Comparative study on Pd(II) and Ru(III) catalyzed oxidation of α-amino-β-hydroxypropionic acid (dl-serine) by acid bromate: A kinetic study

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ABSTRACT

Comparative study on Pd(II) and Ru(III) catalyzed oxidation of dl -serine and dl- threonine by acidic solution of potassium bromate in the presence of mercuric acetate, as a scavenger have been made in the temperature range of 30°-45°C.In case of both catalyst rate shows zero order kinetics in bromate [BrO_3^->] and order of reaction is one with respect to substrate and Pd(II) and Ru(III) 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 amino acid. [$PdCl_2$] being reactive species of Palladium(II) chloride in 1:1 ratio, disproportionates in a slow and rate determining step while in case of Ru(III) a transient complex, formed between [$RuCl_6$]$^{3-}$ and amino acid. ([$RuCl_6$]$^{3-}$ being reactive species of ruthenium (III) chloride) in 1:1 ratio, 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: Palladium(II) Chloride, Ruthanium (III) Chloride, Potassium, bromate, dl-serine, Catalysis.

INTRODUCTION

Potassium bromate has been earlier used as an oxidant in oxidation of some compounds[1-7] in acidic media. Scant attention has been paid to the activity of potassium bromate in the presence of catalyst in the acidic media[8-10] ,but the result have not been interpreted so as to reveal a clear picture of the mode of catalyzed process. The utility of Palladium(II)chloride[11-12] and Ruthaniun(III) chloride[13-14] as a non toxic and homogeneous catalyst has been reported by several workers .

This prompted us to undertake the present investigation, which consists of "Comparative study on Pd(II) and Ru(III) catalyzed oxidation of α – amino-β-hydroxypropionic acid by acid bromate ". Mechanistic steps are discussed.

EXPERIMENTAL

Aqueous solution of amino acids (E. Merck), potassium bromate (BDH,AR), sodium perchlorate and mercuric acetate (all 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.Palladium(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 still were blackened from outside to prevent photochemical effects.
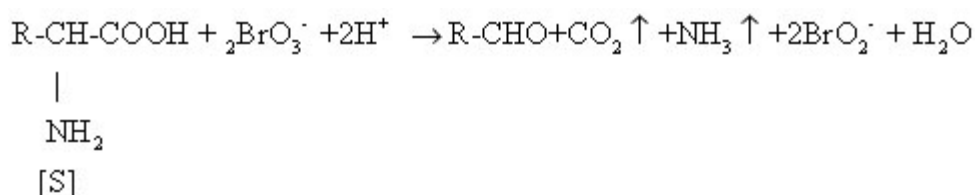
Kinetics

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 potassium bromate solution, which was also maintained seperately at the same temperature, was rapidly poured into the reaction vessel. The kinetics was followed by examining aliquot portion of reaction mixture for potassium bromate iodometrically using starch as an indicator, after suitable time intervals.

RESULT S AND DISCUSSION

In case of both catalyst reaction mixture containing excess of bromate over amino acids in different ratios were allowed to equilibrate at 35°C for about 24 h. The estimation of unconsumed bromate showed that two moles of bromate were consumed per mole of amino acid, according to following stoichiometric, equation –

$$R\text{-}CH\text{-}COOH + _2BrO_3^- + 2H^+ \rightarrow R\text{-}CHO + CO_2 \uparrow + NH_3 \uparrow + 2BrO_2^- + H_2O$$
$$\begin{array}{l} | \\ NH_2 \\ [S] \end{array}$$

Where,
R= CH_2OH-, for dl-serine and
S= $CH_2OH\text{-}CH(NH_2)\text{-}COOH$, for dl-serine
Oxidation products of dl-serine is $CH_2OH\text{-}CHO$
(dl-serine = α –amino-α-hydroxypropionic acid)

Further the product analysis by spotting techniques indicate the presence of aldehyde in the reaction mixture. So the product of oxidation should be the glycolic aldehyde (2-hydroxy ethanal) for dl-serine.

