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PHOSPHOTUNGSTIC ACID CATALYZED KINETICS OF OXIDATION OF o-NITRO BENZALDEHYDE BY N-BROMOSACCHARIN IN ACETIC ACID-WATER MEDIUM

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ABSTRACT

Kinetic investigations in Keggin-type phosphotungstic acid catalyzed oxidation of benzyl alcohol by N-Bromosaccharin, (NBSA) in aqueous acetic acid have been studied. Oxidation kinetics of o-nitro benzaldehyde *by N-Bromosaccharin, in presence of Phosphotungstic acid (PTA) show first order dependence on [NBSA] ,* [o-nitro benzaldehyde] *and [PTA]. The variation of [H^+] and [saccharin] (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 Experimental kinetic data and a plausible mechanism has been proposed.*

INTRODUCTION

The elucidation of reaction mechanism is still one of the most fascinating problems in inorganic and organic chemistry. Kinetics has furnished a pool of precious wealth of information about the nature and course of a reaction[1] *viz.* molecularity, concentration, reaction path, frequency of activated complex, mass, temperature and other properties such as influence of substituent groups and structural alterations, rate equation, salt effect, isotopic effect, activation parameters and various environmental changes etc. like solvent polarity, pH and catalytic changes in a reaction. The above study leads to work at stoichiometry, identification of intermediates and isolation of end-products as an indirect support to reaction mechanism.

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[2-9]have attracted considerable attention of the researchers. 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[10]. *N-Bromosaccharin, (NBSA)* 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[11-22]**.** The kinetics and mechanistic investigations of the oxidation of o-nitro benzaldehydeby various oxidizing agents have been studied earlier[24-25]. It seems that there are no reports about PTA catalyzed the kinetics of oxidation of o-nitro *benzylaldehyde*by NBSA. The present work reports kinetics and mechanism of PTA catalyzed oxidation of o-nitro benzaldehydeby N-*Bromosaccharin*, *(NBSA)* in 40 % acetic acid.

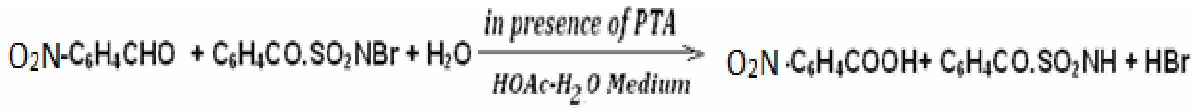
MATERIALS AND METHODS

The solution of N-Bromosaccharin (sigma chemical India)so obtained was prepared by dissolving its weighed quantity in 100% CH_3COOH (B.D.H.) and kept either amber colored flask or black paper wrapped around it to save it from the action of diffused day light which alters appreciably its concentration. The standardization of N-Bromosaccharin was done by taking one ml of its solution in conical flask to which 10 ml of 2% KI solution followed by 5ml of

2N H_2SO_4 added to it. The liberated iodine was titrated against standard sodiumthiosulphate solution using starch solution as an indicator. o-Nitro benzaldehyde, (sigma chemicals India) were used as substrates for the preparation of solution. The solution of o-Nitro benzaldehyde was prepared in requisite volume of glacial acetic acid.

Kinetic measurements: All kinetic measurements were made under pseudo first order conditions, by keeping large excess of o-Nitro benzaldehyde over oxidant N-Bromosaccharin. Mixture containing requisite amounts of solutions of o-Nitro benzaldehyde and PTA in 40 % acetic acid was equilibrated at 313 K. To this mixture was added a measured amount of pre-equilibrated (313 K) standard solution of N-Bromosaccharin. To maintain the desired temperature (within ± 0.1^{o}C) the reaction mixture was kept in a thermo stat water bath and the progress of the reaction was monitored iodometrically by withdrawing aliquots of the reaction mixture at regular time of intervals.

Stoichiometry and Product Analysis: Stoichiometry of the reaction was ascertained by equilibrating the reaction mixture containing an excess of N-Bromosaccharin over o-Nitro benzaldehyde and phosphotungstic acid in 40% acetic acid for 24 hrs.at, 313 K. The un-reacted oxidant was determined by iodometrically. The estimated amount of un-reacted o- N-Bromosaccharin showed that one mole of o-Nitro benzaldehyde consumes one mole of N-Bromosaccharin. The o-nitro benzoic acid was found as the end-product of oxidation. Which was separated, purified and re-crystallized then determines their melting point 145.6 ^{0}C and compared with melting point (145-147.5 ^{0}C) given in the literature.



$$O_2N\text{-}C_6H_4CHO + C_6H_4CO.SO_2NBr + H_2O \xrightarrow[HOAc\text{-}H_2O\ Medium]{in\ presence\ of\ PTA} O_2N\text{-}C_6H_4COOH + C_6H_4CO.SO_2NH + HBr$$

$-NO_2$ at ortho position.

