

Phosphotungstic Acid Catalyzed Oxidation of Benzhydrols by N-Bromophthalimide-A Kinetic Study

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Abstract: Kinetic investigations in Keggin-type phosphotungstic acid catalyzed oxidation of benzhydrol and p-substituted benzhydrols 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 benzhydrols by NBP in presence of PTA (Phosphotungstic acid) shows a first order dependence on NBP and fractional order on benzhydrols and PTA. The variation of ionic strength, $\text{Hg}(\text{OAc})_2$, 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. A mechanism involving transfer of hydride ion in rate determining step is suggested.

Key Words: Kinetics, Oxidation, Benzhydrol, Phosphotungstic acid, N-bromophthalimide.

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 conditions¹⁻⁹ 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 amines¹⁰ aromatic alcohols¹¹, allyl alcohols¹², styrene¹³, oximes¹⁴ etc.

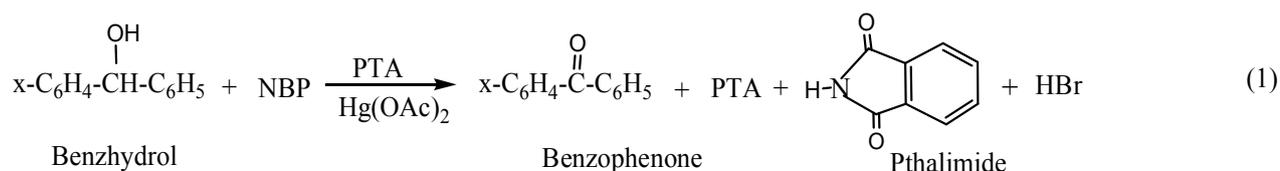
The kinetics of oxidation of substituted benzhydrols by organic halo chromates such as Benzyl triethylammonium Chlorochromate¹⁵, Quinoxalinium bromochromate¹⁶, Quinolinium bromochromate¹⁷, Pyridinium bromochromate¹⁸, Tetrabutylammonium tribromide¹⁹, etc. have been studied earlier. A number of reports on kinetic studies of oxidation of benzhydrols with variety of N-halo compounds such as N-bromosuccinimide²⁰, N-bromosaccharin²¹, N-bromoacetamide²² and Chloramine-T²³ as oxidants

have been reported. N-bromophthalimide (NBP) is a potential oxidizing agent²⁴⁻²⁵ and it seems that there are no reports about the kinetics of oxidation of benzhydrols by NBP. The present work reports kinetics and mechanism of PTA catalyzed oxidation of benzhydrols by NBP in 30 % acetic acid.

Experimental

Materials

Substituted benzhydrols were prepared by the sodium borohydride reduction of corresponding benzophenones²⁶. Purity of benzhydrols was checked by TLC and M.P. The oxidant NBP (Aldrich sample) was used. Acetic acid (A.R. grade) was purified by the literature procedure. The standard solutions of substituted benzhydrols 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 iodometrically²⁷ 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 benzhydrols over oxidant NBP. Mixture containing requisite amounts of solutions of benzhydrol, Hg(OAc)₂ and PTA in 30 % acetic acid were equilibrated at 303 K. To this mixture was added a measured amount of pre-equilibrated (303 K) standard solution of NBP. To maintain the desired temperature (within $\pm 0.1^\circ\text{C}$) 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 intervals. Duplicate kinetic runs showed that the rate constants were reproducible to within $\pm 4\%$.

Stoichiometry and Product Analysis

Stoichiometry of the reaction was ascertained by equilibrating the reaction mixture containing an excess of NBP over benzhydrol, mercuric acetate and phosphotungstic acid in 30 % 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 benzhydrol consumes one mole of NBP.

Benzhydrol (0.2 Mole) and NBP (0.4 Mole) were mixed together with PTA (0.1 Mole) mercuric acetate (0.5 Mole) in 30 % 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 benzophenone by M.P., TLC, HPLC and 2, 4-DNP derivative. Analysis confirmed the formation of benzophenone in quantitative yield. The percentage yield calculated to be 94%.

Results and Discussion

Order on reactants

The kinetics of oxidation of benzhydrol by NBP in 30% acetic acid in presence of phosphotungstic acid (H₃PW₁₂O₄₀) 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 ($r^2 > 0.9985$) 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 benzhydrol and plot of log k' Vs log [Benzhydrol] was linear ($r^2 = 0.999$) with slope less than unity for all the benzhydrols indicating a fractional order ($n = 0.43$) dependence on rate of benzhydrol. (Table 1). The concentration of PTA was varied while the concentration of benzhydrol, [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).

Effect of Hydrogen ion

The dependence of the reaction rate on hydrogen ion concentration has been investigated at different initial concentrations of H₂SO₄ and keeping the concentration of the other reactants constant. 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 the attack of an ion on a neutral molecule in the rate determining step²⁸.

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 bromine²⁹. 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 benzhydrol 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.

