Mechanistic Aspects of Oxidation of 1-Phenylethanol by N-Bromophthalimide in Aqueous Acetic acid – A Kinetic Study

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Abstract: Kinetic investigations of oxidation of 1-Phenylethanol by N-bromophthalimide (NBP) in aqueous acetic acid medium in presence of mercuric (II) acetate as a scavenger have been studied. In absence of mineral acids, the oxidation kinetics of 1-Phenylethanol 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.
Key Words: Kinetics, Oxidation, 1-Phenylethanol, N-bromophthalimide.

Introduction:

Oxidation is a fundamental transformation in organic synthesis and there are numerous methods reported in the literature[1]. The oxidation of alcohols to carbonyl compounds is one of the most important reactions in synthetic organic chemistry and it is usually achieved using harmful different reagents[2]. The conversion of primary and secondary alcohols to the corresponding carbonyl compounds is essential for the preparation of many synthetic intermediates in organic chemistry[3]. The versatile 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[4-7]. 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[8-12].

The kinetics and mechanistic investigations of the oxidation of substituted phenylethanols by various oxidizing agents have been studied earlier[13-18]. It seems that there are no reports about the kinetics of oxidation of 1-Phenylethanol by NBP. The present work reports kinetics and mechanism of oxidation of 1-Phenylethanol by N-Bromophthalimide in 50 % acetic acid.

Experimental:

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[19] using 1 % solution of freshly prepared starch as an indicator.

Kinetic measurements: All kinetic measurements were made under pseudo first order conditions, by keeping large excess of 1-Phenylethanol over oxidant NBP. Mixture containing requisite amounts of solutions of 1-Phenylethanol, $Hg(OAC)_2$ in 50 %

acetic acid were equilibrated at 303 K. To this mixture was added a measured amount of prequilibrated (303 K) standard solution of NBP. To maintain the desired temperature (within $\pm$ 0.1° C) the reaction mixture was kept in a thermostated water bath and the progress of the reaction was monitored iodometrically by withdrawing aliquots of the reaction mixture at regular time of intervals. The pseudo first order rate constants k' were computed from linear least squares plot of -log [a – x] Vs time. Duplicate kinetic runs showed that the rate constants were reproducible to within $\pm$5 %.

Stoichiometry and Product Analysis: 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 hrs. at 30° C. The unreacted oxidant (NBP) was determined by iodometrically. The estimated amount of unreacted NBP showed that one mole of 1-Phenylethanol consumes one mole of NBP.

1-Phenylethanol (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. The residue was confirmed as Acetophenone by m. p., TLC, HPLC and 2, 4-DNP derivative[20]. 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 Hg(OAc)$_2$ was kept higher than 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. 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-Phenylethanol] was linear with slope less than unity for 1-Phenylethanol indicating a fractional order dependence on rate of 1-Phenylethanol (Table 1).
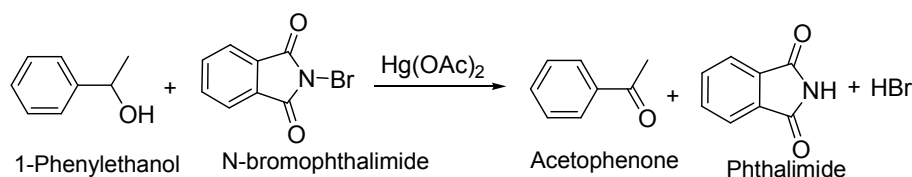

Table 1.   Effect of variation of reactants on pseudo order rate constant k' at 303K
     Hg(OAc)$_2$=2.00x10^3(mol dm^{-3})   50% AcOH medium

10^2[1-Phenylethanol] (mol dm^{-3})	10^3 [NBP] (mol dm^{-3})	k' x 10^4 (s^{-1})
1.00	1.00	2.18
2.00	1.00	3.10
3.00	1.00	3.78
4.00	1.00	4.48
5.00	1.00	5.09
6.00	1.00	5.72
1.00	1.00	2.18
1.00	2.00	4.65
1.00	3.00	7.08
1.00	4.00	10.00
1.00	5.00	11.90
1.00	6.00	14.20

The dependence of the reaction rate on hydrogen ion concentration has been investigated at different initial concentrations of H_2SO_4 and keeping the concentration of the other reactants constant. There was no significant change in rate constant was observed with variation of H^+ ion.

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. This may presumably be due to the attack of an ion on a neutral molecule in the rate determining step[21].

The concentration effect of mercury (II) acetate in our present study showed negligible effect on the reaction rate but found its utility to fix bromide ion during the course of reaction and avoiding the oxidation of the latter to molecule bromine. It is not involve in NBP oxidation, but only act as a scavenger[12d]. Variation of Phthalimide, one of the products of oxidation, had negligible effect on the rate of reaction. The oxidation reactions of 1-Phenylethanol with NBP at different initial concentrations of acrylonitrile have been investigated. The reaction neither induces polymerization nor retards the reaction rate which may be attributed to the inertness shown by free radicals.

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. The plot of log k' Vs 1/D was found to be linear with negative slope (**figure not shown**) 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[21]. A plot of log k' versus (D-1/2D+1) has been found to be linear (**figure not shown**) in accordance with Kirkwood[22] theory of dipole – dipole type reaction.

