Kinetics and Mechanistic Study of Phosphotungstic Acid Catalyzed Oxidation of 2-Phenylethanol by N-Bromophthalimide

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Abstract

Kinetic investigations in Keggin-type phosphotungstic acid catalyzed oxidation of 2-Phenylethanol N-Bromophthalimide (NBP) in aqueous acetic acid medium in presence of mercuric (II) acetate as a scavenger have been studied. Oxidation kinetics of 2-Phenylethanol by NBP in presence of Phosphotungstic acid (PTA) shows a first order dependence on NBP and fractional order on 2-Phenylethanol and PTA. 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 temperature. The rate law has been derived on the basis of obtained data.

Key Words: Kinetics, 2-Phenylethanol, N-Bromophthalimide, phosphotungstic acid.
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INTRODUCTION

In the recent years, studies of oxidation of various organic compounds by heteropoly acids and Polyoxometalates especially those with Keggin type structure under homogeneous and heterogeneous reaction conditions [1-9] have attracted considerable attention of the researchers. Literature survey reveals that phosphotungstic acid (PTA) due to its thermal stability, acidity make it efficient and eco-friendly catalyst in oxidation of organic compounds such as aromatic amines[10], aromatic alcohols[11], cyclic alcohols[12], allyl alcohols[13], oximes[14], styrene[15] etc.

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 [16-19]. N-bromophthalimide (NBP) is a potential oxidizing agent and has some definite advantages over

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other N-halogeno oxidants, which has been extensively used in the estimation of organic substrates [20-24].

The kinetics and mechanistic investigations of the oxidation of substituted phenylethanols by various oxidizing agents have been studied earlier [25-31]. It seems that there are no reports about the kinetics of oxidation of 2-Phenylethanol by NBP. The present work reports kinetics and mechanism of PTA catalyzed oxidation of 2-Phenylethanol by N-Bromophthalimide in 50 % acetic acid.

MATERIALS AND METHODS

The oxidant NBP (Aldrich sample) was used. Acetic acid (A.R.grade) was purified by the literature procedure. The standard solutions of 2-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 [32] 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 2-Phenylethanol over oxidant NBP. Mixture containing requisite amounts of solutions of 2-Phenylethanol, $Hg(OAC)_2$ and PTA 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.   Duplicate kinetic runs showed that the rate constants were reproducible to within ± 4 %.

Stoichiometry and Product Analysis
Stoichiometry of the reaction was ascertained by equilibrating the reaction mixture containing an excess of NBP over 2-Phenylethanol, mercuric acetate and phosphotungstic acid 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 2-Phenylethanol consumes one mole of NBP.
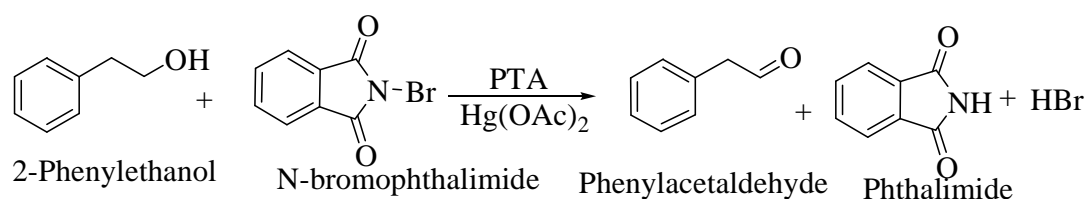
2-Phenylethanol (0.2 Mole) and NBP (0.4 Mole) were mixed together with PTA (0.1 Mole) mercuric acetate (0.5 Mole) in 50 % aqueous acetic acid (total volume 100 ml). The reaction mixture was set aside for about 24 hrs. to ensure completion of the reaction. It was then evaporated and extracted with ether. The layer was separated and dried. The residue was confirmed as Phenylacetaldehyde by m. p., TLC, HPLC and 2, 4-DNP derivative [33]. Analysis confirmed the formation of Phenylacetaldehyde in quantitative yield.

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RESULTS AND DISCUSSION

Order on reactants

The kinetics of oxidation of 2-Phenylethanol by NBP in 50% acetic acid in presence of phosphotungstic acid ($H_3PW_{12}O_{40}$) as a catalyst 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 (${r^2}$ >0.999) 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 2-Phenylethanol and plot of log k' Vs log [2-Phenylethanol] was linear (r^2 = 0.997) with slope less than unity for all the 2-Phenylethanol indicating a fractional order (n = 0.51) dependence on rate of 2-Phenylethanol. (Table 1). The concentration of PTA was varied while the concentration of 2-Phenylethanol, [NBP] and Hg $(OAc)_2$ kept constant. The plot log k' Vs log [PTA] shows slope less than unity indicating fractional order (n = 0.38) dependence of rate on [PTA] (Table 1).