Table 1: Effect of variation of reactants on pseudo order rate constant k' at 303K
Hg(OAc)₂=2.00x10³(mol dm⁻³) 30%AcOH medium

10 ² [benzhydrol] (mol dm ⁻³)	10 ³ [NBP] (mol dm ⁻³)	10 ⁴ [PTA] (mol dm ⁻³)	$k' \times 10^4$ (s ⁻¹)
1.00	1.00	5.00	3.62
2.00	1.00	5.00	4.95
3.00	1.00	5.00	5.93
4.00	1.00	5.00	6.57
5.00	1.00	5.00	7.24
6.00	1.00	5.00	7.86
1.00	1.00	5.00	3.62
1.00	2.00	5.00	7.18
1.00	3.00	5.00	11.40
1.00	4.00	5.00	15.00
1.00	5.00	5.00	18.10
1.00	6.00	5.00	21.40
1.00	1.00	2.50	2.91
1.00	1.00	5.00	3.62
1.00	1.00	7.50	4.46
1.00	1.00	10.00	5.10
1.00	1.00	15.00	5.85

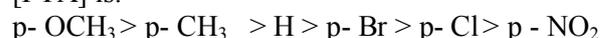
Effect of Solvent Composition

The effect of solvent composition on the reaction rate was studied by varying concentration of acetic acid from 20-70 %. The rate constants (Table 2) suggest that the rate of reaction decreases with increasing acetic acid content of the solvent mixture. Amis²⁸ has shown that a plot of log k' versus $1/D$ is linear with a negative slope for a dipole anion or dipole – dipole interaction. A plot of log k' versus $(D-1/2D+1)$ has been found to be linear in accordance with Kirkwoods³⁰ theory of dipole – dipole type reaction.

Effect of Substituents

The oxidation of benzhydrol and substituted benzhydrol 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. All the substrates obey the same rate law as the parent substrate. Electron donating groups increase the rate while electron withdrawing groups decreases the rate of oxidation. The order of reactivity of different benzhydrols with [NBP] catalyzed by [PTA] is.



The Hammett's plot of log k' Vs σ is linear with a reaction constant $\rho = -0.25$ and correlation coefficient $r^2 = 0.90$. The negative reaction constant ρ indicates the creation of carbonium ion in the transition state; this is in agreement with finding of Sadagopa Ramanujam³¹. The negative reaction constant ρ also supports the loss of secondary hydrogen atom as a hydride in the slow step. If it is so, a better correlation, must be observed in the plot of log k Vs σ .

Table 2. Effect of variation of dielectric constant on reaction rate

AcOH (%)	Dielectric constant (D)	10 ³ /D	10 ² (D-1)/2D+1	$k' \times 10^4$ (s ⁻¹)
20	58.2	17.18	48.7	3.72
30	52.2	19.16	48.6	3.62
40	45.5	21.98	48.4	3.54
50	39.0	25.64	48.1	3.42
60	32.4	30.86	47.7	3.28
70	26.1	38.31	47.2	3.12

Reactive Species and Mechanism



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

$$-\frac{d[\text{NBP}]}{dt} = k[\text{X}] \quad (8)$$

If $[\text{NBP}]_T = \text{Total concentration of [NBP]}$, then $[\text{NBP}]_T = [\text{NBP}] + [\text{X}]$

$$[\text{X}] = \frac{K_2[\text{C}_1] [\text{NBP}]_T}{1 + K_2[\text{NBP}]} \quad (9)$$

But, Rate = $k[\text{x}]$ according to equation (8), substituting value of [X] in it, we have

$$\text{Rate} = \frac{k K_2[\text{C}_1] [\text{NBP}]_T}{1 + K_2[\text{NBP}]} \quad (10)$$

$$\text{C}_1 = \frac{K_1[\text{PTA}][\text{S}]}{1 + K_1[\text{S}]} \quad (11)$$

Substituting $[\text{C}_1]$ in eqⁿ (10)

The order with respect to [NBP] is one and fractional order with [PTA] and [S]. As $[\text{S}] > [\text{NBP}]$, eqⁿ (12) further reduced to,

$$\begin{aligned} \text{Rate} &= \frac{k K_2 K_1[\text{PTA}][\text{NBP}]_T [\text{S}]}{(1 + K_1[\text{S}]) (1 + K_2[\text{NBP}])} \\ &= \frac{k K_2 K_1[\text{PTA}][\text{NBP}]_T [\text{S}]}{1 + K_1[\text{S}] + K_1 K_2[\text{S}] [\text{NBP}]} \end{aligned} \quad (12)$$

$$\frac{-d[\text{NBP}]}{dt} = \frac{k K_2 K_1[\text{PTA}][\text{NBP}]_T [\text{S}]}{1 + K_1[\text{S}] + K_1 K_2[\text{S}]} \quad (13)$$

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

$$k' = \frac{k K_2 K_1[\text{PTA}] [\text{S}]}{1 + K_1[\text{S}] + K_1 K_2[\text{S}]} \quad (14)$$

k' is observed rate constant, and at constant [PTA], double reciprocal of eqⁿ (14),

$$\frac{1}{k'} = \frac{1}{kK_1K_2[S]} + \frac{1}{kK_2} + \frac{1}{k} \quad (15)$$

