Kinetic Studies of Phosphotungstic Acid Catalyzed Oxidation of Some Diols by N-Chloropyarazinamide in Aqueous Acetic Acid Medium Using Spectrophotometer

Sandhya Mishra[1]; S.K. Singh[2]; Santsoh K.Singh[3†]

[1]Govt. Girls PG College, Rewa (M.P.) INDIA
[2]Govt. T.R.S. PG College, Rewa (M.P.) INDIA
[3]Govt.S.V. College Teonthar, Rewa (M.P.) INDIA

Abstract:

In aqueous acetic acid media, the kinetics of N-chloropyrazinamide (NCPZA) oxidation of diols has been investigated. Reaction exhibits first-order dependence with respect to [NCPZA] and [PTA] and Fractional order kinetically obeys the order in the [diol] have been observed. Perchloric acid concentration just little (almost negligibly) catalyzes the process. The rate of oxidation accelerates the medium's dielectric constant increases. Additionally, research has been done on different ionic strengths and pyrazinamide addition as a reduction product. Parameters for Arrhenius activation and thermodynamics have been evaluated. There has been proposed a suitable mechanism that fits the observed kinetics.

**Keywords**: Kinetics, oxidation, mechanism, diol, N-chloropyrazinamide.

INTRODUCTION

Kinetic study provides useful information about the mechanism and rate of chemical reaction, which helps to run a chemical reaction successfully by a way of selecting optimum condition as to get maximum yield. It also helps us to study the factors which influence the rate of reaction such as temperature, pressure, substrate concentration, oxidant concentration, composition of reaction mixture and catalyst. The reaction kinetics plays a very important role in the investigation of the reaction mechanism. diols are used as hard surface treatment disinfectants, sanitizers, a sterilant, virucides, fungicides and mildewides. Kinetics of oxidation of diols by various oxidizing reagents has been well documented[1-12]. The kinetics of oxidation of some diols by a newly synthesized oxidant[13-15], N-chloropyrazinamide (NCPZA) has not been reported so far and hence need for the present investigation.

EXPERIMENTAL

All chemicals were used of Anala R grade. Conductivity water was used throughout the study. All the alcohols were used after their distillation by proper method and purity checked by their boiling point. The solution of perchloric acid was prepared by known volume of acid in water and standardized by sodium hydroxide using phenolphthalein indicator. N-chloropyrazinamide[16] was prepared by chlorinating pyrazinamide using trichloroisocyanuric acid.

N-Chloropyrazinamide was prepared using a straight forward process (NCPZA). 0.6894 g (5.605 m mol) of pyrazinamide (PZA) was dissolved in methyl acetate and put into a 100 mL round-bottom flask. After adding 0.478 g (2.057 mmol) of trichloroisocyanuric acid, cyanuric acid precipitate started to form after 20 minutes. The mixture was vacuum filtered and the solid washed with methylene chloride after 4 hours of stirring. A rotary evaporator had been used to remove the solvent from the filtrate. The solid obtained was washed with diethyl ether to give high purity of N-chloropyrazinamide[21]. Yield 88 %; M.P. 135 °C.
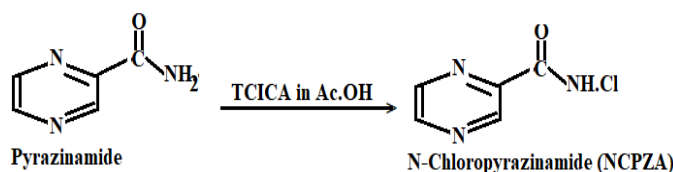
NCPZA solution was prepared by dissolving the known amount of NCPZA in water and standardized by iodometrically using starch indicator.

KINETIC MEASUREMENTS

A thermostat water bath was used to maintain the desired temperature within ±0.1^{0}C. Requisite volume of all reagents including substrate, were taken in reaction vessel and thermostat at 35^{0}C for thermal equilibrium. The kinetics was followed by examining aliquot portion of reaction mixture for NCPZA, spectrophotometrically, after suitable time intervals.

