Int. J. Chem. Sci.: 7(3), 2009, 2141-2150

KINETICS AND MECHANISM OF PHOSPHOTUNGSTIC ACID CATALYZED OXIDATION OF BENZOIN BY N-BROMOPHTHALIMIDE

JAGDISH BHARAD, BALAJI MADJE, FULCHAND CHAVAN, RATNA SHELKE[a] and MILIND UBALE[*]

Post Graduate Department of Chemistry, Vasantrao Naik Mahavidyalaya,
AURANGABAD (M. S.) INDIA
[a]Premraj Sarda College, AHMEDNAGAR (M. S.) INDIA

ABSTRACT

Kinetic investigations in Keggin-type phosphotungstic acid catalyzed oxidation of benzoin by N-bromophthalimide (NBP) in aqueous acetic acid medium in presence of mercuric (II) acetate as a scavenger have been carried out. The oxidation kinetics of benzoin by NBP in presence of PTA (Phosphotungstic acid) shows a first order dependence on NBP and fractional order on benzoin 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 temperatures.

Key words : Kinetics, Oxidation, Benzoin, Phosphotungstic Acid, N-Bromophthalimide.

INTRODUCTION

In the recent years, studies of oxidation of various organic compounds by heteropoly acids and polyoxymetalates especially those with Keggin-type structure under homogeneous and heterogeneous reaction conditions[1-5] have attracted considerable attention of the researchers. Literature survey reveals that phosphotungstic acid (PTA) due to its thermal stability and acidity makes it efficient and eco-friendly catalyst in oxidation of organic compounds such as aromatic amines[6], aromatic alcohols[7], allyl alcohols[8], oximes[9] etc.

Kinetic investigation of benzoin by peroxydisulphate[10], iron (III)[11], Cr (VI)[12], Ce (IV)[13], N-bromosuccinimide[14] and N-bromosulphonamide[15] have been reported.

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[*] Author for correspondence; E-mail: mbubale@yahoo.com

Transition metal complexes of iron (II)[16], nickel[17], vanadium[18], cobalt[19], cerium and chromium[20] oxidize benzoin under various reaction conditions. Benzoin has two flanking phenyl rings, which offers opportunity to study the kinetics and mechanism of oxidation of benzoin under acidic medium.

N-Bromophthalimide (NBP) is a potential oxidizing agent[21] and has some definite advantages over other N-halogeno oxidants, which has been extensively used in the estimation of organic substrates. It seems that there are no reports about the kinetics of oxidation of benzoin by NBP. The present work reports kinetics and mechanism of PTA catalyzed oxidation of benzoin by N-bromophthalimide in 30 % acetic acid.

EXPERIMENTAL

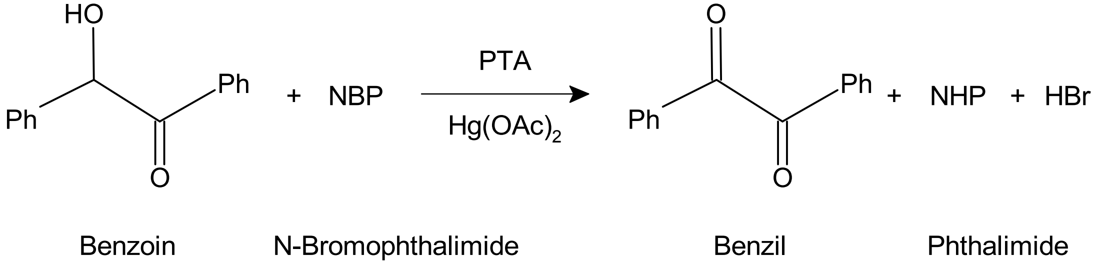
The oxidant NBP (Aldrich sample) was used. Acetic acid (A. R. grade) was purified by the literature procedure. The standard solutions of benzoin (A. R. grade) were prepared in acetic acid. Double distilled water was employed in all kinetic runs. To prevent photochemical effect, the freshly prepared solution of NBP was stored in an amber colored bottle and its strength was checked iodometrically[22] 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 benzoin over oxidant NBP. Mixture containing requisite amounts of solutions of benzoin, $Hg(OAc)_2$ and PTA in 30 % acetic acid were equilibrated at 303 K. To this mixture, a measured amount of prequilibrated standard solution of NBP was added. To maintain the desired temperature (within ± 0.1^{o}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 ± 5%.