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. NBP like other similar N-halo imides may exist in various forms in acid medium viz. free NBP, protonated NBP, Br^+, HOBr, H_2O^+Br. In absence of mineral acid, the possibility of Br^+, $NBPH^+$ or H_2OBr^+ being the reactive oxidizing species is ruled out. If HOBr is the reactive oxidizing species, then the rate of reaction should be an inverse function of phthalimide (NHP) which is not observed in the present study. Also the possibility of brominating action of bromide is ruled out due to the presence of mercury (II) acetate which eliminates Br^- through complexation. The rate constants suggest that the rate of reaction decreases with increasing acetic acid content of the solvent mixture. This observation coupled with slight enhancement in the reaction rate with ionic strength of the medium also supports the participation of neutral molecule in the rate determining step. Therefore (free) NBP is the probable oxidizing species under the present experimental condition[23].

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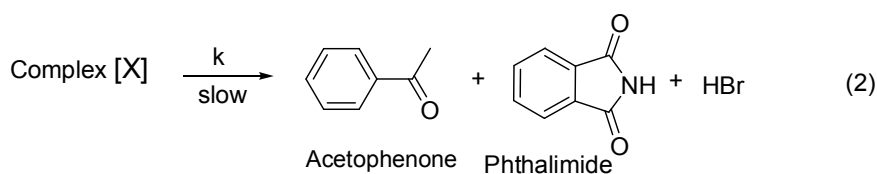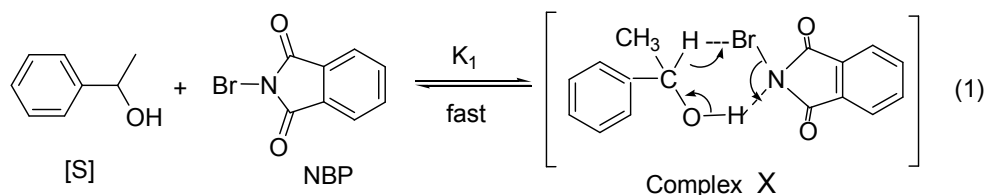
$$\frac{-d[NBP]}{dt} = rate = \frac{kK_1[S][NBP]}{1+K_1[S]} \quad (3)$$

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

Reciprocal of eq[n] (4) gives,

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

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/ [S] (figure 1). 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/ [S] eq[n] (5), the decomposition rate constant k and formation constant K_1 was find out (Table 2).

Table 2. Decomposition rate constant (k) and formation constant (K_1) of 1-Phenylethanol at 303K.

$k \times 10^4$ (s^{-1})				K_1
303K	308K	313K	318K	(dm^{3}mol^{-1})
6.78	8.74	10.49	12.53	46.357

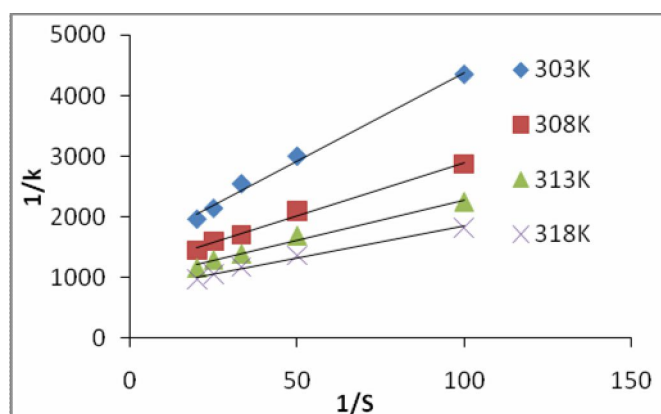**Figure 1. Plot of 1/ [substrate] Vs 1/k' i.e. Double reciprocal plot of 1-Phenylethanol**

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 3). The observed $\Delta S^{\#}$ values are large and negative. It may be interpreted that the fraction of collisions become more stringent and decomposition of activation complex is a quite slow process. $\Delta H^{\#}$ indicates that the reactions are enthalpy controlled. Further the constancy in the calculated values of $\Delta G^{\#}$ for this oxidation reaction indicates that the same type of the reaction mechanism could be operative for the reaction.

Conclusions:

Kinetic study of oxidation of 1-Phenylethanol 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.

Table 3. Activation parameters of 1-Phenylethanol at 303K.

Ea KJmol^{-1}	$\Delta H^{\#}$ KJmol^{-1}	$\Delta G^{\#}$ KJmol^{-1}	$\Delta S^{\#}$ JK^{-1}mol^{-1}	LogA
32.47	29.95	73.69	-243.1	4.86
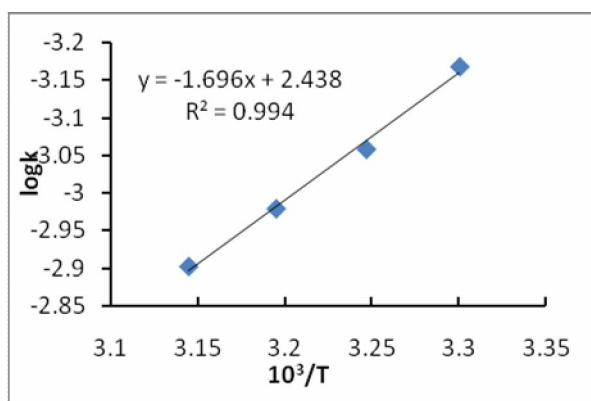
Figure 2. (Plot of 1/T Vs log k); Arrhenius plot for 1-Phenylethanol

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