The reaction was carried out under pseudo-first order conditions [diol] >> [NCPZA] in aqueous acetic acid medium containing phosphotungstic acid. Before performing the kinetic run, instrument was calibrated over $KMnO_4$ to verify Lambert-Beer's Law. The 0.0001M solution of NCPZA was taken in a beaker; all other reagents were added to it, except substrate i.e. diol and a wavelength scan was done. The λ_{max} obtained for present investigation was 310 nm. All kinetic runs were carried out using the same λ_{max} i.e. 310 nm.(fig.1)

Fig. 1: The λ_{max} for NCPZA
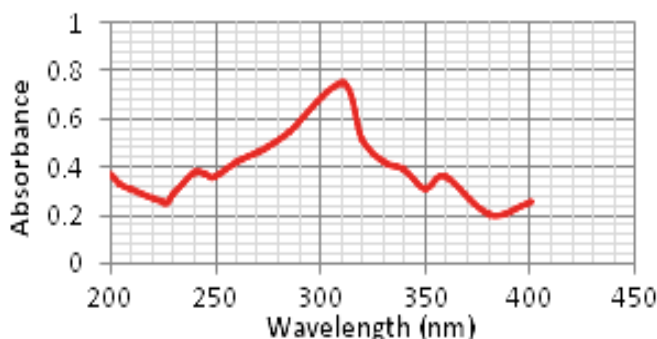
The solutions were kept in the thermostat to acquire the requisite temperature. A mixture of NCPZA, Perchloric acid, phosphotungstic acid, Acetic acid and appropriate quantity of water was taken in a Pyrex boiling tube. The diols solutions were added rapidly, maintaining pseudo order condition i.e. [Diol] >> [NCPZA]. The reaction was maintained using UV-visible double beam spectrophotometer at 310 nm. The rate constants (k_{obS}) were determined from optical density (O.D.) against regular intervals time (t).

The kinetic reactions were allowed for more than 70-80% completion of reaction and first order kinetics was observed. The optical density (D) will be substituted for the concentration changes required the rate law. The optical density (D) of a single chemical species in solution related to its concentration by the Beer-Lambert law to measure first order rate law by equation -

$$k = \frac{2.303}{t} \log \frac{D_0}{(D_0 - D_t)} \quad \ldots \ldots (1)$$

Where, D_0 is the optical density at zero time and, D_t at is the optical density at time 't'. The rate constants, k_{obs} were reproducible within ± 5%.

STOICHIOMETRY AND PRODUCT ANALYSIS

In order to find out the total amount of oxidant consumed by oxidation one mole of substrate, various sets of reaction mixture were taken in which concentration of oxidant was large excess than that of substrate. The entire conical flasks containing the reaction mixture were allowed to stand for several 72Hrs. at room temperature. The NCPZA un-reacted in each reaction mixture is, then estimated separately, periodically by titrating against left a definite volume of the reaction mixture iodometrically[19]. Thus, the amount of NCPZA used up to oxidize a definite quantity of each substrate is completely amount calculated, it is found that for complete oxidation of one mole of each diol, one mole of NCPZA is required. The stoichiometric equations empirically can be therefore, represented as:
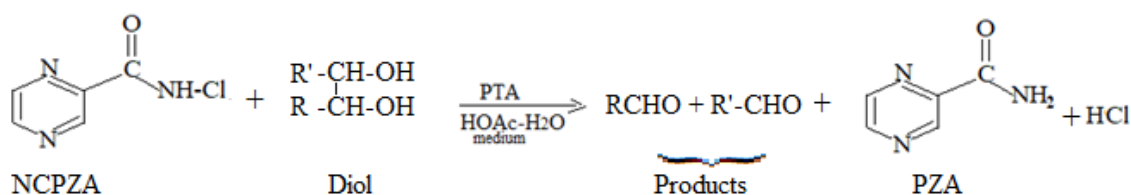
Where, R= -H, R'= -CH$_3$, in case of propan-1, 2-diol and, R'& R stand for -CH$_3$, in case of butan-2, 3-diol

RESULTS AND DISCUSSION

Effect of oxidant concentration: The oxidation is carried out with different initial concentrations of NCPZA. The rate constant in each run is determined by the slope of the tangent line drawn from the graph, which is plotted as log (a-x) versus time or log (D$_0$-D$_t$) versus time. With the help of these observed rate constant values and the corresponding NCPZA concentration, the value of -dc/dt was calculated. The plots of log (a-x) or log (D$_0$-D$_t$) vs. time are linear with nearly uniform slope (Fig.1). Therefore, it is, concluded that the order of reaction is one with respect to oxidant.