RESULTS AND DISCUSSION

Order on reactants: The kinetics of oxidation of o-Nitro benzaldehyde by NBSA in 40% acetic acid in presence of phosphotungstic acid ($H_3PW_{12}O_{40}$) as a catalyst was carried at 313 K under pseudo first order conditions. The Plot of log [NBSA] 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 o-Nitro benzaldehyde and plot of log k' vs. log [o-Nitro benzaldehyde] was linear with unity slope, indicating a first order dependence with respect to the [o-Nitro benzaldehyde] (**Table-1).** The concentration of PTA was varied while the concentration of o-Nitro benzaldehyde and, [NBSA] kept constant. First-order rate constant increases with increase in concentration of phosphotugstic acid i.e. reactions are fully PTA catalyzed. The plot of k_1 vs. [PTA] and log k_1 versus log [PTA] was obtained linear with positive slope (**Fig. 3, Table -1**). PTA is the heteropoly acid; its conjugate base is the $[PW_{12}O_{40}]^{-3}$ anion. Its acidity in acetic acid has been shows that three protons dissociate independently rather than sequentially and acid sites are the same strength.

The first-order rate constant decreases with increase composition of acetic acid i.e. rate slightly retards with increase in dielectric constant of the medium. The plot of log k_1 versus $10^3/D$ were obtained linear with negative slope in each substrate. Reaction rate ebbs on addition of concentration of saccharin. The velocity coefficient increases slightly as the concentration of different salts increase. It is clear that the added neutral salts such as NaCl and KCl have nearly no effect on the rate of reaction. The plots of log k/k_o versus $\sqrt{\mu}$ give straight line with very small positive slope. The presence of free radicals in the system understudy was tested qualitatively by addition of 1-2 ml of acrylonitrile (monomer) in about 5-6 ml of the reaction mixture employing trapping method. The non-occurrence of turbidity and white precipitate clearly indicates the absence of free radicals in the system.

Various activation parameters namely temperature coefficient, energy of activation (Ea), frequency factor (A), enthalpy of activation ($\Delta H^{\#}$), free energy of activation ($\Delta G^{\#}$), and entropy of activation ($\Delta S^{\#}$) for each reaction are calculated for o-Nitro benzaldehyde-NBSA system and according to the reaction mechanism, rate equation and order of reaction have been discussed .

