



## **Kinetics and Mechanistic Study of Oxidation of 1-Phenylethanols by N-Bromophthalimide in Aqueous Acetic acid**

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### **ABSTRACT**

*Kinetic investigations of oxidation of 1-Phenylethanol and substituted 1-Phenylethanols by N-bromophthalimide (NBP) in aqueous acetic acid medium in presence of mercuric (II) acetate as a scavenger have been studied spectrophotometrically. Oxidation kinetics of 1-Phenylethanols by NBP shows a first order dependence on NBP and fractional order on 1-Phenylethanol. The variation of ionic strength,  $Hg(OAc)_2$ ,  $H^+$  and phthalimide (reaction product) have insignificant effect on reaction rate. Activation parameters for the reaction have been evaluated from Arrhenius plot by studying the reaction at different temperatures. A mechanism involving transfer of hydride ion in rate determining step is suggested.*

**Keywords:** Kinetics, Oxidation, 1-Phenylethanol, N-bromophthalimide.

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### **INTRODUCTION**

The oxidation of alcohols to carbonyl compounds is usually achieved using harmful different reagents [1, 2]. The nature of N-halo compounds is due to their ability to act as sources of halonium ions, hypo halite species and nitrogen anions, which act as both bases and nucleophiles. They have been widely used as oxidizing and halogenating reagents in organic compounds [3-5]. N-bromophthalimide (NBP) is a potential oxidizing agent and has some definite advantages over other N-halogeno oxidants, which has been extensively used in the estimation of organic substrates [6-10].

The kinetics and mechanistic investigations of the oxidation of substituted phenylethanols by various oxidizing agents have been studied earlier [11-18]. It seems that there are no reports about the kinetics of oxidation of 1-phenylethanol by NBP spectrophotometrically. The present work reports kinetics and mechanism of oxidation of 1-phenylethanols by N-bromophthalimide in 50 % acetic acid.

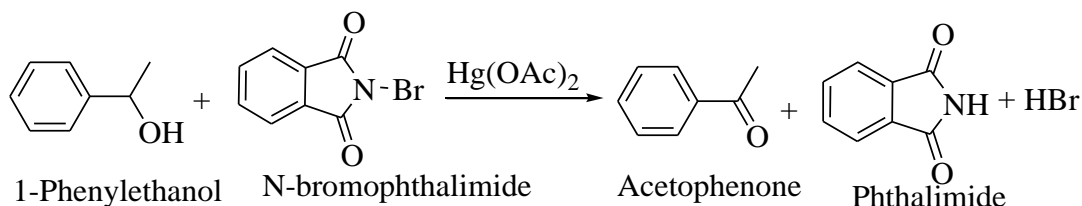
### **MATERIALS AND METHODS**

**Materials:** The oxidant NBP (Aldrich sample) was used. Acetic acid (A.R.grade) was purified by the literature procedure. The standard solution of 1-Phenylethanol (Fluka) was 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.

**Kinetic measurements:** In the present kinetic investigations all experiments were carried out in absence of added mineral acids. All the reactions were carried out in a thermostated water bath adjusted to the desired temperature. The calculated quantities of standard solutions of substrate and mercuric acetate were taken in hard tube by using graduated pipette. The volume 10 mL was adjusted by adding required amount of 50% AcOH. The calculated quantity of standard solution of oxidant (NBP) was taken in another tube by using graduated pipette and the volume 10 mL was adjusted by adding required amount of 50% AcOH. Both the tubes were thermostated at least for 15 min. The reaction was initiated by adding the thermostated solutions from both the flasks. The time of mixing of the solution was recorded as zero time. The maximum absorption ( $\lambda_{\max}$ ) of NBP found to be 284 nm. The absorbance values of the reaction aliquots are then measured throughout the present work at this wavelength. The reaction rate was monitored at  $\lambda_{\max}$  by measuring the absorbance of the unreacted NBP at the respective time. The decrease in absorbance of reaction mixture indicates the amount of NBP undergoing the reaction. The reaction rate was studied upto 70-75% completion of the reaction. A graph of  $1 + \log \text{abs. (O.D.)}$  v/s time was plotted and Rate constant was determined. According to linear least square method graphs were plotted. The absorbance was plotted against time for different initial concentration of NBP.