Effect of Hydrogen ion

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.

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[2-Phenylethanol] (mol dm^{-3})	10^3 [NBP] (mol dm^{-3})	10^4[PTA] (mol dm^{-3})	k' x 10^4 (s^{-1})
1.00	1.00	5.00	2.43
2.00	1.00	5.00	3.51
3.00	1.00	5.00	4.18
4.00	1.00	5.00	4.94
5.00	1.00	5.00	5.46
6.00	1.00	5.00	6.25
1.00	1.00	5.00	2.43
1.00	2.00	5.00	5.06
1.00	3.00	5.00	7.45
1.00	4.00	5.00	10.44
1.00	5.00	5.00	12.98
1.00	6.00	5.00	15.15
1.00	1.00	2.50	2.02
1.00	1.00	5.00	2.43
1.00	1.00	7.50	3.04
1.00	1.00	10.00	3.41
1.00	1.00	15.00	3.89

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

Effect of Mercury (II) Acetate

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.

Effect of Product and Free Radical Inhibitor

Variation of Phthalimide, one of the products of oxidation, had negligible effect on the rate of reaction. The oxidation reactions of 2-Phenylethanol with NBP catalyzed by PTA 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 20-80 %. 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 [34]. A plot of log k' versus (D-1/2D+1) has been found to be linear (figure not shown) in accordance with Kirkwood [35] 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.

The proton released during the reaction by PTA do not alter sufficient reaction rate but are responsible for protonation of NBP. 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.

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Keggin structure allows the molecule to hydrate and dehydrate without significant structural changes. Thus in aqueous solutions the heteropolyacids consists of solvate separated ion-pairs in which the protons are hydrated and linked to the anion as a whole and not to a specific centre in heteropolyanion [36]. Baker and others have shown that such water molecules can be replaced by other ligands [37]. The heteropolyanion structure consists of a charged sphere with a large surface area where the acid protons are accommodated in the form of point charges [38]. In the present study the catalyst $[PW_{12}O_{40}]^{3-}$ Keggin anion gets converted into the oxidized form and acts as an outer sphere reagent. Formation of an outer sphere complex by the replacement of one of the water molecules of hydration is more probable transition state. Since probable transition state is less solvated and also in large size it will be more stabilized in the medium. Therefore irrespective of the nature of 2-Phenylethanol the transition state formed would be the same, making the rate of reaction independent of nature of 2-Phenylethanol. Oxidation of substrate by heteropolyanions occurred via overlap of the aromatic p system with the tungstate frame work [39].
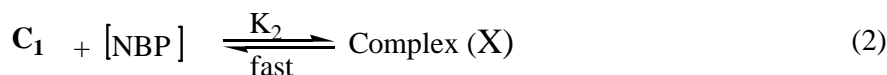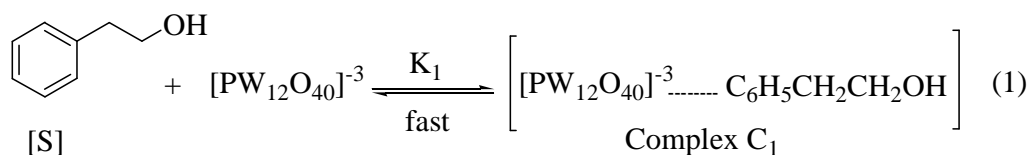
Based upon the experimental observations, the most probable mechanism is as in scheme 1.
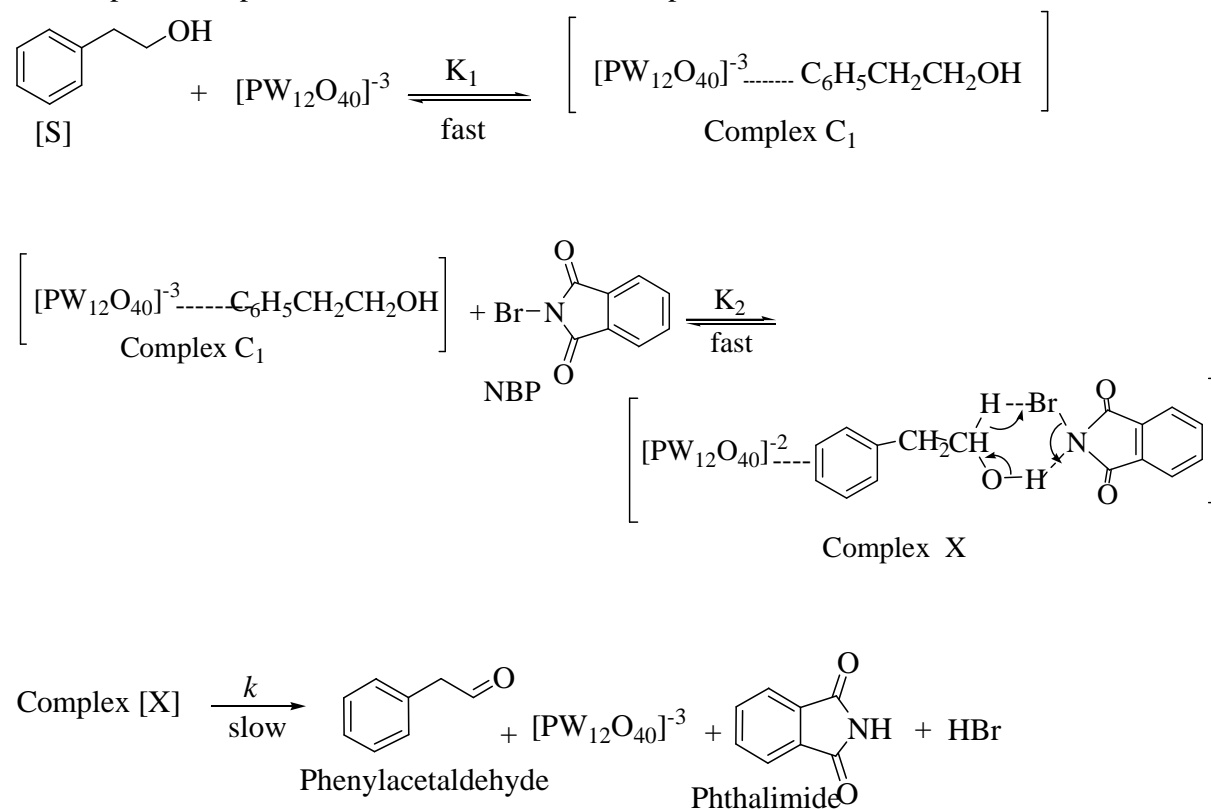
Scheme- 1