Effect of substrate concentration: In order to study the effect of [diol] on the rate of oxidation, the reaction is studied over a five-fold variation in [diol] at constant concentrations of all other reactants at fixed temperature. The plot of k$_1$ vs. [diol] is initially linear but bent towards x-axis (Fig. 3). The double reciprocal plots of 1/k$_1$ vs. 1/[diol] intercepted on y-axis(Fig.4). Suggesting that a rigid complex is formed during the course of oxidation and exhibiting Fractional order kinetics with respect to [diol].

Effect of phosphotungstic acid concentration: The effect of phosphotungstic acid concentration on the rate of oxidation is studied by varying [PTA] while keeping the concentration of other reactants constant (Table: 1). The plots of k$_1$ versus log [PTA] are linear with unit slope indicating first- order dependence of [PTA] on the rate of oxidation.

Effect of HClO$_4$ acid concentration: The influence of variation of acid strength on the reaction rate is studied by varying the concentration of added HClO$_4$. The reaction rate slightly (say negligible as comparison to PTA) increases with increasing acid strength (Table: 2), the plots of k$_1$ versus [HClO$_4$] are linear with positive slope.

Effect of dielectric constant of the medium: An increase in the rate constant slightly(almost negligible) is noticed on increasing the dielectric constant of the medium (Table: 3). The plot of log k1 versus 1/D, where D is the dielectric constant of the medium, gives straight line with positive slope.

Effect of NaClO$_4$·H$_2$O and KCl concentrations: Added sodium perchlorate and KCl has a considerable influence on the rate of oxidation. The rate increases slightly with increase in the concentration of NaClO4·H2O. This result is an indication of the participation of charged species in the rate - determining step.

Effect of pyrazinamide concentrations: The effect of one of the products of the oxidation has been investigated by adding various [pyrazinamide], keeping all other reactant concentration as constant. There is a slight decrease in reactivity with the increase in the initially added concentration of pyrazinamide (PZA). The retardation of rate on the addition of pyrazinamide suggests a pre-equilibrium step that involves a process in which pyrazinamide is one of the products (Table 4).

The addition of acrylonitrile, which is a very good trapper of free radical do not initiate polymerization indicating the absence of free radical species in the reaction sequence. The oxidation of Et.-1,2-diol has been studied at different temperatures (303-318 K). The temperature dependence on the rates of oxidation is determined by plotting log kobs versus 1/T. From the plot, the Arrhenius and thermodynamic activation parameters are evaluated (Table 5).

Reactive species of oxidant and substrate: Before predicting a probable mechanism, the most active oxidizing species has to be identified. This observation coupled with slight enhancement in the reaction rate with ionic strength of the medium also supports the participation of one ionic species in the rate determining step. Therefore H$_2$O$^+$Cl are the probable oxidizing species[13-15] under the present experimental condition. The proton released during the reaction by PTA alter sufficient reaction rate but are responsible for protonation of HOCl, Protonated H$_2$O$^+$Cl. are involved in reaction mechanism which may be attributed to the slightly positive effect of variation of mineral acid on the reaction rate. The neutral molecule form of Ethan-1,2-diols is pronounced as reacting species of substrate .
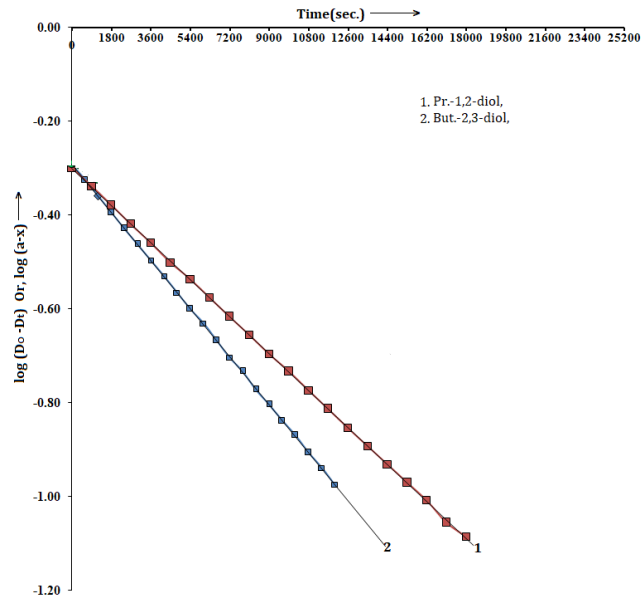
Fig.2: Comparative plot of log $(D_o- D_t)$ or, log (a-x) Vs. Time (sec.) for rate dependency on initial concentrations oxidant [NCPZA]=2.50×10^{-3}(mol.dm.$^{-3}$), (1-2);[Diol]=2.50×10^{-3}(mol.dm.$^{-3}$),(1-2); [PTA] =1.25×10^{-3}(mol.dm.$^{-3}$),(1-2); HOAc-H_2O = 40% (v/v)), (1-2); Temperature=308 K), (1-2).
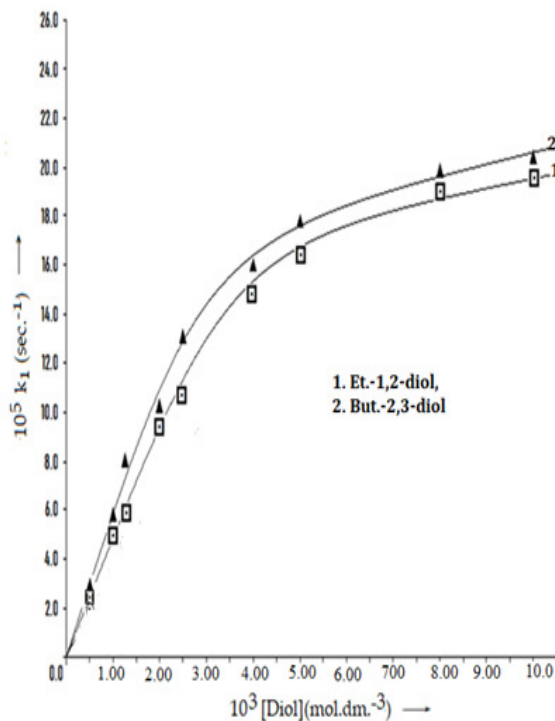
Fig. 3: A comparative plot of k_1 vs. [Diol]

