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Kinetics and mechanism of Ag (I) catalyzed oxidation of phenethyl alcohols and para-substituted phenethyl alcohols by PDP in aqueous nitric acid

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ABSTRACT

Spectroscopic method for the kinetics of Ag (I) catalysed oxidation of phenethylalcohol(PA) by PDP in aqueous nitric acid medium has been reported under different conditions. The reaction is followed spectrophotometrically by measuring the decrease in absorbance of PDP at 350nm to 360nm. The rates show first order dependence on [PDP] and the rate constants evaluated at different [PDP] are found to be almost the same. Increase in [Ag (I)] has linear relation with the rate of oxidation and order in [Ag (I)] has been found to be fractional. Variation in ionic strength of the medium has significant effect on the rate of reaction. The rates of the reaction have been measured at different temperatures and the activation parameters for all the substrates computed. The rates increase in the order $-NO_2 < -Cl < -H < -CH_3 < -OCH_3$ of para substituted phenethyl alcohols. Hammett's plot of log k_{obs} versus σ is found to be valid. The correlation between enthalapies and free energies of activation is reasonably linear with an isokinetic temperature of 425K to 432K. The rate constant k obeys corresponding equation, $k=Q.e^{-\Delta E\#RT}$. $e^{\Delta s\#R}$. Ea increases with introduction of electron-withdrawing groups into the benzene ring. Electron withdrawing groups increases chemical reactivity decreases. The introduction of electron-releasing groups lowers the Ea for the reaction. The reactions were sluggish under ordinary conditions. However, in the presence of Ag (I) catalyst these substrates underwent Oxidation at Kinetically measurable speed. Hence, it is thought worthwhile to study Oxidation of and its substituted derivatives in the presence of Ag(I) PDP in aqueous HNO_3 medium.

Keywords: spectrophotometric, phenethylalcohol, Peroxodiphosphate, Silver catalyst.

INTRODUCTION

Phenethyl alcohol caused Escherichia coli to take up great by increased amount of acriflavine, a compound to which healthy growing cells are impermeable PEA also caused an increased rate of reflux of cellular potassium under conditions which do not leakage greatly after the influx of potassium via the energy dependent potassium pump. We therefore propose the primary effect PEA is a limited breakdown of the cell membrane. The inhibition of deoxyribonucleic acid synthesis and other cellular functions would then be secondary con sequences of the alter ration in the membrane structure.

Oxidation of alcohols has been studied by several workers[1-4]. Aromatic alcohols have found wide applications in synthetic and pharmaceutical industries. Among the aromatic alcohols Phenethyl alcohols are found in a number of essential oils such as champera rose and alleppoine. Richard etal[5] have studied antibacterial activity and found that these are being used as preservatives in Ophthalmic solutions. Due to their Synthetic importance several workers have made attempts to study of these compounds by different Oxidants such as sodium –N bromobenzene sulphonamide[6], sodium hypochlorite and Ce (IV).

But Oxidation of phenethylalcohols by PDP in aqueous nitric acid medium has not has not been reported so far. Further phenethylalcohols are found to be resistant to Oxidation under normal conditions though there are number of reports on the Oxidation of aromatic alcohols like benzyl alcohols[7]. Oxidation of benzyl alcohols are comparatively easy than phenethylalcohols, because stable intermediate benzyl free radical is assumed to be formed in the Oxidation of benzyl alcohols due to addition of one more methylene group Phenethyl alcohols are found to be resistant to Oxidation[8-10]. The reactions were sluggish under ordinary conditions However, in the presence of Ag (I) catalyst these substrates underwent Oxidation at Kinetically measurable speed[11-12]. Hence, it is thought worthwhile to study Oxidation of and its substituted derivatives in the presence of Ag(I) PDP in aqueous HNO₃ medium.

RESULTS AND DISCUSSION

The Kinetics of Oxidation of Ag(I) catalyzed Oxidation of Phenethylalcohols by PDP have been investigated in aqueous nitricated medium spectrophotometrically over the temperature range 298k to 360k.