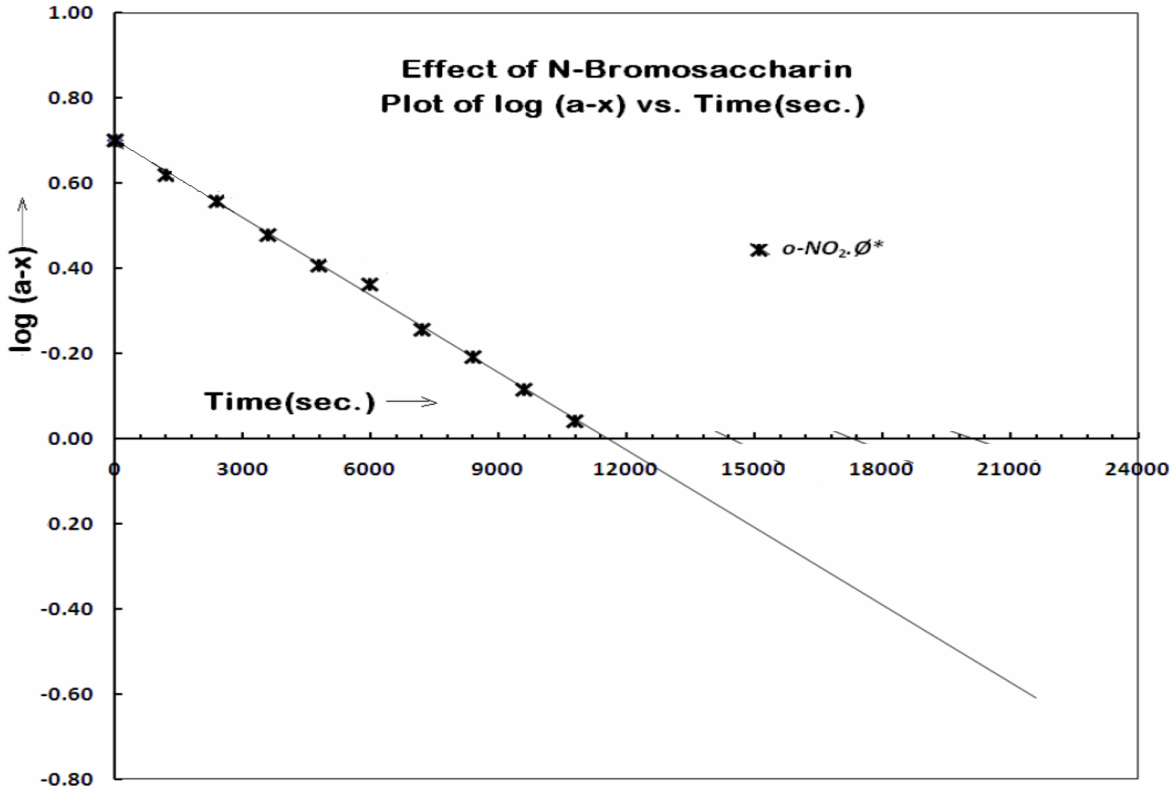


Fig. 1 :Effect of varying in the concentration of NBSA

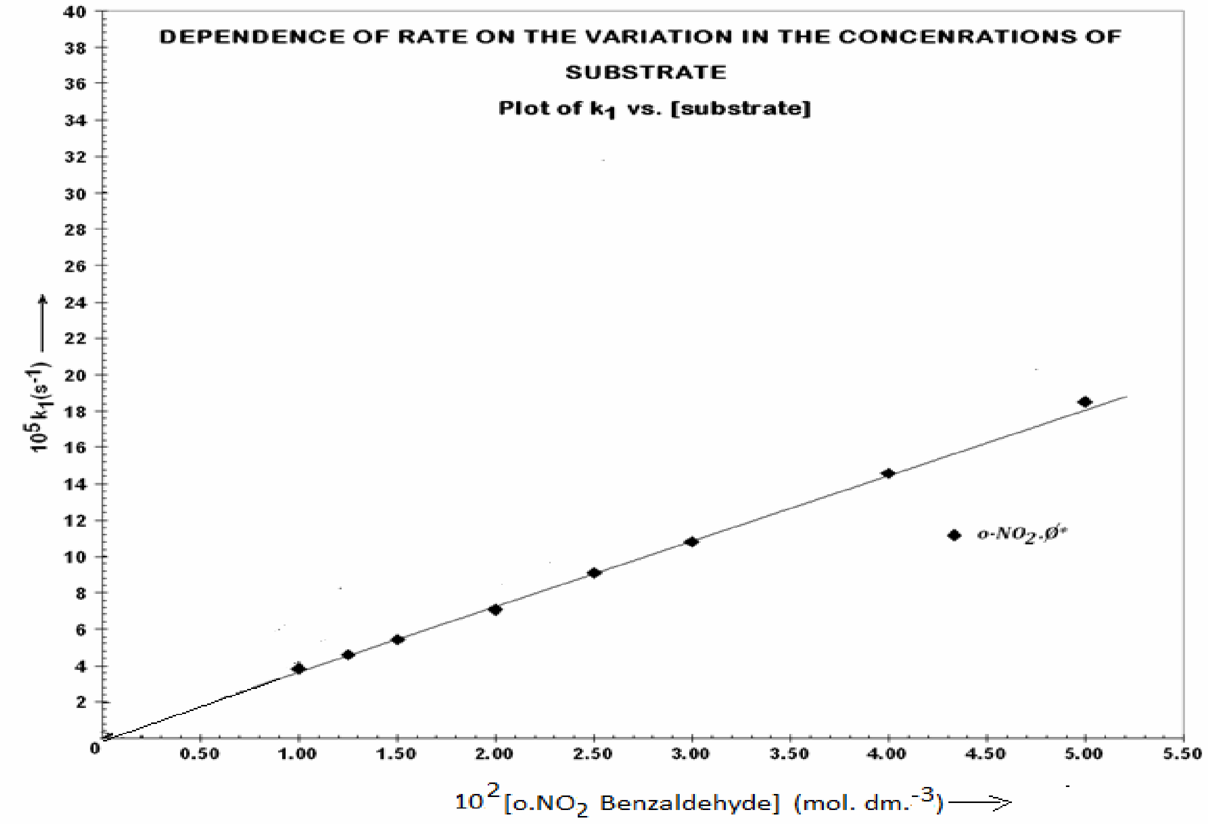


Fig.2: Dependence of rate on the variation in the concentrations of o-nitrobenzaldehyde