The kinetic results were collected at

several initial concentrations of reactants (Table 1). Zero-order rate constants i.e. (-dc/dt) were calculated from the plots of unconsumed bromate Vs. time. It was observed that values of (-dc/dt) were constant at all initial concentrations of bromate, showing thus zero-order dependence on [bromate]. It was found that as we increase the concentration of substrate the –dc/dt value increases and it becomes almost double by doubling the concentration of substrate indicating first order dependence on reaction rate(Fig.1). The kinetic results recorded at various [Pd(II)], [Ru(III)], ionic strengths of the medium along with kinetic effects
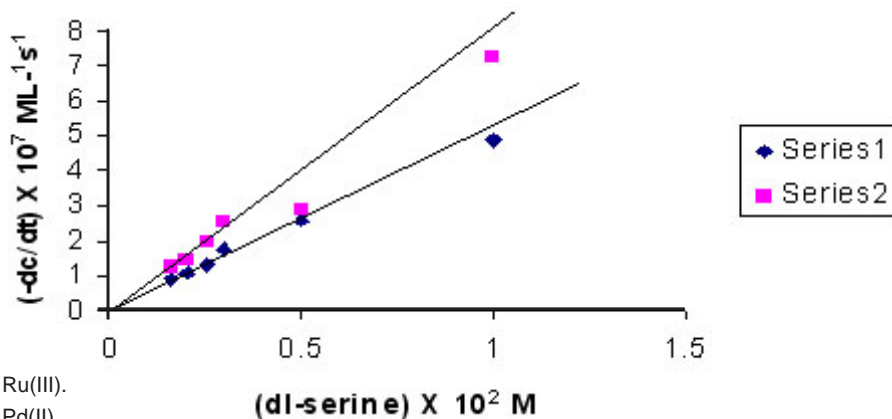
Serise 1 for Ru(III).
Serise 2 for Pd(II).

Fig.1: Plot of (–dc/dt) Vs. substrate(dl-serine) for Pd (II) & Ru(III) catalysts

on successive addition of mercuric acetate, potassium chloride and sodium perchlorate are given in Table2. First order dependence on [Pd(II)] and [Ru(III)] is evident from close resemblance between the slope values (1.88×10^{-2} and 2.59×10^{-2} at 35^0 for dl-serine respectively), of (-dc/dt) Vs. [Pd(II)] and [Ru(III)] plot (Fig.2) and average of experimental k_1 values (1.95×10^{-2} and 2.64×10^{-2} at 35^0 for dl-serine respectively).

The 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 only a marginal effect. Kinetic results obtained on varying concentrations of hydrogen ions indicate negligible effect of hydrogen ion variation, which means rate constant is not effected by increase or decrease of [H$^+$]

concentrations. The rate measurement were taken at 30°-45°C.

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 catalyst or as an oxidant because it does not help the reaction proceed without bromate. Hence the function of mercuric acetate is to act as a scavenger[15] for any Br$^-$ ion formed in the reaction. It helps to eliminate the parallel oxidation by Br_2 which would have been formed as a result of interaction between Br$^-$ and bromate ion.

**Table 1: Effect of variation of reactants on the reaction rate at 35°C**

[Bromate]x10³ M	[Substrate]x10² M	[HClO$_4$]x 10³ MPd(II)	-(dc/dt)x10⁷ ML^{-1}s^{-1}	
			Ru(III)dl-serine	dl-serine
0.80	0.50	1.00	3.61	2.52
1.00	0.50	1.00	2.86	2.56
1.25	0.50	1.00	3.65	2.30
1.67	0.50	1.00	3.57	2.33
2.50	0.50	1.00	3.61	2.65
5.00	0.50	1.00	3.41	2.45
1.00	0.16	1.00	1.23	0.85
1.00	0.20	1.00	1.46	1.05
1.00	0.25	1.00	1.91	1.30
1.00	0.30	1.00	2.52	1.75
1.00	0.50	1.00	2.86	2.56
1.00	1.00	1.00	7.27	4.88
1.00	0.50	0.80	3.51	2.78
1.00	0.50	1.00	2.86	2.56
1.00	0.50	1.25	3.73	2.66
1.00	0.50	1.67	3.65	2.54
1.00	0.50	2.50	3.68	2.72
1.00	0.50	5.00	3.67	2.65

[Hg(OAc)$_2$]	=	1.00×10^{-3} M		
[KCl]	=	1.00×10^{-3}M		
[dl-serine]	=	0.50×10^{-2} M		
[Ru(III)]	=	5.72×10^{-6} M		
[Pd(II)]	=	2.25×10^{-6} M		

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

[Bromate]×10^3 M	[NaClO$_4$]×10^2 M	[Hg(OAc)$_2$]x 10^3 MPd(II)	-(dc/dt)x10^7 ML^{-1}s^{-1}	
			Pd(II)dl-serine	Ru (III) di-serine
0.80	-	1.25	2.42	2.22
1.00	-	1.25	2.86	2.56
1.25	-	1.25	2.96	2.75
1.67	-	1.25	3.30	3.00
2.50	-	1.25	3.58	3.36
5.00	-	1.25	3.82	3.65
1.00	0.80	1.25	3.72	2.60
1.00	1.00	1.25	3.66	2.48
1.00	1.25	1.25	3.70	2.50
1.00	1.67	1.25	3.56	2.58
1.00	2.50	1.25	3.60	2.66
1.00	5.00	1.25	3.78	2.64
1.00	-	0.80	3.66	2.81
1.00	-	1.00	3.60	2.65
1.00	-	1.25	2.86	2.56
1.00	-	1.67	3.50	2.66
1.00	-	2.50	3.56	2.85
1.00	-	5.00	3.50	2.50