Rate Law:

Based on kinetic results and the mechanism proposed, the following rate expression can be derived applying steady state approximation,

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$$C_6H_5CH_2CH_2OH \; [S] \; + \; [PW_{12}O_{40}]^{-3} \xrightleftharpoons[\text{fast}]{K_1} \left[[PW_{12}O_{40}]^{-3} \text{------} C_6H_5CH_2CH_2OH \right] \text{Complex } C_1 \quad (1)$$

$$C_1 \; + \; [NBP] \xrightleftharpoons[\text{fast}]{K_2} \text{Complex (X)} \quad (2)$$

$$\text{Complex } [X] \xrightarrow[\text{slow}]{k} \text{Products} \quad (3)$$

The rate of reaction may be expressed in terms of loss of [NBP] as given below,

$$\frac{-d[NBP]}{dt} = k[x] \quad (4)$$

If $[NBP]_T$ =Total concentration of [NBP], then $[NBP]_T = [NBP] + [X]$

$$[X] = \frac{K_2[C_1][NBP]_T}{1 + K_2[NBP]} \quad (5)$$

But, Rate = $k[x]$ according to equation (4), substituting value of [X] in it, where [S] is substrate concentration, we have,

$$\text{Rate} = \frac{k \, K_2[C_1][NBP]_T}{1 + K_2[NBP]} \quad (6)$$

$$C_1 = \frac{K_1[PTA][S]}{1 + K_1[S]} \quad (7)$$

$$\text{Rate} = \frac{k \, K_2 K_1[PTA][NBP]_T[S]}{(1 + K_1[S])(1 + K_2[NBP])}$$

$$= \frac{k \, K_2 K_1[PTA][NBP]_T[S]}{1 + K_1[S] + K_1 K_2[S][NBP]} \quad (8)$$

The order with respect to [NBP] is one and fractional order with [PTA] and [S]. As [S]> [NBP] Eq^n (8) further reduced to,

$$\frac{-d[NBP]}{dt} = \frac{k \, K_2 K_1[PTA][NBP]_T[S]}{1 + K_1[S] + K_1 K_2[S]} \quad (9)$$

$$\text{rate} = k'[NBP]_T \quad \text{and} \quad k' = \frac{\text{rate}}{[NBP]_T}$$

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$$k' = \frac{k\,K_2\,K_1[PTA]\,[S]}{1 + K_1[S] + K_1 K_2[S]} \qquad (10)$$

k' is observed rate constant, and at constant [PTA], double reciprocal of Eq^n (10),

$$\frac{1}{k'} = \frac{1}{kK_1 K_2[S]} + \frac{1}{kK_2} + \frac{1}{k} \qquad (11)$$

