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Pd(II) catalysis in oxidation of D-ribose and arabinose by chloramine-T in acidic medium: A kinetic study

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ABSTRACT

Kinetic investigations on Pd(II) catalyzed oxidation of D-ribose and D-arabinose by acidic solution of chloramine-T in the presence of mercuric acetate, as a scavenger have been made in the temperature range of 30°-45°C. The rate shows first order kinetics in case of chloramine-T and order of reaction is zero and one with respect to substrate and Pd(II) respectively. Increase in [Cl-] showed positive effect, while [H^+] showed zero effect. Negligible effect of mercuric acetate and ionic strength of the medium was observed. A transient complex, formed between $PdCl_2$ and chloramine-T. $PdCl_2$ being the reactive species of Palladium(II) chloride, disproportionates in a slow and rate determining step. Various activation parameters have been calculated. A suitable mechanism in agreement with observed kinetics has been proposed.

Key words: Pd(II) chloride, Chloramine-T, D-Ribose and D-Arabinose.

INTRODUCTION

Kinetics and Mechanism of palladium(II) catalyzed oxidation of some compounds by chloramine-T in perchloric acid medium has been reported[1-3.].Chloramine-T has been used as an oxidant in oxidation of some compounds such as amino alcohols[4] and α- amino acids[5] etc . The catalytic as well as inhibition action of Pd(II) in various redox reactions has been reported over the past decade, there has been a considerable interest on the speciation of aqueous $PdCl_2$ solutions and complexes[6-8] of Pd(II) with Cl^- ions. The use of palladium(II) chloride as a non toxic and homogeneous catalyst has been reported by several workers[9-12]. Scant work has been done for Pd (II) catalyzed oxidation by Chloramine-T which prompted us to undertake the kinetic study of Pd(II) catalyzed oxidation of sugars by Chloramine-T in acidic medium.

EXPERIMENTAL

Aqueous solution of sugars (E. Merck), Chloramine-T (CDH grade), and mercuric acetate (E. Merck) were prepared by dissolving the weighed amount of sample in triple distilled water. Perchloric acid (60%) of E. Merck grade was used as a source of hydrogen ions. Palladous(II) chloride (Johnson Matthey) was prepared by dissolving the sample in hydrochloric acid of known strength. All other reagents of analytical grade were available. Sodium perchlorate(E. Merck) was used to maintain the ionic strength of the medium. The reaction stills were blackened from outside to prevent photochemical effects.

Kinetics

A thermostated water bath was used to maintain the desired temperature within ±0.1°C. Requisite volume of all reagents including substrate, were taken in reaction vessel and thermostated at 35°C for thermal equilibrium. A measured volume of chloramine-T solution, which was also maintained separately at the same temperature, was rapidly poured into the reaction vessel. The kinetics was followed by examining aliquot portion of reaction mixture for chloramine-T iodometrically using starch as an indicator, after suitable time intervals.

RESULTS AND DISCUSSION

Reaction mixture containing excess of chloramine-T over sugars in different ratios were allowed to equilibrate at 35°C for about 24 h. The estimation of unconsumed oxidant showed that one moles of oxidant were consumed per moles of D-Fructose, according to following stoichiometric equation -

$$\mathrm{RCHO + H_2O + RNHCl \rightarrow RCOOH + RNH_2 + HCl}$$

Where, R= $C_4H_9O_4$. Identification of the end product formed in the above reaction i.e corresponding acids (1,2,3 trihydroxy butyric acid and arabonic acid for ribose and arabinose respectively) was carried out as follows-

Neutralised 5ml of acid with excess of ammonia in a boiling test tube.Then boiled the solution to remove excess of ammonia cooled and

Table 1: Effect of variation of oxidant, Substrate, Catalyst & perchloric acid at 35^{0}C