Under the conditions [PDP]<<[PA] the plot of log [PDP] versus time was linear indicating a first order dependence in [PDP] (Table 1, fig 1). From the slopes of such plots, Pseudo first order constants (K^1) have been evaluated at different [PA]. The plots of log K^1 versus [PA] were linear, and from the slopes of such plots the order dependence in [PA] were evaluated to be fractional.

Table. 1: Order in [PDP] in Ag(I) catalyzed PA-Ag(I) reaction

 $\begin{array}{l} [PDP] = \ 3 \ x \ 10^{-3} \ mol \ dm^{-3} \\ [PA] = \ 10.00 \ x \ 10^{-2} \ mol \ dm^{-3} \\ [H^+] = \ 5 \ x \ 10^{-1} \ mol \ dm^{-3} \\ [Ag(I)] = \ 7.25 \ x \ 10^{-5} \ mol \ dm^{-3} \\ Temp = 298k \end{array}$

Time	Absorbance	1+log (abs)
0	0.604	0.781
10	0.494	0.694
20	0.405	0.608
30	0.309	0.488
40	0.224	0.350
50	0.168	0.225



Fig. 1: Order in [PDP] in Ag(I) catalyzed PDP-PA reaction



(Table 2, fig 2) keeping [PDP] and [PA] constant increased in [Ag(I)] increased the rate and the order in [Ag(I)] was found to be fractional. This indicates that PA may be involved in the formation of complex either with Ag(I) has been confirmed by shifting absorption maximum of Ag(I) from 305 to 420 nm.

$\begin{array}{l} [PDP] = \ 3 \ x \ 10^3 \ mol \ dm^{\cdot 3} \\ [PA] = \ 4 \ x \ 10^{\cdot 2} \ mol \ dm^{\cdot 3} \\ [H^+] &= \ 5 \ x \ 10^{\cdot 1} \ mol \ dm^{\cdot 3} \\ [Ag(I)] = \ 7.25 \ x \ 10^{\cdot 5} \ mol \ dm^{\cdot 3} \\ Temp = \ 298k \end{array}$

Substrate	Temp(K)	$10^{3}/T$	$10^4 \mathrm{x} \mathrm{K}^1$	$5 + \log K^1$
	298	3.35	4.22	1.62
	3.03	3.30	5.50	1.74
Phenethyl alcohol	308	3.25	6.92	1.84
-	313	3.19	8.92	1.95
	318	3.14	16.3	2.21
	298	3.35	11.3	2.05
	303	3.30	16.0	2.20
Para-CH ₃ PA	308	3.25	21.8	2.34
	313	3.20	29.0	2.46
	318	3.14	38.9	2.59
	298	3.35	16.9	2.22
	303	3.30	22.0	2.34
Para-OCH ₃ PA	308	3.25	30.2	2.46
	313	3.20	32.0	2.50
	318	3.14	56.0	2.75
	298	3.35	3.30	1.51
	303	3.30	4.90	1.69
Para-NO ₂ PA	308	3.25	7.60	1.88
	313	3.20	11.0	2.04
	318	3.14	19.5	2.29
	298	3.35	4.35	1.63
	303	3.30	5.90	1.77
Para-ClPA	308	3.25	8.92	1.98
	313	3.20	12.3	2.09
	318	3.14	24.0	2.38

Table. 2: Temperature effect on $K^1 \operatorname{Ag}(I)$ catalyzed PA-PDP

This complex is supposed to react with PDP in the rate determining step to form Ag(II) complex.

The Ag(II) complex was un molecularly decomposes into intermediate free radical and Ag(1). Which on further Oxidation in a sequence of one electron yield the product, phenyl acetic acid. Formation of such higher Oxidation on states of Ag(I) has also been reported by earlier workers in the Oxidation studies with PDP, acid bromated and period ate.

