

Phosphotungstic Acid Catalyzed Oxidation of Substituted 1-Phenylethanols by N-Bromophthalimide- A Kinetic Study

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(Acceptance Date 20th November, 2013)

Abstract

Kinetic investigations in kegginn-type phosphotungstic acid catalyzed oxidation of 1-Phenylethanol and p-substituted 1-Phenylethanols by N-bromophthalimide (NBP) in aqueous acetic acid medium in presence of mercuric acetate as a scavenger have been studied. Oxidation kinetics of 1-Phenylethanols by NBP in presence of PTA (Phosphotungstic acid) shows a first order dependence on NBP and fractional order on 1-Phenylethanols and PTA. The variation of ionic strength, $\text{Hg}(\text{OAc})_2$, H^+ and phthalimide (reaction product) have no significant effect on reaction rate. Activation parameters for the reaction have been evaluated from Arrhenius plot by studying the reaction at different temperature.

Key words: Kinetics, Oxidation, 1-Phenylethanol, Phosphotungstic acid, N-bromophthalimide.

Introduction

In the recent years, studies of oxidation of various organic compounds by heteropoly acids and polyoxometalates especially those with kegginn-type structure under homogeneous and heterogeneous reaction conditions have attracted considerable attention of the researchers¹⁻⁴. 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 amines⁵, aromatic alcohols⁶,

allyl alcohols⁷, *p*-methyl Benzyl Alcohol⁸ etc.

The kinetics of oxidation of substituted 1-Phenylethanols by organic halo chromates such as Benzyl triethylammonium Chlorochromate⁹, Quinoxalinium bromochromate¹⁰, Benzimidazolium Fluorochromate¹¹, Tetrabutyl ammonium tribromide¹², etc. have been studied earlier. A number of reports on kinetic studies of oxidation of 1-Phenylethanols with variety of N-halo compounds such as N-bromosuccinimide¹³, N-bromosaccharin¹⁴, N-bromoacetamide¹⁵

and Chloramine-T¹⁶ as oxidants have been reported.

N-bromophthalimide (NBP) is a potential oxidizing agent¹⁷⁻¹⁹ and it seems that there are no reports about the kinetics of oxidation of 1-Phenylethanols by NBP. The present work reports kinetics and mechanism of PTA catalyzed oxidation of 1-Phenylethanols by N-bromophthalimide in 50 % acetic acid.

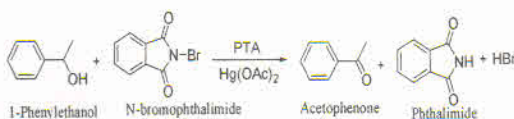
Experimental

Materials: The oxidant NBP (Aldrich sample) was used. Acetic acid (A.R.grade) was purified by the literature procedure. The standard solutions of substituted 1-Phenylethanols 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 iodometrically²⁰ 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-Phenylethanols over oxidant NBP. Mixture containing requisite amounts of solutions of 1-Phenylethanol, Hg(OAc)₂ and PTA in 50% acetic acid were equilibrated at 303 K. To this mixture was added a measured amount of pre-equilibrated (303 K) standard solution of NBP. 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 maximum absorption (λ_{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.

Stoichiometry: Stoichiometry of the reaction was ascertained by equilibrating the reaction mixture containing an excess of NBP over 1-Phenylethanol, mercuric acetate and phosphotungstic acid in 50 % acetic acid. The 1:1 stoichiometry is represented by following equation.



Results and Discussion

The kinetics of oxidation of 1-Phenylethanol by NBP in 50% acetic acid in presence of phosphotungstic acid (H₃PW₁₂O₄₀) as a catalyst was carried at 303 K under pseudo first order conditions. The reactions were carried out in presence of PTA under pseudo first order conditions of [1-Phenylethanol] >> [NBP]. The Plot of log [NBP] Vs time found to be linear ($r^2 > 0.995$) 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 [1-Phenylethanol] was linear ($r^2 = 0.996$) with slope less than unity for all the 1-Phenylethanols indicating a fractional order ($n = 0.49$) dependence on rate of 1-Phenylethanol. The concentration of PTA was varied while the concentration of 1-Phenylethanol, [NBP] and Hg(OAc)₂ kept constant. The plot log k' Vs log [PTA] shows slope less than unity indicating fractional order dependence of rate on [PTA] (Table 1).