Oxidantx10^{3}M	**[Sub.] x 10^{2}M**	**[Pd(II)]x 10^{6}M**	**[HClO$_4$]x10^{3}M**	**(-dc/dt)x10^{7}ML^{-1}s^{-1}**	
		Ribo./Arabi		**Ribo.**	**Arabi.**
0.80	2.00	2.25	1.00	1.98	2.00
1.00	2.00	2.25	1.00	2.10	2.33
1.25	2.00	2.25	1.00	2.95	2.80
1.67	2.00	2.25	1.00	3.15	3.00
2.50	2.00	2.25	1.00	4.25	4.33
5.00	2.00	2.25	1.00	7.66	7.35
1.00	0.33	2.25	1.00	2.25	2.12
1.00	0.44	2.25	1.00	2.50	1.95
1.00	0.55	2.25	1.00	2.00	2.16
1.00	0.66	2.25	1.00	2.16	1.98
1.00	1.00	2.25	1.00	2.05	2.75
1.00	2.00	2.25	1.00	2.10	2.33
1.00	2.00	1.12	1.00	1.25	1.39
1.00	2.00	2.25	1.00	2.10	2.33
1.00	2.00	3.37	1.00	3.00	3.21
1.00	2.00	4.50	1.00	3.95	4.10
1.00	2.00	5.72	1.00	5.12	5.25
1.00	2.00	6.74	1.00	6.00	6.30
1.00	2.00	2.25	0.80	1.80	2.00
1.00	2.00	2.25	1.00	2.10	2.33
1.00	2.00	2.25	1.25	2.15	2.13
1.00	2.00	2.25	1.67	1.79	2.05
1.00	2.00	2.25	2.50	2.21	2.20
1.00	2.00	2.25	5.00	2.50	2.57

[Substrate] = 2.00 x 10^{-2} M
[HClO$_4$] = 1.00 x10^{-3} M
[Pd(II)] = 2.25 x 10^{-6} M
Temp. = 35^0

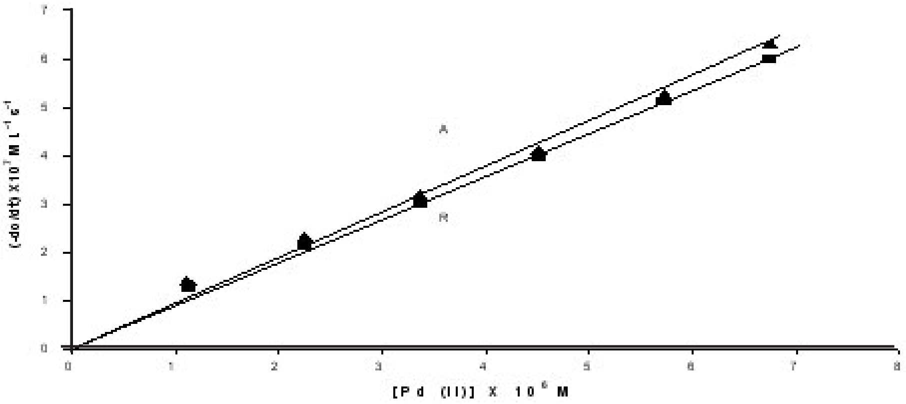

Fig. 1: Plot between [Pd(II)] x 10^6 M and (-dc/dt) x 10^7 mol l^{-1} s^{-1} for oxidation of D-ribose and D-arabinose

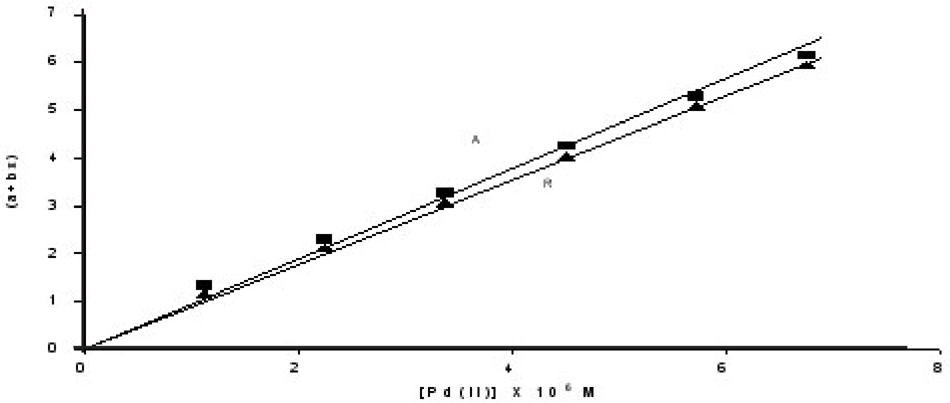

Fig. 2: Plot between [Pd(II)] x 10^6 M and (a+bx) for oxidation of D-ribose and D-arabinose