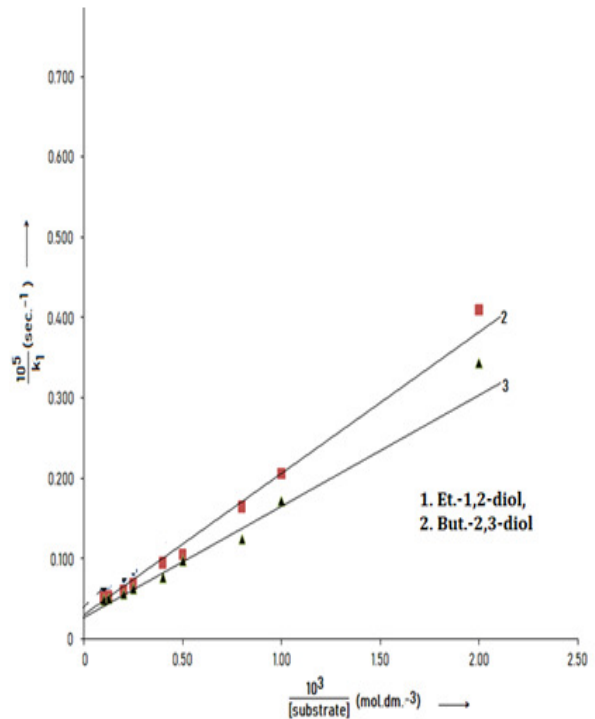| [NCPZA]$\times 10^4$ | = | 2.50(mol.dm.$^{-3}$) , (1,2) ; |
[PTA]$\times 10^4$	=	1.25 (mol.dm.$^{-3}$), (1,2) ;
HoAc-H_2O)	=	40% (v/v) , (1,2) ;
Temperature	=	308 K , (1,2) ;

Fig. 4: A comparative double reciprocal plot of 1/ k_1 vs. 1/[Diol]

[NCPZA]$\times 10^4$	=	2.50(mol.dm.$^{-3}$) , (1,2) ;
[PTA]$\times 10^4$	=	1.25 (mol.dm.$^{-3}$), (1,2) ;
HoAc-H_2O	=	40% (v/v) , (1,2) ;
Temperature	=	308 K , (1,2) ;

Table: 1

Effect of phosphotungstic acid concentration

[Diol]=1.25×10^{-3}(mol.dm.$^{-3}$), (1,2); [NCPZA]=2.00×10^{-3}(mol.dm.$^{-3}$) (1,2);

HOAc-H_2O=40 % (v/v),(1,2); Temperature=308 K (1,2) .