Table 1. Effect of variation of substrate, oxidant, and catalyst concentration on pseudo order rate constant k' at 303KHg(OAc)₂=2.00x10³ (mol dm⁻³) 50% AcOH medium

10 ² x [1-Phenylethanol] (mol dm ⁻³)	10 ³ x [NBP] (mol dm ⁻³)	10 ⁴ x[PTA] (mol dm ⁻³)	k' x 10 ⁴ (s ⁻¹)
1.00	1.00	5.00	2.42
2.00	1.00	5.00	3.28
3.00	1.00	5.00	3.96
4.00	1.00	5.00	4.67
5.00	1.00	5.00	5.26
6.00	1.00	5.00	5.88
1.00	1.00	5.00	2.42
1.00	2.00	5.00	4.83
1.00	3.00	5.00	7.28
1.00	4.00	5.00	11.90
1.00	5.00	5.00	13.90
1.00	6.00	5.00	16.12
1.00	1.00	2.50	1.84
1.00	1.00	5.00	2.42
1.00	1.00	7.50	2.80
1.00	1.00	10.00	3.17
1.00	1.00	15.00	3.62

The dependence of the reaction rate on hydrogen ion concentration has been investigated at different initial concentrations of H₂SO₄. There was no significant change in rate constant was observed with variation of H⁺ ion.

Effect of Ionic Strength: The ionic strength of the reaction was varied by the addition of NaClO₄ 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 attack of

an ion on a neutral molecule in the rate determining step²¹.

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 1-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 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.

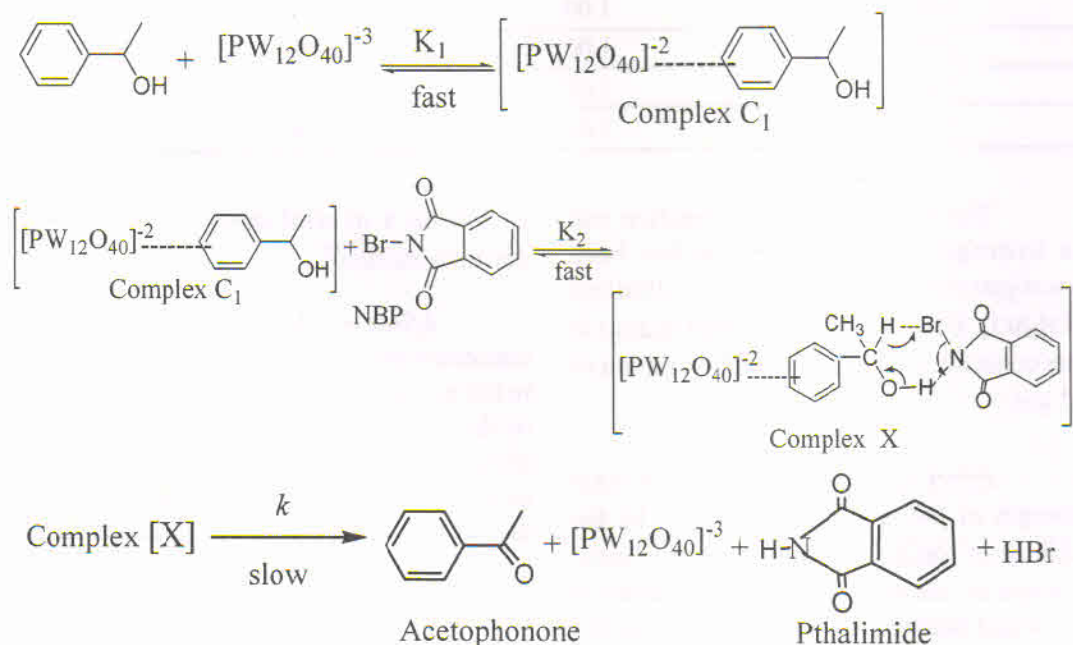
Effect of Substituent: The oxidation of 1-Phenylethanol and substituted 1-Phenylethanol by [NBP] were carried out in the

temperature range 30–45°C. The observed rate constants found to be increase with temperature for all the compounds. Electron donating groups increase the rate while electron withdrawing groups decreases the rate of oxidation. The order of reactivity of different 1-Phenylethanol with [NBP] catalyzed by [PTA] is.