Stoichiometry and product analysis

Stoichiometry of the reaction was ascertained by equilibrating the reaction mixture containing an excess of NBP over benzoin, mercuric acetate and phosphotungstic acid in 30 % acetic acid for 24 hrs. at 30^{0}C. The unreacted oxidant (NBP) was determined iodometrically. The estimated amount of unreacted NBP showed that one mole of benzoin consumes one mole of NBP.



Benzoin (0.2 mole) and NBP (0.4 mole) were mixed together with PTA (0.1 mole) and 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 benzil by m. p., TLC, HPLC and 2, 4-DNP derivative. Analysis confirmed the formation of benzil in quantitative yield.

RESULTS AND DISCUSSION

The kinetics of oxidation of benzoin by NBP in 30 % 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 was found to be linear indicating first order dependence of the reaction rate and from the slopes of such plots, pseudo first order rate constants were evaluated. The rate constant (k') have been found to increase with increase in the concentration of benzoin and plot of log k' vs log [Benzoin] was linear ($r^2 = 0.9939$) with slope less than unity for benzoin indicating a fractional order (n = 0.49) dependence on rate of benzoin (Table 1).

The concentration of PTA was varied while the concentrations of benzoin, [NBP] and $Hg(OAc)_2$ were kept constant. The plot log k' vs log [PTA] shows slope less than unity indicating fractional order dependence of rate on [PTA] (Table 1). The dependence of the reaction rate on hydrogen ion concentration has been investigated at different initial concentrations of H_2SO_4, keeping the concentration of the other reactants constant. 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[23].

The concentration effect of mercury (II) acetate in 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[24]. It is not involved in NBP oxidation, but only acts as a scavenger. Variation of phthalimide, one of the products of oxidation, had negligible effect on the rate of reaction. The oxidation reactions of benzoin 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 303 K $Hg(OAc)_2 = 2.00 \times 10^3$(mol dm^{-3}), 30%AcOH-$H_2O$ medium

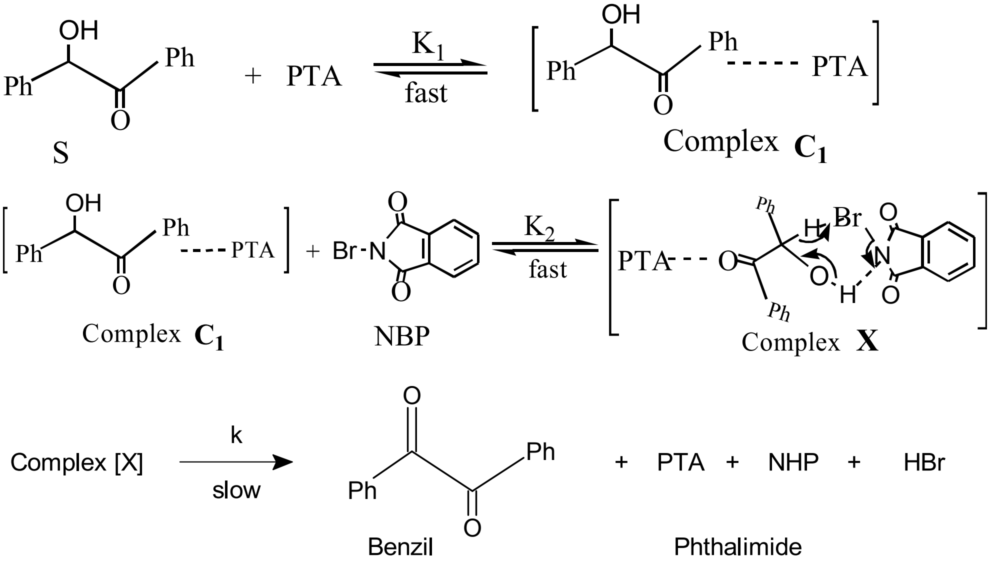
[Benzoin] x 10^2 (mol dm^{-3})	[NBP] x 10^3 (mol dm^{-3})	10^4 x [PTA] (mol dm^{-3})	k' x 10^4 (s^{-1})
1.00	1.00	5.00	2.52
2.00	1.00	5.00	3.47
3.00	1.00	5.00	4.12
4.00	1.00	5.00	4.88
5.00	1.00	5.00	5.40
6.00	1.00	5.00	6.24
1.00	1.00	5.00	2.52
1.00	2.00	5.00	4.98
1.00	3.00	5.00	7.38
1.00	4.00	5.00	10.33
1.00	5.00	5.00	12.95
1.00	6.00	5.00	14.97
1.00	1.00	2.50	2.08
1.00	1.00	5.00	2.52
1.00	1.00	7.50	3.10
1.00	1.00	10.00	3.54
1.00	1.00	15.00	4.22

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.