Table. 3: Order in [HNO₃] in Ag(I) catalyzed PA-PDP reaction

 $\begin{array}{l} [PDP] = \ 3 \ x \ 10^{-3} \ mol \ dm^{-3} \\ [PA] = \ 10.00 \ x \ 10^{-2} \ mol \ dm^{-3} \\ [Ag(I)] = \ 7.25 \ x \ 10^{-5} \ mol \ dm^{-3} \\ Temp = 298k \end{array}$

10[NHO ₃] mol \bar{dm}^{3}	2+log [NHO ₃]	$10^4 \ge K^1(S^{-1})$	5+log K
5	1.70	5.85	1.76
1.74	1.25	5.48	1.73
1.45	1.16	5.12	1.71
1.15	1.06	4.97	1.69
8.85	0.93	4.59	1.66
0.55	0.74	4.41	1.64

At constant [PDP], [PA] and [Ag(I)] an increase in $[H^+]$ increased the rate of Oxidation (Table 3, fig 3). But increase in $[NO^{-3}]$ resulted in decrease in the rate of Oxidation . Similar effects of $[H^+]$ and $[NH_3^-]$ was reported in the literature s well as in our earlier studies. These results could be explained by proposing the following equilibrium.



Fig. 3: Effect of [HNO₃] on Ag catalyzed PDP-PA reaction





Fig. 4: Arrhenius plot for PDP – PA reaction conditions are same as Table. 3

Thus it is assumed that rate could be increased in $[H^+]$ as it will influence the existence of Oxidant reactive species. Further it is very well know from literature that Ag(I) in aqueous nitric acid medium exist in various forms but $[Ag(H_2O)_5cl]$ was considered to be a reactive species.



 $\begin{array}{l} [PA] = \ 4.00 \ x \ 10^{-2} \ mol \ dm^{-3} \\ [H^+] & = \ 5 \ x \ 10^{-1} \ mol \ dm^{-3} \\ [Ag(I)] = \ 7.25 \ x \ 10^{-5} \ mol \ dm^{-3} \\ Temp = 298k \end{array}$

10 ³ [PDP]	3+log[PDP]	10^4 x K^1	5+logK ¹
1.50	0.177	4.26	1.62
2.00	0.302	4.25	1.63
3.00	0.478	4.29	1.63
6.00	0.779	4.23	1.63
7.58	0.876	4.30	1.64

Stoichiometry:

Stoichiometry of PA-PDP reaction was determined by allowing Ag(I) catalyzed Oxidation to go to completion at room temperature by maintaining PA and PDP in 1:4 molar ratio. The observed Stoichiometry was found to be

$$C_6H_5CH_2CH_2OH + PDP \xrightarrow{Ag(I)} C_6H_5CH_2COOH$$

Product analysis:

Oxidation product of Phenethyl alcohol was detected by thin layer chromate graphy using but an 1-ol-ethyl acetatewater (4:1:5) v/v/v) as the solvent and iodine as detecting agent (Rf = 0.86). The reported Rf value is consistent with the value of authentic sample as the reference one. In a typical experiment the solution of PA (0.2 mol), PDP (0.05 mol) and Ag(I) (0.008 mol) were dissolved in 50 ml water acetonitrile mixture (60:40 v/v) and allowed to stand for Ca.24h to ensure completion of the reaction. Then it was treated with excess (100 ml) of CHCl₃ to separate the organic layer. After separation of organic layer the solvent was evaporated and the residue was purified with silic gel column (eluent: but an 1-of-ethylacelate-water (4:1:5 v/v/v)). Evaporation of the solvent afforded the pure compound. The product was characterized as phenyl acetic acid based on HNMR (CCDCL₃) data: 83.65 (S₂ 2H, -CH₂-) 87.20 -7.40 (m, 5H, aromatic); 811.25 (bs, 1H, COOH) (fig 13A). The products were also identified by characteristic ferric hydroxamic test. The weight of the product obtained iso 967g which account for 78% yield. Based on experimental facts such as the Stoichiometry, induced polymerization, rate data, order of the species and activation parameters, the most probable mechanism proposed is as shown below in Scheme – I



Assuming that Eq (4) in scheme 1 to be the ret determining step, the rate law could be written as follows

$$-\frac{d[PDP]}{dt} = \frac{KK[PDP][PA][Ag(I)]}{1+K[PA]+K[Ag(I)]}$$
OR

$$-\frac{2.303d\log[PDP]}{dt} = K^{1} = \frac{KK[PA][Ag(I)]}{1 + K[PA] + K[Ag(I)]}$$