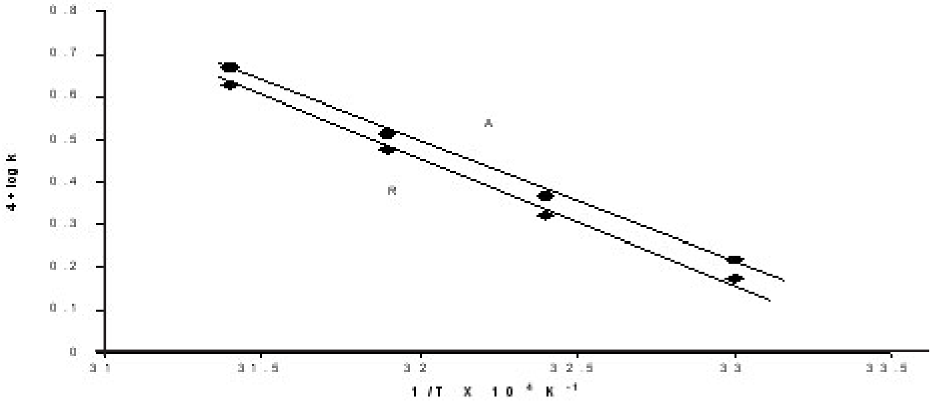

Fig. 3: Plot between log k and 1/T x 10^4 K^{-1} for oxidation of D-ribose and D-arabinose

added few drops of neutral $FeCl_3$ solution.A reddish brown colour ppt. is obtained, which confirms presence of carboxylic group.

The kinetic results were collected at several initial concentrations of reactants (Table 1). First-order rate constants i.e. (-dc/dt) were calculated from the plots of unconsumed chloramine-T Vs. time. It was observed that values of(-dc/dt) were doubled when the concentration of chloramine-T was made two

Table 2: Effect of variation of [KCl], mercury(II) acetate and sodium perchlorate at 35°C

[KCl] x 10^3M	[$NaClO_4$]x10^3M	[$Hg(OAc)_2$]x10^3M	(-dc/dt)x10^7ML^{-1}s^{-1}	
			Ribo.	Arabi.
0.80	-	1.25	1.91	2.00
1.00	-	1.25	2.10	2.33
1.25	-	1.25	2.13	2.40
1.67	-	1.25	2.40	2.51
2.50	-	1.25	3.00	2.80
5.00	-	1.25	3.33	2.95
1.00	0.80	1.25	2.11	2.16
1.00	1.00	1.25	1.98	2.50
1.00	1.25	1.25	2.15	2.21
1.00	1.67	1.25	2.05	2.00
1.00	2.50	1.25	2.50	2.31
1.00	5.00	1.25	2.33	2.05
1.00	-	0.80	1.97	2.00
1.00	-	1.00	2.40	2.11
1.00	-	1.25	2.10	2.33
1.00	-	1.67	2.31	2.16
1.00	-	2.50	2.11	2.21
1.00	-	5.00	2.00	2.18

[$Hg(OAc)_2$] = 1.25 x 10^{-3} M [KCl] = 1.00 x10^{-3} M Temp. = 35^0

Table 3: Activation parameters for D-Ribose and D-Arabinose

Rate constant(-dc/dt)x10^7ML^{-1} s^{-1} atdifferent T (°C)	D- Ribose	D- Arabinose
30°	1.49	1.65
35°	2.10	2.33
40°	3.00	3.27
45°	4.24	4.67
Arrhenius parameters		
ΔE^* , kJ mol $^{-1}$	63.75	57.45
log A	11.13	10.12
ΔS^* , JK^{-1} mol^{-1}	-8.57	-13.13
ΔG^*, kJ mol^{-1}	74.84	74.44
ΔH^*, kJ mol^{-1}	72.20	70.39
At 35°C		

[$HClO_4$] = . 1.00 x 10^{-3} M [Chloramine-T] = 1.00 x 10^{-3} M

[KCl] = 1.00 x 10^{-3} M [Pd(II)] = 2.25 x10^{-6} M times, showing thus first-order dependence on chloramine-T. The kinetic results recorded at various [Pd(II)], ionic strengths of the medium along with kinetic effects on successive addition of mercuric acetate, potassium chloride and sodium perchlorate are given in Table2.First order dependence on [Pd(II)] is evident from close resemblance between the slope values (6.25 x $10^{-2}$for ribose and 2.75 x 10^{-2} for D-arabinose at 35º),of (-dc/dt) Vs [Pd(II)] (Fig.1) and average of experimental k_1 (dc/dt/[Pd(II)])values (6.33 x 10^{-2} for D-ribose and 2.80 x10^{-2} for D-arabinose at 35^0 respectively). This can also justified by least square method. (Fig.2)

Negligible effect of variation of ionic strength of the medium, addition of mercuric acetate and positive effect of chloride ions on reaction rate was obvious from the kinetic data in Table 2. Change in ionic strength has a negligible effect. Kinetic results obtained on varying concentrations of hydrogen ions indicate negligible effect of hydrogen ion variation, which means rate of reaction is not affected by increase or decrease of [H^+] concentrations.