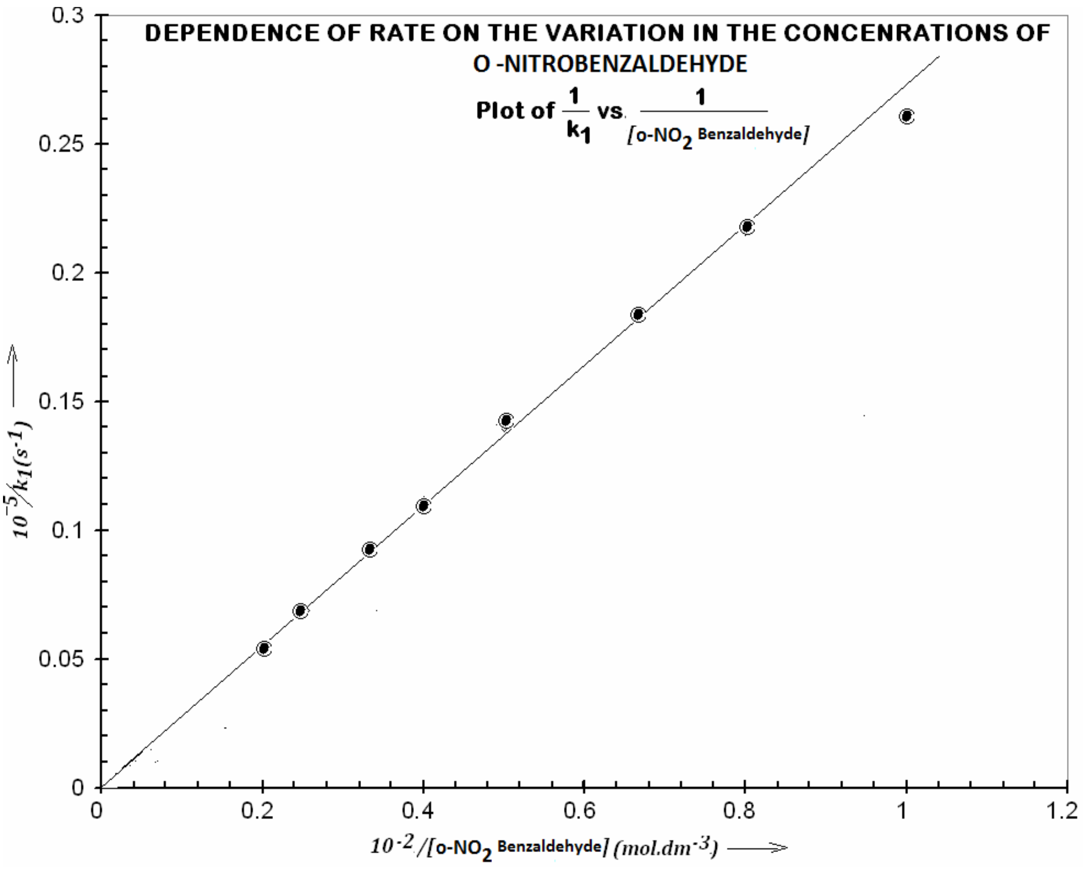


Fig.3: Dependence of rate on the variation in the concentrations of o-nitrobenzaldehyde