10^4[PTA] (mol.dm.$^{-3}$)	Pr.-1, 2-diol	But.- 2, 3-diol
	← $10^5 k_1$(sec.$^{-1}$) →	
0.50	6.50	8.40
1.00	8.50	10.70
1.25	10.11	13.09
2.00	11.60	15.80
2.50	13.00	17.00
4.00	18.40	23.20
5.00	19.80	27.60
8.00	30.60	38.00
10.00	35.30	46.20

Table: 2

Effect of $HClO_4$ acid concentration

[Diol]=1.25×10^{-3}(mol.dm.$^{-3}$), (1,2); [NCPZA]=2.00×10^{-3}(mol.dm.$^{-3}$) (1,2);

[PTA]=1.25×10^{-4}(mol.dm.$^{-3}$) (1,2);HOAc-H_2O=40 % (v/v),(1,2); Temperature=308 K (1,2) .

10^4[H^+](mol.dm.$^{-3}$)	Pr.-1, 2-diol	But.- 2, 3-diol
	← $10^5 k_1$(sec.$^{-1}$) →	
0.50	10.19	13.13
1.00	10.26	13.18
1.25	10.33	13.20
2.00	10.41	13.23
2.50	10.54	13.31
4.00	10.78	13.49
5.00	10.83	13.54
8.00	11.12	13.62
10.00	11.20	13.81

Table: 3

Effect of dielectric constant of the medium:

[Diol]=1.25×10^{-3}(mol.dm.$^{-3}$)(1,2); [NCPZA]=2.00×10^{-4}(mol.dm.$^{-3}$) (1,2);

[PTA]=1.25×10^{-4}(mol.dm.$^{-3}$) (1,2); Temperature=308K(1,2)

HOAc-H_2O % (v/v)	1/D	Pr.-1, 2-diol	But.- 2, 3-diol
		← $10^5 k_1$(sec.$^{-1}$) →	
20	17.17	9.63	12.75
30	19.15	9.92	12.92
40	21.98	10.11	13.09
50	25.64	10.13	13.19
60	30.36	10.25	13.24

Table: 4
Effect of pyrazinamide concentrations:
[Diol]=1.25×10^{-3}(mol.dm.$^{-3}$), (1,2); [NCPZA]=2.00×10^{-3}(mol.dm.$^{-3}$) (1,2);
HOAc-H_2O=40 % (v/v),(1,2); Temperature=308 K (1,2) .

Table: 5

10^4[PZA] (mol.dm.$^{-3}$)	Pr.-1, 2-diol	But.- 2, 3-diol
	$\longleftarrow$ $10^5 k_1$(sec.$^{-1}$) $\longrightarrow$	
0	10.11	13.09
1.00	10.05	13.02
1.25	10.01	12.94
2.00	9.97	12.88
2.50	9.86	12.78
4.00	9.80	12.68
5.00	9.73	12.53
8.00	9.60	12.49
10.0	9.53	12.41

Thermodynamic activation parameters
[Diol]=1.25×10^{-3}(mol.dm.$^{-3}$), (1,2); [NCPZA]=2.00×10^{-3}(mol.dm.$^{-3}$) (1,2);
HOAc-H_2O=40 % (v/v),(1,2); Temperature=308 K (1,2) .

Diol	E_a KJ mol^{-1}	A s^{-1}	$\Delta H^{\#}$ KJ mol^{-1}	$\Delta G^{\#}$ KJ mol^{-1}	$\Delta S^{\#}$ JK^{-1} mol^{-1}
Pr.-1,2-diol	55.90 ±0.76	4.134×10^4 ±0.22	57. 61 ±0.64	-82.37 ±0.598	-101.75 ±0.98
But.-2,3-diol	52.64 ±0. 63	3.815×10^5 ±0.35	48. 95 ±0.63	-78.26 ±0.60	-96.52 ±0. 76