**Stoichiometry and Product Analysis of 1-Phenylethanol:** Stoichiometry of the reaction was ascertained by equilibrating the reaction mixture containing an excess of NBP over 1-Phenylethanol and mercuric acetate in 50 % acetic acid for 24 h. at 30° C. The unreacted oxidant (NBP) was determined and the estimated amount of unreacted NBP showed that one mole of 1-Phenylethanol consumes one mole of NBP.



1-Phenylethanol (0.2 mol) and NBP (0.4 mol) were mixed together with mercuric acetate (0.5 mol) in 50 % aqueous acetic acid (total volume 100 mL). The reaction mixture was set aside for about 24 h. to ensure completion of the reaction. It was then evaporated and extracted with ether. The layer was separated and dried. The residue was confirmed as Acetophenone by b. p., TLC, HPLC and 2, 4-DNP derivative. Analysis confirmed the formation of Acetophenone in quantitative yield.

## RESULTS AND DISCUSSION

The kinetics of oxidation of 1-Phenylethanol by NBP in 50 % acetic acid was carried at 303 K under pseudo first order conditions. The concentration of  $\text{Hg(OAc)}_2$  was kept higher than NBP. The Plot of  $\log [\text{NBP}]$  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. The rate constant ( $k'$ ) have been found to increase with increase in the concentration of 1-Phenylethanol and plot of  $\log k'$  Vs  $\log [1\text{-Phenylethanol}]$  was linear with slope less than unity for 1-Phenylethanol indicating a fractional order dependence on rate of 1-Phenylethanol (Table 1).

The dependence of the reaction rate on hydrogen ion concentration has been investigated at different initial concentrations of  $\text{H}_2\text{SO}_4$ . The variation of hydrogen ion concentration has not affected the rate; it may be attributed to the absence of any protonation equilibrium with the reactant species. In order to see the effect

of ionic strength of the medium on the rate of oxidation reactions were studied in the presence of an electrolyte like sodium perchlorate and it was observed that the ionic strength of the reaction medium has negligible effect on the reaction rate. This may presumably be due to the attack of an ion on a neutral molecule in the rate determining step.

**Table 1.** Effect of variation of reactants on pseudo order rate constant  $k'$  at 303K

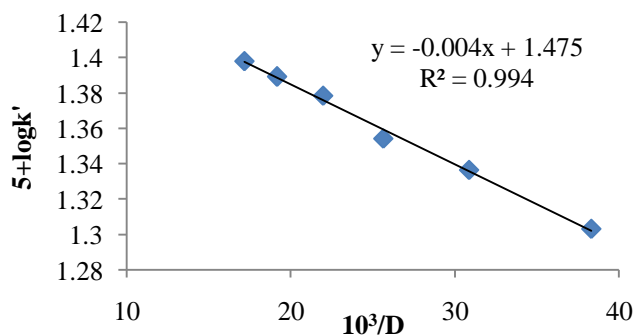
Hg(OAc) <sub>2</sub> =2.00x10 <sup>3</sup> (mol dm <sup>-3</sup> )		50% AcOH medium
10 <sup>2</sup> [1-Phenylethanol] (mol dm <sup>-3</sup> )	10 <sup>3</sup> [NBP] (mol dm <sup>-3</sup> )	$k' \times 10^4$ (s <sup>-1</sup> )
1.00	1.00	2.26
2.00	1.00	3.05
3.00	1.00	3.62
4.00	1.00	4.31
5.00	1.00	4.88
6.00	1.00	5.13
1.00	1.00	2.26
1.00	2.00	4.58
1.00	3.00	7.15
1.00	4.00	10.12
1.00	5.00	12.34
1.00	6.00	14.45

To ascertain that there is no interaction between Hg(OAc)<sub>2</sub> ions and 1-Phenylethanol. The concentration effect of mercury (II) acetate in our present study showed negligible effect on the reaction rate proves that it did not influence the reaction in any way other than fixing bromide ion during the course of reaction and avoiding the oxidation of the latter to molecule bromine.

It is observed that the variation of Phthalimide, one of the products of oxidation, has negligible effect on the rate of reaction. The reaction neither induces polymerization nor retards the reaction rate by variation of acrylonitrile, which may be attributed to the inertness shown by free radicals. A free scavenger rules out the possibility of free radical formation, therefore, the reaction proceeds with two electron transfers.

**Effect of Solvent Composition:** The effect of changing solvent composition on the reaction rate was studied by varying concentration of acetic acid from 20-70 %. The rate constants suggest that the rate of reaction decreases with increasing acetic acid content of the solvent mixture. This observation helps up in picturing the reaction events. The plot of  $\log k'$  Vs  $1/D$  was found to be linear with negative slope (figure 1) indicating the involvement of two dipoles or a negative ion – dipole reaction.