Eq^n (10) can be transformed into the rearranged Eq^n (12) at fixed [S],

$$\frac{[PTA]}{rate\ (k')} = \frac{1}{kK_1 K_2[S]} + \frac{1}{kK_2} \qquad (12)$$

The kinetics results suggest the possibility of formation of ternary complex involving of each of oxidant, substrate and catalyst is strongly favored. However, such a ternary complex is of transient life time due to fast interaction of catalyst and oxidant, and then former undergoes redox decomposition to the end of products intramolecularly. Such a mechanism however, leads to the rate law Eq^n (9) which is in good agreement with the work reported by Binyahia [40]. The spectral evidence for complex formation between catalyst-substrate and oxidant was obtained from UV-vis spectra of the mixture. One sharp intense peak for mixture indicates formation of complex. Such complex formation was also proved kinetically by the non-zero intercept of the double reciprocal plot of 1/k' Vs 1/ [S] and [PTA] / k' Vs 1/ [S]. Evidence is also provided by the fractional order found in substrate. As per Eq^n (11), double reciprocal plot of 1/k' Vs 1/[S] (Figure 1), decomposition rate constant **k** was find out from intercept and K_2 was obtained by substituting $1/k$ in intercept of plot [PTA]/k' Vs 1/[S] and also from Eq^n(12), the value of K_1 (formation constant) was determined (Table 2) from slope of it, K_1, K_2 and *k* was found to be 58.098 ($dm^3 mol^{-1}$), 2×10^3 ($dm^3 mol^{-1}$) and $6.54 \times 10^4 (s^{-1})$ respectively for 2-Phenylethanol at 303K.
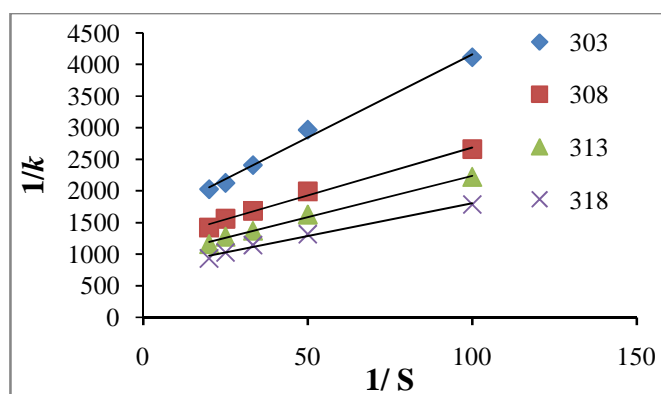

Figure 1. Plot of 1/k' Vs 1/ [substrate] i.e. Double reciprocal plot of 2-Phenylethanol

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

$k \times 10^4$ (s^{-1})				K_1 (dm^{3}mol^{-1})
303K	308K	313K	318K	
6.54	8.55	10.71	13.00	58.098

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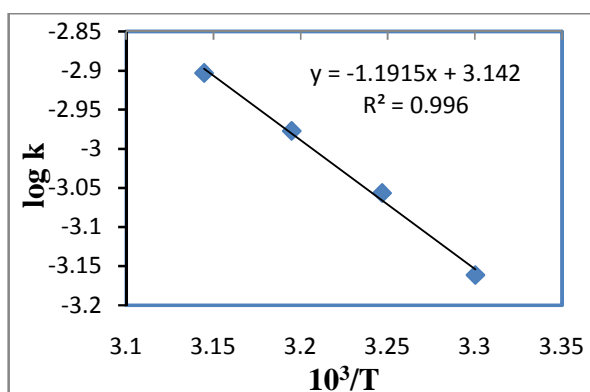
Figure 2. (Plot of log k Vs 1/T); Arrhenius plot for 2-Phenylethanol

Table 3. Activation and Thermodynamic parameters of 2-Phenylethanol at 303K

Ea KJmol^{-1}	$\Delta H^{\#}$ KJmol^{-1}	$\Delta G^{\#}$ KJmol^{-1}	$\Delta S^{\#}$ JK^{-1}mol^{-1}	LogA
22.81	20.29	75.25	-248.30	4.37

CONCLUSION

Kinetic studies demonstrate that the ternary complex of Keggin-anion, substrate and oxidant decomposes in a slow rate determining step to give Phenylacetaldehyde as the main product. The experimental stoichiometry is in good agreement. First order to oxidant and fractional order to

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catalyst and substrate is supported by derived rate law. Keggin anion act as an outer sphere electron transfer reagent in the present study. The Keggin-type phosphotungstic acid catalyst is efficient homogenous catalyst for oxidation of 2-Phenylethanol and it is participating in the reaction as Keggin anion.

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