MECHANISM: In view of the above experimental kinetic data, facts and finding, a suitable mechanism has been proposed for the PTA catalyzed oxidation of diols–NCPZA system as:
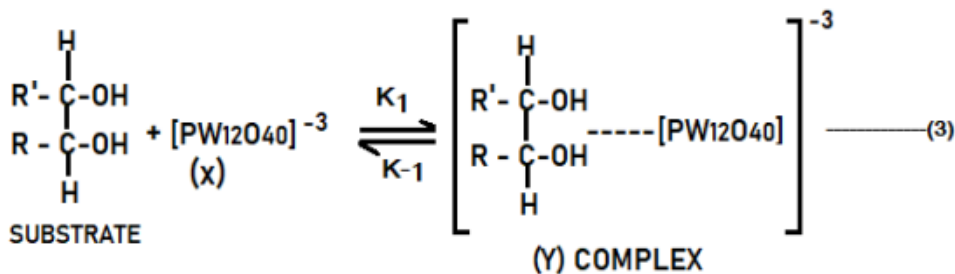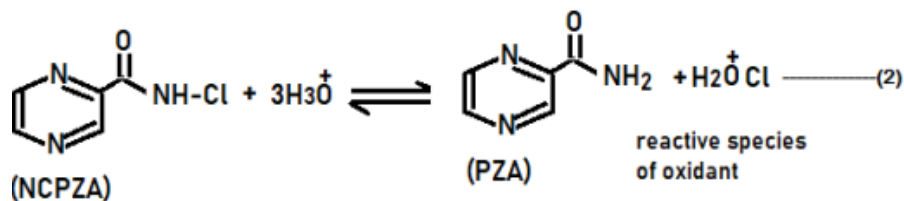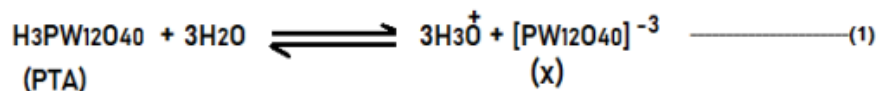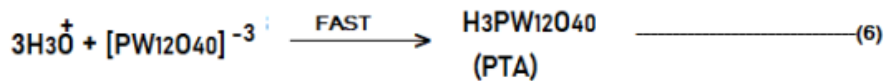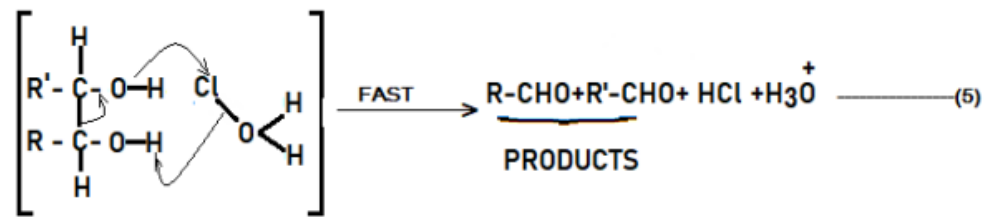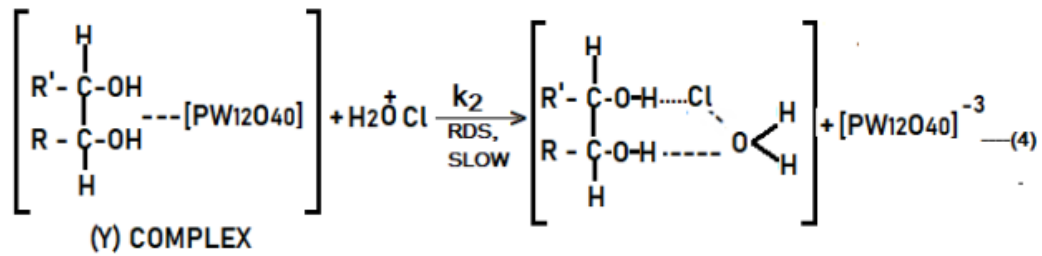
R- and R' are standing for H and CH3-, in case of propane-1,2-diol and , R- and R' are standing for CH3-, in case of butane-2,3-diol.

RATE LAW:

The reaction rate in term of consumption of concentration of reaction during species H_2O^+Cl of oxidant (NCPZA) may be expressed as:

$$-\frac{d}{dt}[H_2O^+Cl] = k_2[Y] \dots\dots\dots\dots\dots. (7)$$

Applying steady state treatment to the concentration of [Y], we can determine the concentration of [Y] as;

$$\frac{d[Y]}{dt} = K_1[X][S] - K_{-1}[Y] - k_2[Y] = 0 \quad --- (8)$$

Or,

$$[Y] = K_{-1} + k_2 = K_1[X][S] \quad ----(9)$$

Or,

$$[Y] = \frac{K_1[X][S]}{K_{-1} + k_2} \quad ----(10)$$

On substituting the value of [Y]in equation (7) we get-

$$-\frac{d}{dt}[H_2O^+Cl] = \frac{k_2 K_1[X][S]}{(K_{-1} + k_{2)}} \quad ----(11)$$