Where K is the bimolecular rate constant for the slow step (4) and K is the formation constant for Ag(I) complex in the fast step(3). Eq (11) accounts for the first order dependence of the rate on [PDP] and fractional order with respects [PA] and [Ag(I)]

Taking the reciprocal of Eq-12 we get

$$-\frac{1}{K^{1}} = \frac{1}{[PA]} = \left[\frac{1}{KK[Ag(I)]} + \frac{1}{K}\right] + \frac{1}{K[Ag(I)]}$$

A large variation was observed in the rate of Oxidation of PA by PDP with change of substituent at para position. The rate were higher for PA with electron donating substituents in the benzene ring and lower for electron with drawing substituents. At constant [Ag(I)] the plot of $1/K^1$ versus 1/[PA] was found to be linear and from the slope and intercept the values of formation constant K and bimolecular constant K were calculated.

Effect of temperature:

The reaction rate of Oxidation of phenethylalcohols increased with increase in temperature and the values of K¹ increased with temperature. Activation parameters were evaluated from arhenius plots. The large negative Δ ST values attributed to the formation of more ordered transition state. These results indicated that transition state must be more ordered than reactants. Such large values were not common in nature.

Table. 5: Effect of temperature on K and k in Ag(I) Catalyzed PA-PDP reaction.

 $\begin{array}{l} [PDP] = \ 3 \ x \ 10^{-3} \ mol \ dm^{-3} \\ [H^+] &= \ 5 \ x \ 10^{-1} \ mol \ dm^{-3} \\ [Ag(I)] = \ 7.25 \ x \ 10^{-5} \ mol \ dm^{-3} \\ [PA] = \ 0.04 - 0.12 \ mol \ dm^{-3} \\ Temp = 298K \end{array}$

Unit of K are dm^3 mol⁻¹, Unit of k are dm^3 mol⁻¹S⁻¹

Temp (K)	PA		P-0	DCH ₃	P-	CH ₃	P	-Cl	P-N	IO_2
	K	$K \times 10^4$	K	$K \times 10^4$	Κ	K×10 ⁴	K	K×10 ⁴	K	K×10 ⁴
298	29.0	7.69	77.1	21.9	20.0	24.8	2.46	41.9	14.5	9.03
303	2.92	9.20	77.3	28.4	23.0	26.5	4.07	42.5	15.0	10.0
308	30.1	11.6	82.8	33.4	24.8	28.9	55.26	4.60	15.3	10.4
313	31.4	13.9	86.8	40.6	25.9	29.5	5.96	6.78	15.36 +	11.8
318	35.6	15.1	88.7	52.6	27.4	34.8	8.58	9.16	18.6	13.4



It may be interpreted that the formation of collisions that have appropriate molecular Orientations become more stringent and may leads to slow rate even though the activation energy is relatively low and the concentration are enough to ensure many collisions.

The rate constant K may be shown by the equation

$K = Q.e^{\Delta E/RT} \cdot e^{\Delta S = /R}$.

The calculated rate constant K was \cong 4.0 dm³ mol⁻¹ s⁻¹ where Q can be treated as rate constant, which relates to number of molecular collisions per second (frequency factor)

In the present investigation finding $\Delta G^{\#}$ values more than 84 KJ Mol⁻¹ is may be considerable evidence to explain the rate of Oxidation increases with increase in temperature. Further constancy in calculated value so $\Delta G^{\#}$ for the Oxidation reaction indicates that the same type of the reaction mechanism could be operative for the Oxidation reactions. For the purpose of comparison the Ea values of all the substituted Phenethyl alcohols were optimized corresponding to parent PA at 298K through the relation

Log A = log K obs + Ea/2.303RTEa = 2.303RT (log A - log K obs)

Isokinetic phenomena:

The iso Kinetic temperature can be defined as a temperature at which the reaction rates are same for all the substrates in a reaction series. The validity of iso kinetic temperature explained on the basis of leffler and exner equations. According to the leffler the iso kinetic temperature obtained from the slope of linear plot of $\Delta H^{\#}$ versus $\Delta S^{\#}$

 $\Delta H^{\#} = \Delta H_{O}^{\ \#} + \beta \Delta S^{\#}$

However the method has limitations determinations of β from the plots of Δ H[#] versus Δ S[#] is not accurate because these values are essentially obtained from the similar values of Δ G[#]. Hence the accurate iso kinetic temperature can be evaluated from the Exner's linear plot of log K₁, versus log K₂ using the following equation.

Table. 6: Optimized activation and Thermodynamic properties of Ag(I) catalyzed PA-PDP reaction

 $\begin{array}{l} [PDP] = \ 3 \ x \ 10^{-3} \ mol \ dm^{-3} \\ [H^+] &= \ 5 \ x \ 10^{-1} \ mol \ dm^{-3} \\ [Ag(I)] = \ 7.25 \ x \ 10^{-5} \ mol \ dm^{-3} \\ [PA] = \ 0.04 - 0.12 \ mol \ dm^{-3} \\ Temp = 298k \end{array}$

Parameters	Н	4-OCH ₃	4-CH ₃	4-Cl	$4-NO_2$
$K \ge 10^4 (dm^3 mol^{-1} S^{-1})$	7.69	21.9	24.8	41.9	90.3
Eexp (Kjmol ⁻¹)	57.5	45.6	57.6	61.3	66
$\Delta H^{\#}$ (Kjmol ⁻¹)	54.9	43	49	51	64.5
$\Delta S^{\#}$ (Kjmol ⁻¹)	-130	-156	-141	-137	-120
$\Delta G^{\#} (Kjmol^{-1})$	93.7	90.3	91.3	99.5	100

Table. 7: Optimized activation and Thermodynamic properties of Ag(I) catalyzed PA-PDP reaction

 $\begin{array}{l} [PDP] = \ 3 \ x \ 10^{-3} \ mol \ dm^{-3} \\ [PA] = \ 4.00 \ x \ 10^{-2} \ mol \ dm^{-3} \\ [H^+] = \ 5 \ x \ 10^{-1} \ mol \ dm^{-3} \\ [Ag(I)] = \ 7.25 \ x \ 10^{-5} \ mol \ dm^{-3} \\ Temp = \ 298k \end{array}$

Parameters	Н	4-OCH ₃	4-CH ₃	4-Cl	$4-NO_2$
Ea(Kjmol ⁻¹)	57.2	53.7	54.0	57.1	57.8
Log A	6.5	7.1	6.9	6.5	6.4
$\Delta H^{\#}$ (Kjmol ⁻¹)	54.9	43.4	58.9	57.1	63.9
$\Delta S^{\#}$ (Kjmol ⁻¹)	-127	-157	-142	-142	-121

$$\beta = \frac{T_1 T_2 (1-b)}{T_1 - b T_2}$$

Whereas log K_1 and log K_2 are the rate constants at T_1 and T_2 temperatures and 'b" is the slope of exner plots (Fig 7) indicates that the Oxidation of Phenethyl alcohols follows similar mechanism. iso kinetic temperatures evaluated from both the plots leftler plot ($\beta = 425k$) and exner plot ($\beta = 432k$)



Fig. 7: Exner plot for isokinetic temperature, PDP- PA reaction

For rate determining step (Eq.4) is Scheme-I, are higher than experimental temperature range which indicates that the rate determining steps is largely influenced by enthalpy change. Above finding are reasonably agree with two approaches indicating that Oxidation of all the title substrates could follow the identical mechanism.

Effect of substituents:

The observed order of reactivity for the Oxidation of Phenethyl alcohols was shown that

P-methoxy PA>P-methyl PA> PA>P-chloro PA> P-nitro PA. The effect of substituents on the rate const ant (K) could be explained by using Hammettis equation

 $Log(k/K/K_0) = \rho\sigma$

Where K₁ and K₀ are rate constants for substituted and un substituted Phenethyl alcohols.