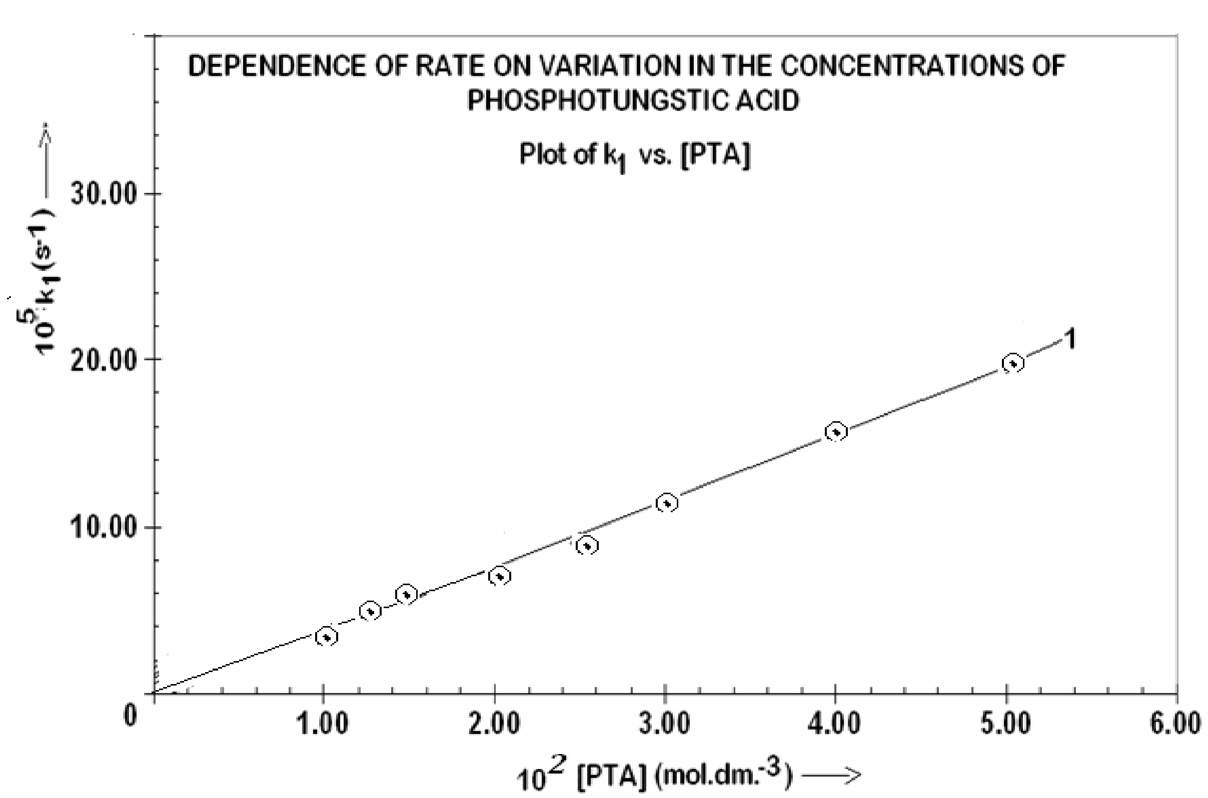


Fig.4: Dependence of rate on the variation in the concentrations of PTA

Table: 1 Experimental Kinetics Data

[NBSA]10^3 (mol.dm.$^{-3}$)	[***o-NO$_2$.***]10^2 (mol.dm.-^{3})	[PTA]10^2 (mol.dm.-^{3})	**HOAc-H$_2$O % (v/V)**	[HClO$_4$]10^3 (mol.dm.-^{3})	$10^5 k_1 (s^{-1})$
1.00	2.00	2.00	40	0	7.07
1.25	2.00	2.00	40	0	7.09
2.00	2.00	2.00	40	0	7.06
2.50	2.00	2.00	40	0	7.09
4.00	2.00	2.00	40	0	7.08
5.00	2.00	2.00	40	0	7.07
8.00	2.00	2.00	40	0	7.06
10.00	2.00	2.00	40	0	7.07
2.50	1.00	2.00	40	0	3.83
2.50	1.25	2.00	40	0	4.60
2.50	1.50	2.00	40	0	5.44
2.50	2.00	2.00	40	0	7.09
2.50	2.50	2.00	40	0	9.07
2.50	3.00	2.00	40	0	10.80
2.50	4.00	2.00	40	0	14.56
2.50	5.00	2.00	40	0	18.52
2.50	2.00	1.00	40	0	3.78
2.50	2.00	1.25	40	0	4.93

2.50	2.00	1.50	40	0	6.02
2.50	2.00	2.00	40	0	7.09
2.50	2.00	2.50	40	0	9.07
2.50	2.00	3.00	40	0	11.74
2.50	2.00	4.00	40	0	15.69
2.50	2.00	5.00	40	0	19.84
2.50	2.00	2.00	20	0	6.62
2.50	2.00	2.00	30	0	6.90
2.50	2.00	2.00	40	0	7.09
2.50	2.00	2.00	50	0	7.19
2.50	2.00	2.00	60	0	7.34
2.50	2.00	2.00	40	1.00	8.02
2.50	2.00	2.00	40	1.25	8.27
2.50	2.00	2.00	40	1.50	8.56
2.50	2.00	2.00	40	2.00	9.15
2.50	2.00	2.00	40	2.50	9.54
2.50	2.00	2.00	40	3.00	10.27
2.50	2.00	2.00	40	4.00	11.72
2.50	2.00	2.00	40	5.00	13.11

