechanism and Derivation of Rate Law:

Based upon the experimental observations, the most probable mechanism and rate expression can be derived applying steady state approximation. The kinetics results suggest the possibility of formation of binary complex involving oxidant and substrate is strongly favored.

However, such a binary complex is undergoes redox decomposition to the end of products intramolecularly. Such complex formation was also proved kinetically by the non-zero intercept of the double reciprocal plot of  $1/k'$  Vs  $1/[S]$ . Evidence is also provided by the fractional order found in substrate.

### Effect of Temperature:

The rate of oxidation was determined at different temperatures and the Arrhenius plots of  $\log k$  versus  $1/T$  were all linear. From these plots, the activation and thermodynamic parameter for equilibrium step and rate  $\Delta A$  determining step of the scheme was evaluated. The observed  $\#$  values are large and negative. It may be interpreted that the fraction of collisions become more stringent and decomposition of activation  $H\Delta$  complex is a quite slow process.  $\#$  indicates that the reactions are enthalpy controlled. Further the constancy  $G\Delta$  in the calculated values of  $\#$  for this oxidation reaction indicates that the same type of the reaction mechanism could be operative for the reaction. Arrhenius Plot for Benzyl alcohol .

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