 ρ is the reaction constant and σ is the substituent constants. The values of pseudo first order rate constants (K¹) varied symmetrically, the Hammett's plot (Fig 11A) of log K¹ versus ' σ ' was linear (0.9994) with ρ = -2.083

Table. 8: Effect of substituents on K and k, thermodynamic and activation parameters. $[PDP] = 3 \times 10^{-3} \text{ mol dm}^{-3}$

 $\begin{array}{ll} [H^+] &= 5 \; x \; 10^{-1} \; mol \; dm^{-3} \\ [Ag(I)] &= \; 7.25 \; x \; 10^{-5} \; mol \; dm^{-3} \\ [PA] &= \; 0.04 - 0.12 \; mol \; dm^{-3} \\ Temp &= \; 298 K \end{array}$

Parameters	Н	4-OCH ₃	4-CH ₃	4-Cl	4-NO ₂
$k \times 10^{4} (dm^{3}mol^{-1}S^{-1})$	7.69	21.9	24.8	41.9	90.3
Eexp (Kjmol ⁻¹)	57.5	45.6	57.6	61.3	66
$\Delta H^{\#}$ (Kjmol ⁻¹)	54.9	43	49	51	64.5
$\Delta S^{\#}$ (Kjmol ⁻¹)	-130	-156	-141	-137	-120
$\Delta G^{\#} (Kjmol^{-1})$	93.7	90.3	91.3	99.5	100

A negative value of ρ suggests the development of an electron deficient reaction centre in the activated complex. It was observed that electron donating groups like –OCH₃, CH₃ increase the rate of the Oxidation and electron with drawing groups –Cl, -NO₂ groups decrease the rate of Oxidation as it may be seen from the date, values of Ea increase with the electron withdrawing groups while electron releasing groups lowered the Ea values (Table 8)

CONCLUSION

The Kinetics of Oxidation of Ag(I) catalyzed Oxidation of Phenethylalcohols by PDP have been investigated in aqueous nitrated medium spectrophotometrically over the temperature range 298k to 360k. Under the conditions [PDP] << [PA] the plot of log [PDP] versus time was linear indicating a first order dependence in [PDP]. Keeping [PDP] and [PA] constant increased in [Ag(I)] increased the rate and the order in [Ag(I)] was found to be fractional.

At constant [PDP], [PA] and [Ag(I)] an increase in $[H^+]$ increased the rate of Oxidation. But increase in $[NO_3^-]$ resulted in decrease in the rate of Oxidation. it is assumed that rate could be increased in $[H^+]$ as it will influence the existence of Oxidant reactive species. The rate of reactivity decreases with increasing of electron withdrawing groups on PA.

REFERENCES

- [1] Vijaya Bhaskar Rao N, Anand Rao M, Oxidation Commun, 26(4) (2003) 580.
- [2] Edward J O, McIssac J E, J Org Chem, 34 (1969) 2565.
- [3] House D A, Chem Rev, 62 (1962) 185.

[4] Levitt L S, Malinowski E R, J Am Chem Soc, 77 (1955) 4517; 80 (1958) 5334.

- [5] Srivastava S K, Singhal S K, Sharma R G, Proc Nat Acad Sci India, 47(A) (1977) 111.
- [6] Richard R M E, J Pharm Pharmacol, 21(1969)681.
- [7] Rama Chandra H, Mahadevappa D S, Rangappa K S, Proc Nat Acad Sci, 108(5) (1996) 485.

[8] Sakai, Ayano, Hendrickson, *Tetrahedron letter*, 41(16) (2000) 2759.

- [9] Srivastava S P, Acta Cienc Indica, 5(1) (1979) 50.
- [10] Cady H H, Connik R E, J Am Chem Soc, 80 (1958) 2646.
- [11] Sung Soo Kim, Igor Trushkov and Santosh Kumar Sar, Bull. Korean Chem. Soc, 23(9), (2002) 1331.
- [12] Barton, D. J. R.; Doller, D. Acc. Chem. Res. 1992, 25, 504