Table: 2 Thermodynamics parameters

[NBSA] = $2.50X10^{-3}$ (mol.dm.$^{-3}$),
[o-nitrobenzaldehyde] = $2.0.0X10^{-2}$ (mol.dm.$^{-3}$),
[PTA] = $2.00X10^{-2}$ (mol.dm.$^{-3}$),
HOAc-H_2O = 40% (v/V)

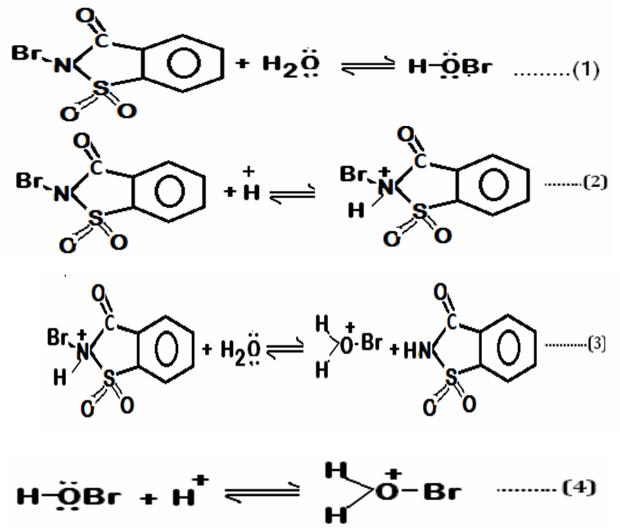
Substrate	Ea (kJ mol^{-1})	A (s^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$-\Delta G^{\#}$ (kJ mol^{-1})	$-\Delta S^{\#}$ JK mol^{-1}
o-NO_2. C_6H_4. CHO	57.45 ±0. 56	$3.45X10^{3}$ ±0.28	56.23 ±0.59	92.05 ±0.47	116.95 ±0.82

Active species of oxidant

PTA is the heteropoly acid; its conjugate base is the $[PW_{12}O_{40}]^{-3}$ anion. The reaction is PTA catalyzed, similar to the $HClO_4$ acid but it is pointed out that the PTA catalyzed reaction rate is observed 10 times slower as comparison to $HClO_4$ acid. Its acidity in acetic acid has been shows that three protons dissociate independently rather than sequentially and acid sites are the same strength. At low pH this evidence indicated that PTA must ionize to gives H^+ ions as:

$$H_3[PW_{12}O_{40}] \rightleftharpoons [PW_{12}O_{40}] + 3H^+ \quad \text{at low pH}$$

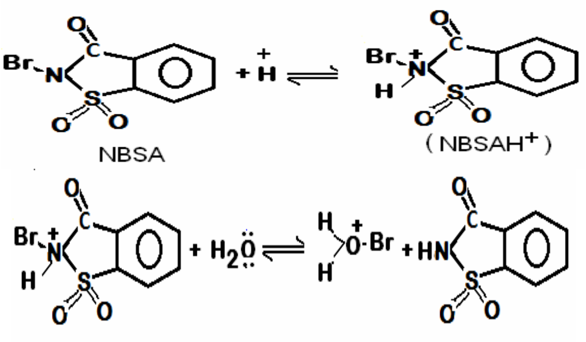
In aqueous acetic acid containing phshotungstic acid, N-bromosaccharin exists in following equilibrium:



The dependence of rate on the acidity and [sac.] helps in selection of active oxidant species. In the oxidation of o-nitro benzaldehyde the involvement of molecular NBSA or protonated NBSA in the mechanistic pathway is ruled out as the reaction rate of retarded by added saccharin concentration. This is suggested that the formation of saccharin in a pre-equilibrium step along with HOBr. The plot of log k vs. log[sac.] is linear for each substrate and thus supports HOBr as active species of oxidant.

The dependence of rate on acidity suggests that some positive species such as Br^+ or protonated HOBr is active species of oxidant. The formation of H_2O^+Br from NBSA may be in two ways:

1. In first way, the molecular NBSA is first protonated and then protonated NBSA suffers nucleophilic attack by water(H_2O) yielding H_2O^+Br as:



2. In second way, NBSA suffers nucleophilic attack by water(H_2O) yielding HOBr, which in next step is protonated. It is kinetically difficult to distinguish between two paths of formation H_2O^+Br.