The rate measurement were taken at 30°-45°C and specific rate constants were used to draw a plot of log k Vs. 1/T, which was linear (Fig.3). The value of energy of activation (ΔE*), Arrhenius factor (A), entropy of activation (ΔS*) and free energy of activation (ΔG*) were calculated from rate measurement at 30°, 35°, 40°, 45°C, and these values have been recorded in Table 3.

Negligible effect of mercuric acetate excludes the possibility of its involvement either as a catalyst or as an oxidant because it does not help the reaction proceed without chloramine-T. Hence the function of mercuric acetate is to act as a scavenger[11] for any Cl^- ion formed in the reaction. It helps to eliminate the parallel oxidation by Cl_2 which would have been formed as a result of interaction between Cl^- and RNHCl ion.

Pd(II) chloride has been reported to give a number of possible chloro species dependent on pH of the solution. Under the experimental pH range in the present investigation [$PdCl_2$] has been proposed and confirmed as the reactive species[13] dominant in the pH range 1.00 to 3.00.

In acidic solution of chloramine-T quick formation of RNHCl[14] has been reported. First-order dependence on [chloramine-T] suggests that RNHCl is itself involved in slow step as an oxidant. The kinetic results reported in Table 1, 2 and 3 and the above statements lead us to suggest the following reaction scheme which gives the details of various steps in title reaction.

Rate Law

Cl^- exist as the following equilibrium in acidic solution of palladium(II) chloride-

$$\underset{[C_1]}{PdCl^+} + Cl^- \underset{k_{-2}}{\overset{k_1}{\rightleftharpoons}} \underset{[C_2]}{PdCl_2} \qquad ...(1)$$

Positive effect with respect to Cl^- in the present investigation suggests that the equilibrium would shift to the right. Therefore [$PdCl_2$] is the active species of palladium(II) chloride in acidic media.

$$k_2$$

$$\underset{[C_2]}{[PdCl_2]} + RNHCl \xrightarrow[\text{slow step}]{k_2} \underset{[C_3]}{[RNHCl\text{---}PdCl_2]} \qquad ...(2)$$

$$\underset{[C3]}{[RNHCl.......PdCl_2]} + RCHO + H_2O \rightarrow PdCl_2 + RCOOH + RNH_2 + HCl \qquad ...(3)$$

Now considering the above steps and applying the steady- state treatment with reasonable approximation, the rate law may be written in term as-

$$\frac{-d[RNHCl]}{dt} = k_2[C_2][RNHCl]$$

$$Rate = k_2\ [C_2]\ [RNHCl] \qquad ...(4)$$

$$[Pd(II)]T = [C_1] + [C_2] \qquad ...(5)$$

$$\frac{d[C_1]}{dt} = k_{-1}[C_2] - k_1[C_1]\ [Cl^-] \qquad ....(6)$$

$$[C_1] = \frac{k_{-1}[C_2]}{k_1[Cl^-]} \qquad ...(7)$$

By putting the value of $[C_1]$ in equation (5)

$$[Pd(II)]_T = \frac{k_{-1}[C_2]}{k_1[Cl^-]} + [C_2] \quad [K_1 = k_1 \backslash k_{-1}]$$

$$[Pd(II)]_T = \frac{[C_2]}{k_1[Cl^-]} + [C_2]$$

$$[Pd(II)]_T = \frac{[C_2] + K_1[Cl^-][C_2]}{k_1[Cl^-]} \qquad ...(8)$$

$$[C_2] = \frac{[Pd(II)]_T\ K_1[Cl^-]}{1+K_1[Cl^-]}$$

By putting the value of $[C_2]$ in equation (4)

$$\text{Rate} = \frac{k_2\ K_1\ [Pd(II)]_T\ [Cl^-]\ [RNHCl]}{1+K_1[Cl^-]}$$

CONCLUSION

The experimental results as shown reveal that the reaction rate doubles when the concentration of catalyst is doubled. The rate law equation is in conformity with all kinetic observations and proposed mechanistic steps are supported by the negligible effect of ionic strength. The high positive values of free energy of activation (ΔG*) indicates highly solvated transition state, while fairly high negative values of entropy of activation (ΔS*) suggest the formation of an activation complex with reduction in the degree of freedom. From the present investigation, it is concluded that RNHCl is the reactive species of chloramine-T in acidic medium and the reactive species of Pd(II) in acidic medium is $[PdCl_2]$ under the experimental pH range.

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