$$[X]_T = [X]\left(1 + \frac{K_1[S]}{(K_{-1} + k_2)}\right) \quad ----(12)$$

$$[X]_T = \frac{[X] + K_1[X][S]}{(K_{-1} + k_2)} \quad ----(13)$$

$$[X] = \frac{[X]_T + (K_{-1} + k_2)}{(K_{-1} + k_2) + K_1[S]} \quad ----(14)$$

On comparing equation (11) and (14) we get as:

$$-\frac{d}{dt}[H_2O^+Cl] = \frac{k_2 K_1[X]_T[S]\{K_{-1} + k_2\}}{\{K_{-1} + k_2\}(K_{-1} + k_2) + K_1[S]} \quad --(14)$$

$$-\frac{d}{dt}[H_2O^+Cl] = \frac{k_2K_1[X]_T[S]}{(K_{-1}+k_2) + K_1[S]} \qquad ----(15)$$

On assuming $k_2 >> K_{-1} + K_1[S]$

The neglecting the second term in the equation (14) we get-

$$-\frac{d}{dt}[H_2O^+Cl] = k_2[X]_T[S] \qquad ----(16)$$

$$k_{obs.} = k_2[X]_T[S] \qquad ----(17)$$

Above rate equation (17) explain all the facts of chemical kinetics observed experimentally.

CONCLUSION

Highly negative value of the free energy of activation and the enthalpy of activation indicate that the transition state is highly solvated, whereas the negative entropy of activation indicates that the transition state is highly solvated and the activated complex is more rigid.

The complexing capability of catalyst PTA was explained.

The stoichiometric ratio 1:1 of substrate and oxidant (NCPZA) was observed in the reaction kinetics. Oxidation product as acetic acid was isolated. Arrhenius plot has been discussed. In addition to order thermodynamic parameters have been evaluated, which supported our proposed mechanism and rate law. Study is probably the most useful in the field of pharmaceutics' for industrial application because of aliphatic aldehyde and diols are widely used as a fixative in the perfume industry and intermediates in pharmaceuticals (including antihistamines), agrochemicals.

REFERENCES

1. Jaya Gosain and Pradeep K Sharma ; Proc. Indian Acad. Sci. (Chem. Sci.), Vol. 115, No. 2, April 2003, pp 135–145.
2. Hemlata Gangwani, Pradeep K. Sharma and Kalyan K. Banerji, J. Chem. Research (S), 1999, 180-181
3. I. Yavari and D. Shaabani, J. Chem. Res. (S), 1994, 274.
4. B. P. Bandgar, S. B. Admane and S. S. Jare, J. Chem. Res. (S), 1998, 154.
5. A. Pareek, S. Kothari and K. K. Banerji, Indian J. Chem.Sect. B 1996, 35, 970
6. Indu Bhatia ,K.K.Benerji; J.Chem.Soc., 1999, Issue 12, Page 2655 to 2817
7. Jyoti Solanki , Namrata Joshi , Divya Chandora , Ammilal Rao , Laszlo Kotai and Pradeep K. Sharma; J. Appl. Chem., 2018, 7 (6):1762-1770S.
8. Pohani, P. Pancharia, P. Purohit, Shweta Vyas and Pradeep K. Sharma. Int. J. Chem. Sci., 2010, 8(3) 1365–1378.
9. Praveen K. Tandon , Shaista Zarrin Khanam and Santosh Bahadur Singh; The Open Catalysis Journal, 2012, 5,
10. K.K.Sen Gupta,Tapashi samanatha, S.N.Basu;Tetrahedron vol.42, issue 20, 1986, pp 5707-5714.
11. Rajeshwari, H.V.,Nandibewoor, S.T., Chimatadar, S.A., J. Ind. Chem. Soc.vol. 86, Issue 9, 2009, pp 936-941
12. Dayo Felix Latona; Adv. J.Chem. Sec.A, 2019, 2(3), 225-233
13. S. Parimala Vaijayanthi and N. Mathiyalagan Int. J. Chem Tech. Res. 2014,6(1), pp 01-07,
14. S. Parimala Vaijayanthi, N. Mathiyalagan; Int. J. Chem Tech. Res.2014,6(1),pp 08-15,
15. S. Parimala Vaijayanthi, N. Mathiyalagan *International Letters of Chemistry, Physics and Astronomy 2013, Vol. 16, pp*