One cannot ignore Br+ as active oxidant species, the formation of which may be formulated as:

$$\text{NBSA} + \overset{+}{\text{H}} \rightleftharpoons \text{Br}^+ + \text{saccharin}$$

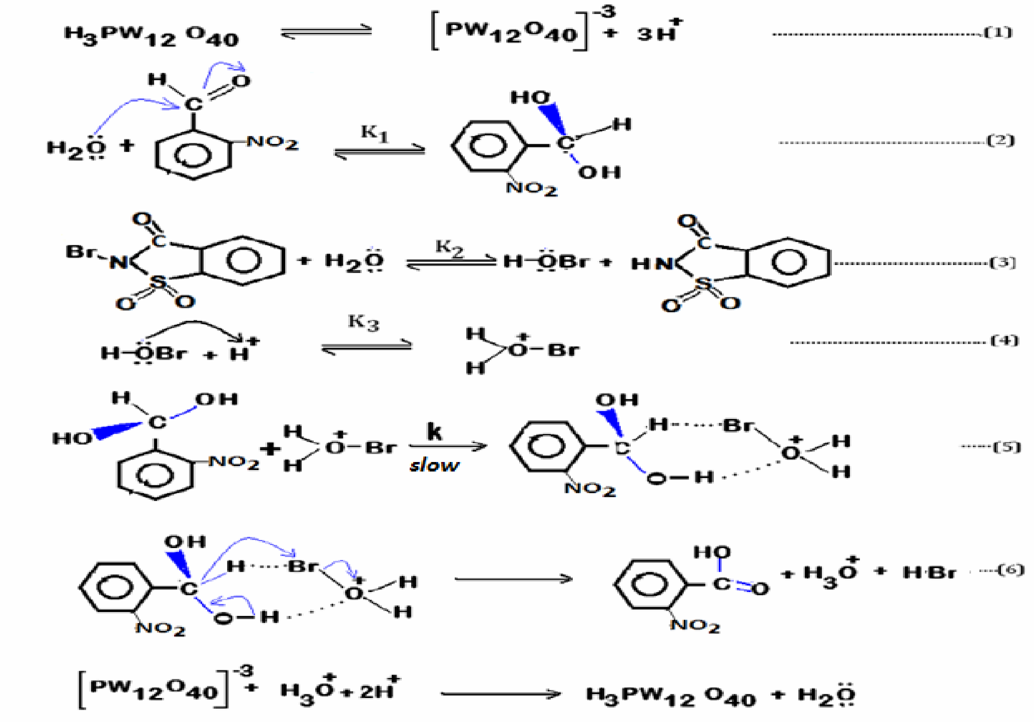
The above equilibrium explains acid catalysis as well as retarding trend of added saccharin. In aqueous solution it is difficult to distinguish between Br+ and H_2O^+Br because they differ only by a molecule of water but it is well documented that H_2O^+Br is more potential electrophile than Br+. Wilson and soper[28] studied that the bromination of benzene by brominr and HOBr in water. They have observed that bromination by HOBr is slow, but HOBr reacts faster than Br_2 on addition of acid concentration. The faster rate is due to formation H_2O^+Br in presence of acid. Several other workers also proved that $H_2O^+Br$are the powerful electrophile than Br+ and preferred one.

Active species of substrate

Further, the present investigation is an aldedehyde molecule in which in aqueous solution may exist as an aldehyde, as an enol, as hydrated molecule. In aqueous acetic acid and in presence of PTA protonated form of electron deficient carbonyl carbon species of aldehyde or hydrated form of aldehyde expected to exist.Substrate in almost completely unionized form, therefore, it is concluded that the protonated form of electron deficient carbonyl carbon specieso-nitro benzaldehyde may undergo react with HOBr or hydrated form of neutral substrate molecule react with the protonated species of H_2O^+Br.