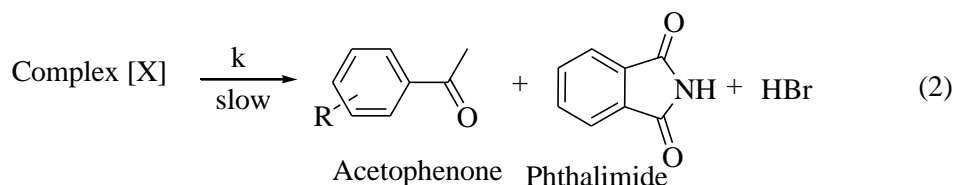
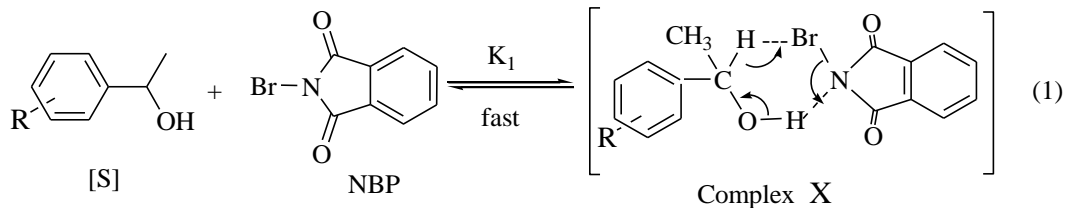
This reveals that there is formation of a charge separated complex in the rate limiting step which is in agreement with Amis [19]. A plot of  $\log k'$  versus  $(D-1/2D+1)$  has been found to be linear (figure not shown) in accordance with Kirkwood [20] theory of dipole – dipole type reaction.



**Fig. 1.** Amis Plot

**Reactive Species and Mechanism:** Earlier reports reveal that NBP, N-bromosuccinimide and N-bromosaccharin are stable oxidizing and brominating agents and behave in a similar way. Free NBP is the probable oxidizing species under the present experimental condition [21].

**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.



$$\frac{-d[\text{NBP}]}{dt} = \text{rate} = \frac{kK_1[\text{S}][\text{NBP}]}{1+K_1[\text{S}]} \quad (3)$$

$$k' = \frac{kK_1[\text{S}]}{1+K_1[\text{S}]} \quad (4)$$

Reciprocal of eq<sup>n</sup> (4) gives,

$$\frac{1}{k'} = \frac{1}{kK_1[\text{S}]} + \frac{1}{k} \quad (5)$$

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  $1/[\text{S}]$ . Evidence is also provided by the fractional order found in substrate. The spectral evidence for complex formation between oxidant and substrate was obtained from UV-Vis spectra of the mixture. One sharp intense peak for mixture indicates formation of complex. As per double reciprocal plot of  $1/k'$  Vs  $1/[\text{S}]$  eq<sup>n</sup> (5), the decomposition rate constant  $k$  and formation constant  $K_1$  was find out (Table 2).

**Table 2.** Decomposition rate constant ( $k$ ), formation constant ( $K_1$ ) and Activation parameters of substituted 1-Phenylethanols at 303K.

Substituent x	$k \times 10^4$ ( $\text{s}^{-1}$ )	$K_1$ ( $\text{dm}^3\text{mol}^{-1}$ )	$E_a$ $\text{KJmol}^{-1}$	$\Delta H^\ddagger$ $\text{KJmol}^{-1}$	$\Delta G^\ddagger$ $\text{KJmol}^{-1}$	$\Delta S^\ddagger$ $\text{JK}^{-1}\text{mol}^{-1}$
4-OCH <sub>3</sub>	11.56	79.55	21.58	19.06	75.18	-248.08
4-CH <sub>3</sub>	9.14	83.81	22.48	19.96	75.17	-244.72
H	6.46	52.81	34.80	32.89	75.27	-248.30
4-Br	7.79	77.94	22.00	19.48	75.23	-248.23
4-Cl	6.12	61.16	37.15	34.63	75.28	-248.34
4-NO <sub>2</sub>	6.39	63.93	18.26	15.74	75.25	-248.32

**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 (figure 2). From these plots, the activation and thermodynamic parameter for equilibrium step and rate determining step of the scheme was evaluated (Table 2).

