

Chemical Kinetic Study of some Substituted Alcohols with N - Bromophthalimide in Aqueous Acetic acid medium

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ABSTRACT

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

kinetic investigations of oxidation of p-substituted benzyl alcohols by n-bromophthalimide (NBP) in aqueous acetic acid medium . kinetics of benzyl alcohols by NBP shows a first order dependence on NBP and fractional order on benzyl alcohols. the variation of ionic strength, H^+ and phthalimide 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.

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], nbromoacetamide[10]

EXPERIMENTAL

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.

Methods:- Thesis includes the contents of preparation of various solution of reagents such as oxidant, substrates etc. required in kinetic studies of the oxidation of unsaturated acids by NBP.

N-bromophthalimide:- It was prepared by passing slow stream of bromine gas into a suspension of phthalimide in presence of sodium hydroxide and acetic acid at low temperature. The precipitated NBP was filtered off; the process of repeatedly passing of Br_2 gas was stopped when no more precipitate is obtained. It is recrystallised from carbon tetra chloride and hexan the solution of N-bromophthalimide was prepared by dissolving its weighted quantity in 100% acetic acid (B.D.H.) and kept in black paper wrapped bottle to save it from the action of diffused day light which alters appreciably its concentration.

The standardization of N-bromophthalimide was carried by taking 1 ml of its solution in conical flask to which 10ml of 2% KI solution followed by 5 ml of 2N H₂SO₄. The liberated iodine was titrated against standard Na₂S₂O₃ solution using starch solution as an indicator iodometrically.²

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.

Kinetic Measurements:

All kinetic measurements were made under pseudo first order conditions, by keeping large excess of substituted alcohols over oxidant NBP. Mixture containing requisite amounts of solutions of substituted alcohol 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 mixture at regular time of intervals. The reaction rate was monitored at λ_{max} of NBP by measuring the absorbance of the unreacted NBP at the respective time.

Typical Kinetic Runs- Three substrate viz., alpha phenyl propyl alcohol, beta phenyl methanol, alpha phenyl ethanol [some substituted alcohols] by N-bromophthalimide (NBP) have been studied in aqueous acetic acid medium. The rate constant was determined by employing graphical, integration and Oswald's dilution methods. The typical kinetics runs pertaining to the oxidation of the substrates as representative sets have been mentioned in the following ways :

Table:

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

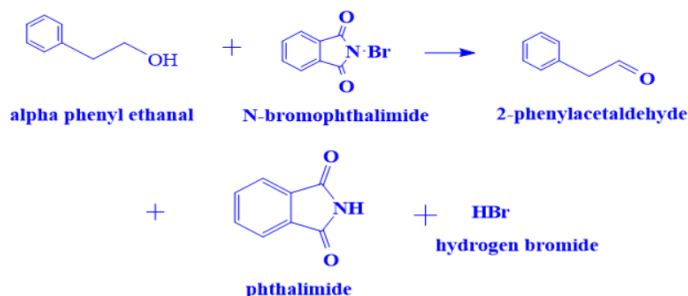
[Alpha phenyl propyl alcohol]	=	2.50 × 10 ⁻² (mol dm ⁻³);
[NBP]	=	2.50 × 10 ⁻³ (mol dm ⁻³);
[H ⁺]	=	1.00 × 10 ⁻³ (mol dm ⁻³);
HOAc-H ₂ O	=	30% (v/v);
Temp.	=	313 K

S. No.	Time (sec)	Vol. of $\frac{N}{1000}$ hypo (ml)	10 ⁴ k ₁ (s ⁻¹)
1.	0	5.0	-
2.	600	3.95	3.92
3.	1200	3.20	3.71
4.	1800	2.50	3.85
5.	2400	1.95	3.92
6.	3000	1.55	3.90
7.	3600	1.25	3.85
8.	4200	1.00	3.83

Average k₁ = 3.85 × 10⁻⁴ (s⁻¹), Graphical k₁ = 3.83 × 10⁻⁴ (s⁻¹)

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 30° 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. 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.



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 $\log [\text{Benzyl alcohol}]$ 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 $NaClO_4$ and 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.

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 Δ 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 HA 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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