In the absence of mineral acid, the probable oxidizing specious is free NBP under the present experimental condition[25].

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



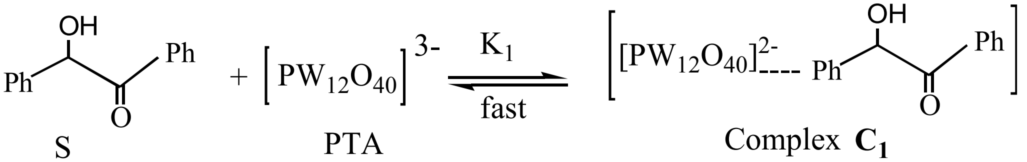
…(1)

…(2)

…(3)

Scheme 1

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



…(4)

$$C_1 + [NBP] \underset{fast}{\overset{K_2}{\rightleftharpoons}} \text{Complex (X)} \qquad \text{…(5)}$$

$$\text{Complex (X)} \xrightarrow[slow]{k} \text{Products} \qquad \text{…(6)}$$

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

$$\frac{-d\,[NBP]}{dt} = k\,[x] \qquad \ldots(7)$$

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

$$[X] = \frac{K_2\,[C_1]\,[NBP]_T}{1 + K_2\,[NBP]} \qquad \ldots(8)$$

But, Rate = k [**x**] according to equation (8), substituting value of [X] in it, we have

$$\text{Rate} = \frac{k\,K_2\,[C_1]\,[NBP]_T}{1 + K_2\,[NBP]} \qquad \ldots(9)$$

$$\text{but} \quad C_1 = \frac{K_1\,[PTA]\,[S]}{1 + K_1\,[S]} \qquad \ldots(10)$$

Substituting $[C_1]$ in eq^n (9)

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

$$= \frac{k\,K_2\,K_1\,[PTA]\,[NBP]_T\,[S]}{1 + K_1\,[S] + K_1\,K_2\,[S]\,[NBP]} \qquad \ldots(11)$$

The order with respect to [NBP] is one and fractional order with [PTA] and [S]. As [S] > [NBP], eq^n (11) is further reduced to,

$$\frac{-d\,[NBP]}{dt} = \frac{k\,K_2\,K_1\,[PTA]\,[NBP]_T\,[S]}{1 + K_1\,[S] + K_1\,K_2\,[S]} \qquad \ldots(12)$$

Rat = k' $[NBP]_T$ and $k' = \frac{\text{Rate}}{[NBP]_T}$

$$k' = \frac{k\,K_2\,K_1\,[PTA]\,[S]}{1 + K_1\,[S] + K_1\,K_2\,[S]} \qquad \ldots(13)$$

k' is observed rate constant and at constant [PTA], double reciprocal of eq^n (13),

$$\frac{1}{k'} = \frac{1}{k\,K_1K_2[S]} + \frac{1}{k\,K_2} + \frac{1}{k} \qquad \ldots(14)$$

Eq^n (13) can be transformed into the rearranged eq^n (15) at fixed [S],

$$\frac{[\text{PTA}]}{\text{rate }(k')} = \frac{1}{k\,K_1\,K_2\,[S]} + \frac{1}{k\,K_2} \qquad \ldots(15)$$