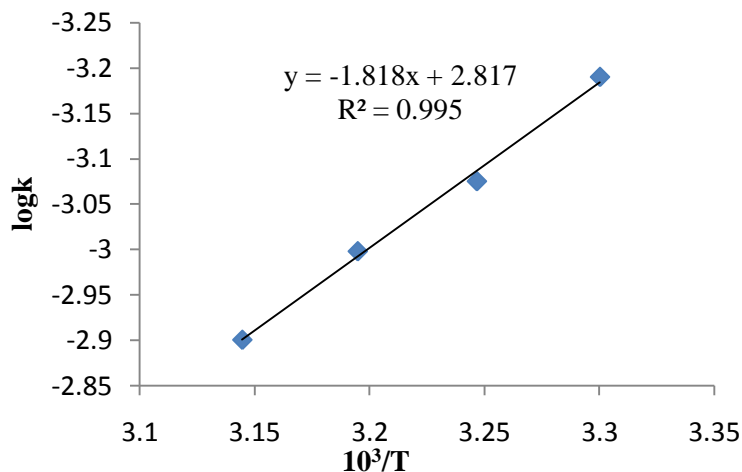
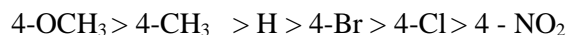


Fig. 2. (Plot of  $1/T$  Vs  $\log k$ ); Arrhenius plot for 1-Phenylethanol

The relatively small value of  $\Delta H^\ddagger$  and the negative  $\Delta S^\ddagger$  values are consistent with the reactions which generally proceed through highly organized transition state. The negative values of entropy of activation also indicate that the reaction involves the transfer of electron between ions of like charges. Moderate values of  $\Delta H^\ddagger$  and entropy of activation  $\Delta S^\ddagger$  indicates outer sphere nature of the mechanism. Further constancy in the calculated values of  $\Delta G^\ddagger$  for these oxidation reactions indicates that the same type of reaction mechanism could be operative for the oxidation reactions.

**Effect of Substituent:** The oxidation of 1-phenylethanol and substituted 1-phenylethanols by NBP were carried out in the temperature range 303–318K. The observed rate constants found to be increase with temperature for all the compounds. The rate of reaction is accelerated by electron donating substituents which help delocalise this forming positive charge in the intermediate complex and correspondingly retarded by electron withdrawing substituents. The introduction of electron releasing group caused an increase in the rate of oxidation, whereas electron withdrawing groups caused a decrease in their rates. The major result of electronic effect of substituents is to stabilize or destabilize the transition state. Thus compounds with electron donating substituents 4-OCH<sub>3</sub>, 4-CH<sub>3</sub> show an enhanced rate of reaction and those with electron-withdrawing -NO<sub>2</sub>, -Cl, -Br substituents are least reactive. The order of reactivity is,



The Hammett's plot of  $\log k'$  Vs  $\sigma$  is linear with a reaction constant  $\rho = -0.21$  and correlation coefficient  $r^2 = 0.80$ . The negative  $\rho$  values in the reaction indicate the development of positive charge at reaction centre. The rate of reaction is accelerated by electron donating substituents which help delocalise this forming positive charge in the intermediate complex and correspondingly retarded by electron withdrawing substituents.

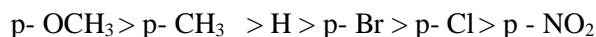
The validity of the isokinetic relation can be tested graphically by plotting Exner plot  $\log k(303)$  Vs  $\log k(313)$ . The isokinetic temperature  $\beta$  evaluated from Exner criterion was found to be 361.7K (slope = 0.794 and  $r^2 = 0.803$ ). Which was more than the experimental temperature; this indicates that the reaction mechanisms in different reactions. It was reported that a linear relationship exists between enthalpies and entropies of activation of a series of related reactions.

## APPLICATIONS

The present work reports kinetics and mechanism of oxidation of 1-phenylethanols by N-bromophthalimide in 50 % acetic acid.

## CONCLUSIONS

Kinetic study of oxidation of 1-Phenylethanols by NBP in 50% acetic acid medium shows first order dependence on NBP and fractional order on 1-Phenylethanol. Mercuric (II) acetate acts as a scavenger and showed negligible effect on the reaction rate. Free NBP is the probable oxidizing species under the present experimental condition. The order of reactivity of different 1-Phenylethanols with [NBP] is,



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