HClO$_4$	=	1.00×10^{-3}M
[dl-serine]	=	0.50×10^{-2} M
[Ru(III)]	=	5.72×10^{-6} M
[Pd(II)]	=	2.25×10^{-6} M

Table 3: Activation parameters for acid bromate oxidation of amino acids

Rate constant(-dc/dt)×10^{7}ML^{-1} s^{-1} atdifferent T (°C)	Pd(II) dl-serine	D- Arabinose
30°	1.99	1.86
35°	2.86	2.56
40°	5.15	3.81
45°	7.59	5.15
Arrhenius parameters		
ΔE* , kJ mol^{-1}	54.70	52.18
log A	9.84	9.25
ΔS* , JK^{-1} mol^{-1}	-14.37	-17.05
ΔG *, kJ mol^{-1}	73.30	74.26
Δ H*, kJ mol^{-1}	68.90	68.015
At 35°C		

[HClO$_4$]	=	1.00×10^{-3} M	[KBrO$_3$]	=	1.00×10^{-3} M
[KCl]	=	1.00×10^{-3} M	[dl- serine]	=	0.50×10^{-2} M
[Ru(III)]	=	5.72×10^{-6} M	[Pd(II)]	=	2.25×10^{-6} M
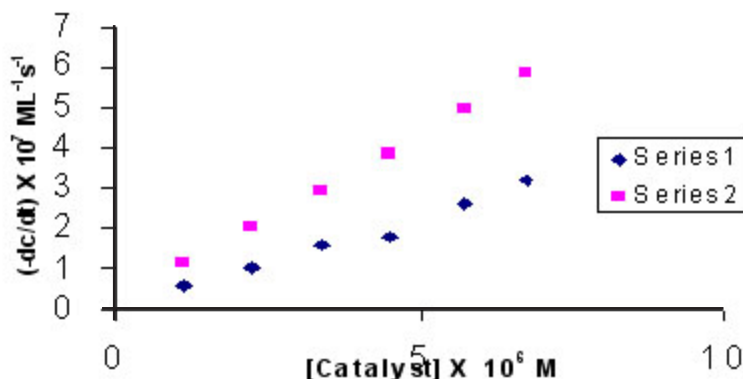
Serise 1 for Ru(III).
Serise 2 for Pd(II).

Fig. 2: Plot of (–dc/dt) Vs. catalysts for substrate(dl-serine)
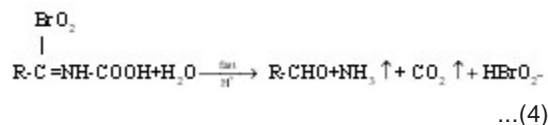
Pd(II) chloride has been reported to give a number of possible chloro species dependent on pH of the solution. Under the experimental pH range in the present investigation [PdCl$_2$] has been proposed and confirmed[16] as the reactive species dominant in the pH range 1.00 to 3.00.
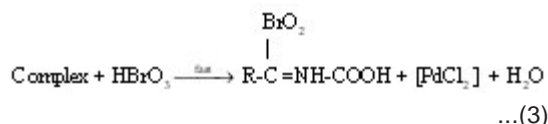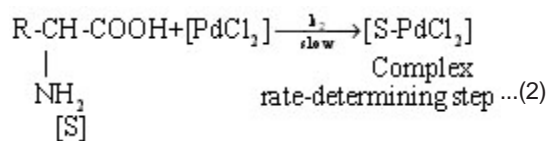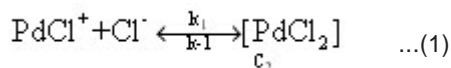
Ru(III) chloride has been reported to give a number of possible chloro species dependent on pH of the solution. Under the experimental pH range in the present investigation [RuCl$_6$]$^{3-}$ has been proposed and confirmed[17] as the reactive species dominant in the pH range 1.00 to 3.00.

In acidic solution of potassium bromate quick formation of HBrO$_3$ has been reported[5]. Zero-order dependence on [bromate] suggests that HBrO$_3$ formed in a fast step is itself involved in fast step as an oxidant.