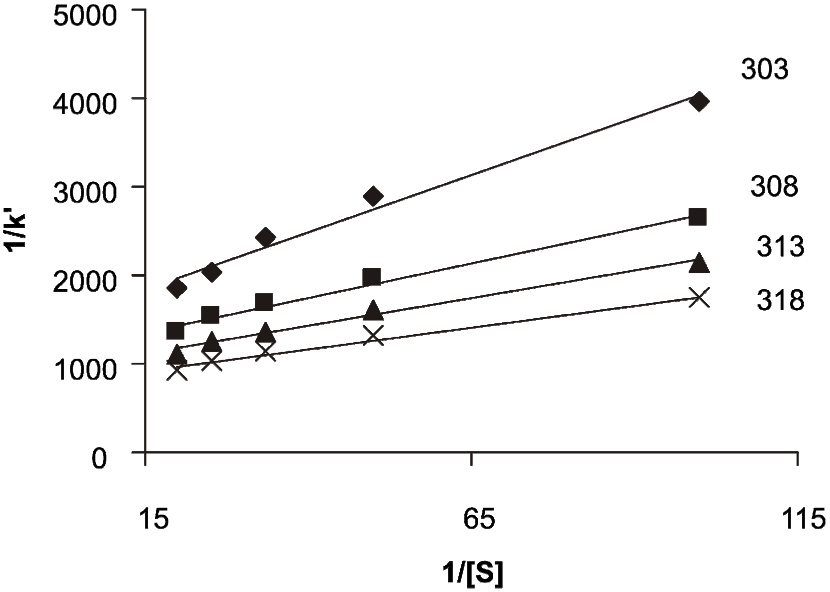


Fig. 1 : Double reciprocal plot of benzoin

The kinetics results suggest the possibility of formation of ternary complex involving each; 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 complex formation was also proved kinetically by the non-zero intercept of the double reciprocal plot (Fig. 1) of 1/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 eq^n (14), 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 eq^n (15), the value of K_1 (formation constant) was determined (Table 2) from slope of it. K_2 was found to be 1.998×10^3 (dm^3mol^{-1}) for benzoin at 303 K.

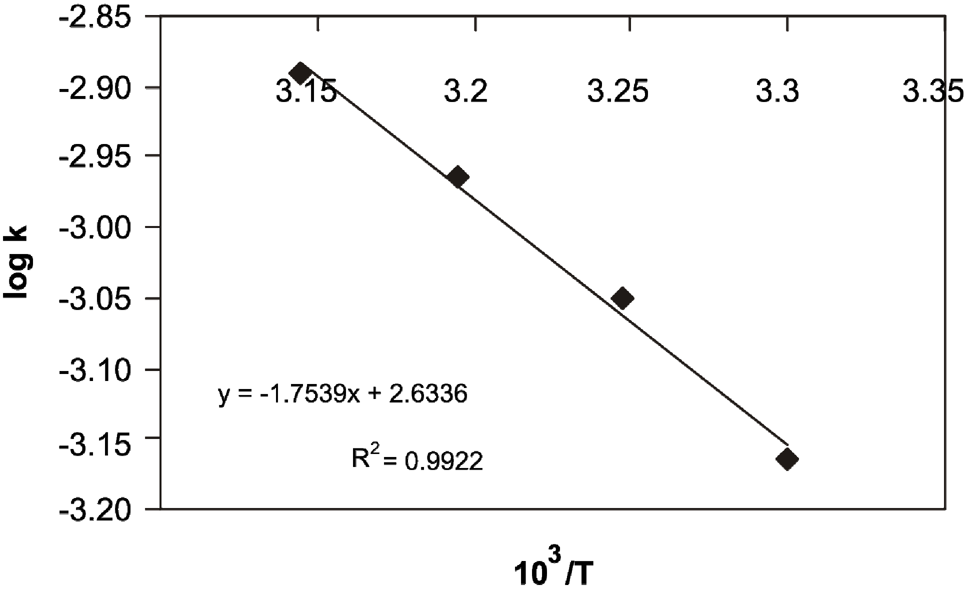


Fig. 2 : Arrhenius plot for benzoin

Table 2 : Decomposition rate constant (*k*), formation constant (K_1) and activation parameters at 303K

k x10^4 (s^{-1})	K_1 (dm ^{3} mol^{-1})	Ea (KJ mol^{-1})	$\Delta H^\#$ (KJ mol^{-1})	$\Delta G^\#$ (KJ mol^{-1})	ΔS# (JK^{-1} mol-1)	log A
6.85	56.78	33.58	31.06	75.26	-248.28	4.92

The rate of oxidation was determined at different temperatures and the Arrhenius plots of log *k* versus 1/T were all linear (Fig. 2). From these plots, the activation and thermodynamic parameters for equilibrium step and rate determining step of the scheme was evaluated (Table 2). 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.

ACKNOWLEDGEMENT

We are thankful to Principal, Vasantrao Naik Mahavidyalaya and Principal, Maulana Azad College, Aurangabad for providing the laboratory facilities.

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Accepted : 21.05.2009