Mechanistic paths for the oxidation of o-nitrobenzaldehyde

The kinetic data as summarized in the Tables:1 and 2,Therefore, it is, concluded that, for the oxidation of o-nitro benzaldehyde with NBSA in presence of PTA, the mechanism could be proposed as per following two schemes as:



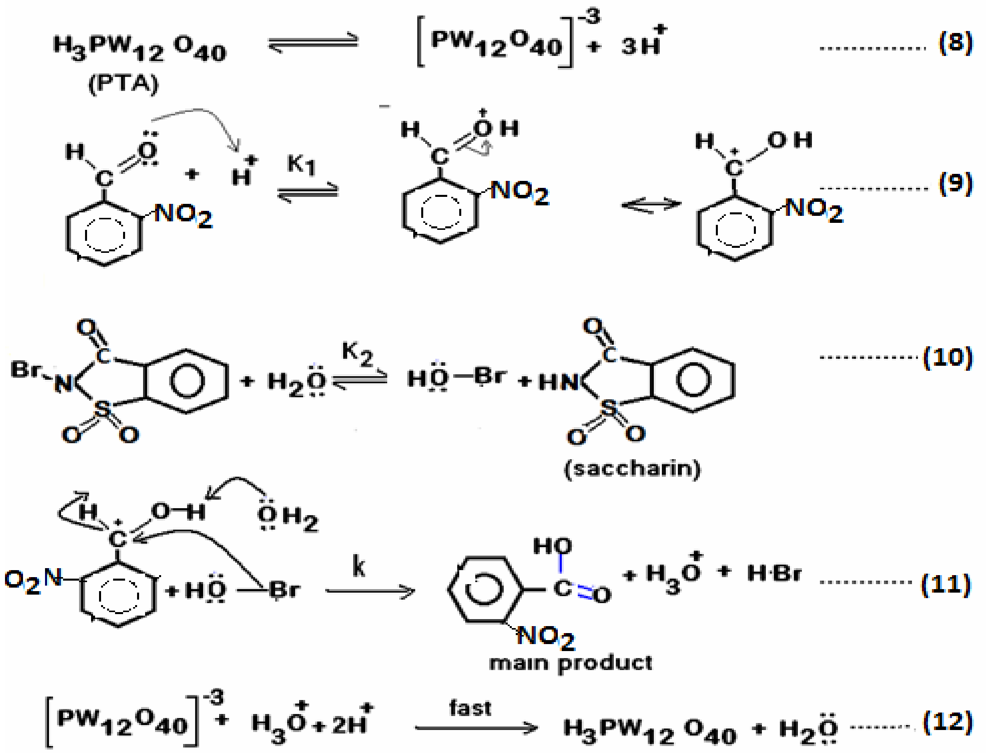
$H_3PW_{12}O_{40} \rightleftharpoons [PW_{12}O_{40}]^{-3} + 3H^+$ ……(1)
H₂Ö + NO₂ K1 HO H C OH NO₂ ……(2)
Br N C O S O O + H₂Ö K2 H–ÖBr + HN ……(3)
H–ÖBr + H⁺ K3 H H O–Br ……(4)
H OH HO C NO₂ H H O–Br k slow OH H Br O H H C NO₂ O–H ……(5)
OH H Br O H H C NO₂ O–H HO C=O NO₂ + H₃O⁺ + H·Br ……(6)
$[PW_{12}O_{40}]^{-3} + H_3O^+ + 2H^+ \longrightarrow H_3PW_{12}O_{40} + H_2O$

Rate expression for scheme-1

The derived rate law for the above scheme-1 explains all the kinetics findings.

$$k_{obs} = \frac{k\ K_1\ K_2\ K_3\ [O_2N\text{-}C_6H_4.CHO]\ [PTA]}{[Sac.] + K_2} \qquad \text{..........(7)}$$

SCHEME-2



Rate expression for scheme-2

The derived rate expression for the above mechanism (scheme-2) can be express as:

$$k_{obs.} = \frac{Rate}{[NBSA]_T} = \frac{K_1K_2k[O_2NC_6H_4.CHO]}{[sac] + K_2} \qquad (13)$$

$$\frac{1}{k_{obs.}} = \frac{1}{K_1K_2k[O_2NC_6H_4.CHO]}\left[\frac{[sac.]}{K_2\ [PTA]} + 1\right] \qquad \text{......(14)}$$

$$k_{obs.} = \frac{Rate}{[NBSA]_T} = \frac{K_1K_2k[O_2NC_6H_4.CHO]}{[sac] + K_2} \qquad (13)$$

$$\frac{1}{k_{obs.}} = \frac{1}{K_1K_2k[O_2NC_6H_4.CHO]}\left[\frac{[sac.]}{K_2\ [PTA]} + 1\right] \qquad \text{......(14)}$$

The derived rate expressions (7), (13) and (14) are good agreement of both the mechanism scheme-1 and 2 and scheme-2; explain all the facts of kinetic finding.

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