Rate law

In case of Pd(II) the kinetic results obtained lead us to suggest the following reaction scheme which gives the details of various steps in title reaction.

$$\text{PdCl}^+ + \text{Cl}^- \underset{\text{k-1}}{\overset{\text{k}_1}{\longleftrightarrow}} \underset{C_2}{[\text{PdCl}_2]} \qquad ...(1)$$

$$\begin{array}{c} \text{R-CH-COOH} + [\text{PdCl}_2] \xrightarrow[\text{slow}]{\text{k}_2} [\text{S-PdCl}_2] \\ | \qquad\qquad\qquad\qquad\qquad\qquad \text{Complex} \\ \text{NH}_2 \qquad\qquad\qquad \text{rate-determining step} ...(2) \\ [\text{S}] \end{array}$$

$$\underset{|}{\overset{\text{BrO}_2}{\text{Complex}}} + \text{HBrO}_3 \xrightarrow{\text{fast}} \text{R-C}=\text{NH-COOH} + [\text{PdCl}_2] + \text{H}_2\text{O} \qquad ...(3)$$

$$\overset{\text{BrO}_2}{\underset{|}{\text{R-C}}}=\text{NH-COOH} + \text{H}_2\text{O} \xrightarrow[\text{H}^+]{\text{fast}} \text{R-CHO} + \text{NH}_3 \uparrow + \text{CO}_2 \uparrow + \text{HBrO}_2^- \qquad ...(4)$$

Now considering the above steps and applying the steady – state treatment with a reasonable approximation, the rate law may be written in term of rate of consumption of [BrO$_3^-$] as eq :-

$$\text{Rate} = \frac{k_2\, K_1\, [\text{Pd(II)}]_T\, [\text{Cl}^-]\, [\text{S}]}{1 + K_1\, [\text{Cl}^-]}$$
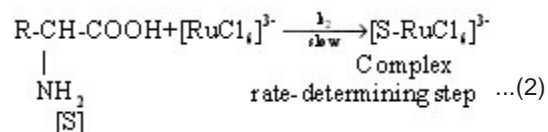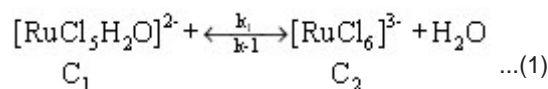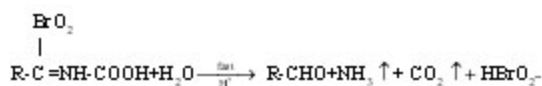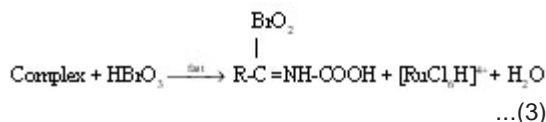
While in case of Ru(III) the kinetic results obtained lead us to suggest the following reaction scheme which gives the details of various steps in title reaction.

$$\underset{C_1}{[\text{RuCl}_5\text{H}_2\text{O}]^{2-}} + \underset{\text{k-1}}{\overset{\text{k}_1}{\longleftrightarrow}} \underset{C_2}{[\text{RuCl}_6]^{3-}} + \text{H}_2\text{O} \qquad ...(1)$$

$$\begin{array}{c} \text{R-CH-COOH} + [\text{RuCl}_6]^{3-} \xrightarrow[\text{slow}]{\text{k}_2} [\text{S-RuCl}_6]^{3-} \\ | \qquad\qquad\qquad\qquad\qquad\qquad \text{Complex} \\ \text{NH}_2 \qquad\qquad\qquad \text{rate-determining step} ...(2) \\ [\text{S}] \end{array}$$

$$\text{Complex} + HBrO_3 \xrightarrow{\text{fast}} \overset{\overset{\textstyle BrO_2}{\textstyle |}}{R\text{-}C} = NH\text{-}COOH + [RuCl_2H]^+ + H_2O$$
...(3)

$$\overset{\overset{\textstyle BrO_2}{\textstyle |}}{R\text{-}C} = NH\text{-}COOH + H_2O \xrightarrow{\text{fast}}{H^+} R\text{-}CHO + NH_3 \uparrow + CO_2 \uparrow + HBrO_2$$

Now considering the above steps and applying the steady-state treatment with a reasonable approximation, the rate law may be written in term of rate of consumption of $[BrO_3^-]$ as eq :-

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

CONCLUSION

The experimental results as shown reveal that the reaction rate doubles when concentration of the catalyst is doubled. The rate law equation is in conformity with all kinetic observations and the proposed mechanistic steps are supported by the negligible effect of ionic strength, which also explains the involvement of a dipole in the rate determining step. From present investigation it is concluded that $HBrO_3$, $[PdCl_2]$ and $[RuCl_6]^{3-}$ are reactive species of $KBrO_3$, palladium(II) chloride and ruthenium (III) chloride respectively in acidic media.

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