Reactive Species and Mechanism:

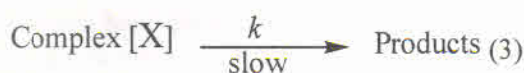
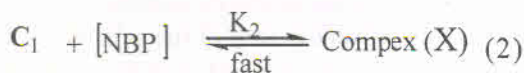
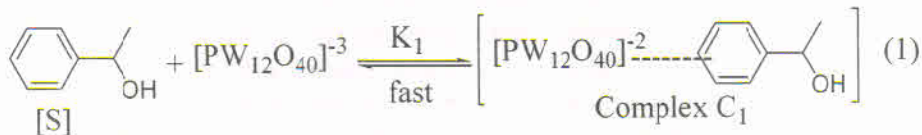
As reported earlier²² on the basis of experimental results, the probable reactive oxidizing species in the present investigation is free NBP. Based upon the experimental observations, the most probable mechanism is as in scheme 1.



Scheme-1

Rate Law

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



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 $[NBP]_T = \text{Total concentration of [NBP]}$, 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, 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 $[S] \gg [NBP]$ equation (8) further reduced to,

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

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

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

k' is observed rate constant and at constant [PTA], double reciprocal of equation (11),

$$\frac{1}{k'} = \frac{1}{k K_1 K_2[S]} + \frac{1}{k K_2} + \frac{1}{k} \quad (11)$$

Equation (10) can be transformed into the rearranged equation (12) at fixed [S],

$$\frac{[PTA]}{\text{rate}(k')} = \frac{1}{k K_1 K_2[S]} + \frac{1}{k K_2} \quad (12)$$

The kinetics results suggest the possibility of formation of ternary complex involving of each of NBP, 1-phenylethanol and Keggin anion of PTA is strongly favored. Such a mechanism however, leads to the rate law equation (11). They have reported the formation of cyclic transition state, in absence of mineral acid and 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. In present study, the double reciprocal plot of $1/k'$ Vs $1/[S]$ with non zero and positive intercept supports the complex formation.

Effect of temperature and isokinetic

phenomenon:

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 parameters-Energy of activation (E_a), enthalpy of activation (ΔH^\ddagger), free energy of activation (ΔG^\ddagger), entropy of activation (ΔS^\ddagger) and pre exponential factor (Log A) were evaluated (Table 2). The thermodynamic parameter for equilibrium step and rate determining step of the scheme was evaluated. The observed ΔS^\ddagger 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. ΔH^\ddagger indicates that the reactions are enthalpy controlled.

Table-2 Activation and thermodynamic parameters for oxidation of 1-phenylethanol at 303K.

Substituents X	E_a KJmol ⁻¹	ΔH^\ddagger KJmol ⁻¹	ΔG^\ddagger KJmol ⁻¹	ΔS^\ddagger JK ⁻¹ mol ⁻¹	LogA
4-OCH ₃	20.61	18.09	75.31	-248.47	4.43
4-CH ₃	21.12	18.61	75.16	-248.49	4.47
H	22.02	19.50	75.32	-248.51	4.54
4-Br	21.58	19.06	75.32	-248.54	4.55
4-Cl	21.81	19.29	75.33	-248.56	4.57
4-NO ₂	23.62	21.10	75.34	-248.58	4.69

The validity of the isokinetic relation can be tested graphically by plotting Exner plot $\log k$ (303) Vs $\log k$ (318). The isokinetic temperature β evaluated from Exner criterion was found to be 325.5K (slope = 0.318 and $r^2 = 0.963$). Which is above the experimental

temperature, it implies that all the compounds are oxidized by the same mechanism. Further the constancy in the calculated values of ΔG^\ddagger for this oxidation reaction indicates that the same type of the reaction mechanism could be operative for the reaction.

Conclusion

Kinetic studies demonstrate that the [PTA---NBP---Ph-CH(OH)CH₃] complex decomposes in a slow rate determining step to give acetophenone as the main product. Low dielectric constant of the medium facilitates the reactivity. The experimental stoichiometry is in good agreement. First order to oxidant and fractional order to catalyst and substrate is supported by derived rate law. The Keggin-type phosphotungstic acid catalyst is efficient homogenous catalyst for oxidation of 1-Phenylethanols. The rate of oxidation of 1-Phenylethanols was found to be in the order of

p- OCH₃ > p-CH₃ > H > p-Br > p- Cl > p- NO₂

Acknowledgement

The authors gratefully acknowledge financial support from UGC (WRO) Pune for minor research project and Principal, Vasantrao Naik Mahavidyalaya Aurangabad for providing the laboratory facilities.

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