Eqⁿ (14) can be transformed into the rearranged eqⁿ (16) at fixed [S],

$$\frac{[PTA]}{\text{rate}(k')} = \frac{1}{kK_1K_2[S]} + \frac{1}{kK_2} \quad (16)$$

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 eqⁿ (13) which is in good agreement with the work reported by Binyahia³⁶ and Hiran²⁰ reports formation of cyclic transition state, in absence of mineral acid. Such complex formation was also proved kinetically by the non-zero intercept of the double reciprocal plot (figure 1) of $1/k'$ Vs $1/[S]$ and $[PTA]/k'$ Vs $1/[S]$. Evidence is also provided

by the fractional order found in substrate. 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. As per eqⁿ (15), double reciprocal plot of $1/k'$ Vs $1/[S]$, 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 eqⁿ(16), the value of K_1 (formation constant) was determined (Table 3) from slope of it. K_1 , K_2 and k was found to be $65.23(\text{dm}^3\text{mol}^{-1})$, $2 \times 10^3 (\text{dm}^3\text{mol}^{-1})$ and $9.07 \times 10^4 (\text{s}^{-1})$ respectively for benzhydrol at 303K.

Table 3. Decomposition rate constant (k), formation constant (K_1) and Activation parameters of substituted benzhydrols at 303K.

Substituent x	$k \times 10^4$ (s^{-1})	K_1 ($\text{dm}^3\text{mol}^{-1}$)	E_a KJmol^{-1}	ΔH^\ddagger KJmol^{-1}	ΔG^\ddagger KJmol^{-1}	ΔS^\ddagger $\text{JK}^{-1}\text{mol}^{-1}$	LogA
p-OCH ₃	11.70	85.44	21.56	19.04	75.18	-248.05	4.05
p-CH ₃	9.27	92.77	21.21	18.69	75.20	-248.15	4.14
H	9.07	65.23	21.61	19.09	75.21	-248.16	4.17
p-Br	7.49	65.13	24.90	22.38	75.24	-248.25	4.43
p-Cl	6.40	50.81	35.96	33.44	75.27	-248.31	5.07
p-NO ₂	6.15	29.76	21.93	19.41	75.34	-248.33	4.35

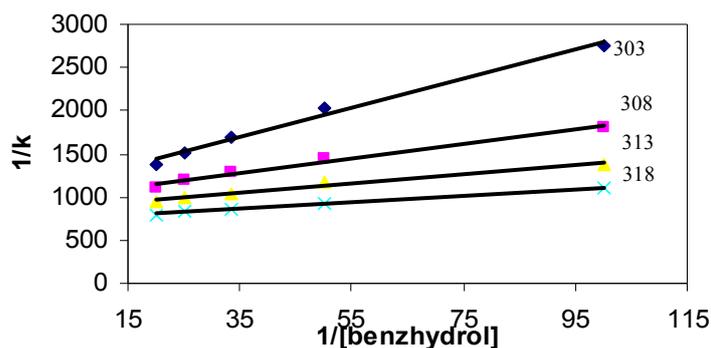


Fig. 1. Double reciprocal plot of benzhydrol

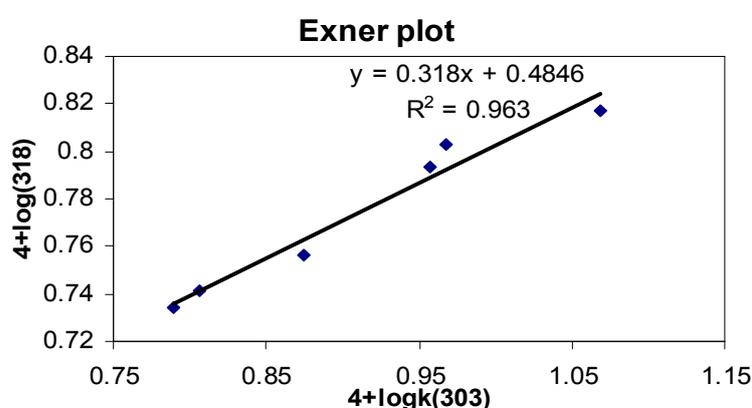


Fig. 2. Exner plot

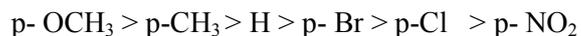
Effect of temperature and isokinetic phenomenon

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 and thermodynamic parameters for equilibrium step and rate determining step of the scheme was evaluated (Table 3). 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. 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 exner³⁷ criterion was found to be 325.51K (slope = 0.32 and $r^2 = 0.963$) as shown in (figure 2). Which is above the experimental temperature, it implies that all the compounds are oxidized by the same mechanism³⁸. 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.

Conclusions

Kinetic studies demonstrate that the ternary complex of Keggin-anion, substrate and oxidant decomposes in a slow rate determining step to give benzophenone as the main product. 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 rate of oxidation of benzhydrols was found to be in the order of



The Keggin-type phosphotungstic acid catalyst is efficient homogenous catalyst for oxidation of benzhydrols and it is participating in the reaction as Keggin anion.

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