

KINETIC INVESTIGATIONS ON Pd(II) CATALYZED OXIDATION OF SOME AMINO ACIDS BY ACID BROMATE

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ABSTRACT: Kinetic investigations on Pd(II) 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. The rate shows zero order kinetics in bromate $[\text{BrO}_3^-]$ and order of reaction is one with respect to substrate and Pd(II) respectively. Increase in $[\text{Cl}^-]$ showed positive effect, while $[\text{H}^+]$ showed zero effect. Negligible effect of mercuric acetate and ionic strength of the medium was observed. A transient complex, formed between $[\text{PdCl}_2]$ and amino acid. Palladium chloride $[\text{PdCl}_2]$ being reactive species of Palladium (II) 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/phrases: Acidic medium, mercuric acetate, Pd catalyst, potassium bromated,

INTRODUCTION

Potassium bromate has been earlier used as an oxidant in oxidation of some compounds. in acidic media (Anandan and Gopalan, 1985; Reddy and Sundaram, 1985; Reddy and VijayaKumar, 1996; Sastri and Anrews, 1998; Veeraiah and Sondu, 1998; Srivastava *et al.*, 2001; Debnath *et al.*, 2002). Scant attention has been paid to the activity of potassium bromate in the presence of several catalyst in the acidic media (Singh and Srivastava, 1988; 1989a and b), but the results have not been interpreted so as to reveal a clear picture of the mode of catalyzed process.

The utility of Palladium (II) chloride as a non-toxic and homogeneous catalyst has been reported by several workers (Srivastava and Singh, 2008a and b).

We know that amino acids are molecules containing an amine group, a carboxylic acid group and a side-chain that varies between different amino acids. The key elements of an amino acid are carbon, hydrogen, oxygen, and nitrogen. The carbon atom next to the carboxyl group is called the α -carbon and amino acids with a side-chain bonded to this carbon are referred to as *alpha amino acids*. An alpha-amino acid has the generic formula $\text{H}_2\text{NCHRCOOH}$, where R is an organic substituent. These are the most common form found in nature. The amine and carboxylic acid functional groups found in amino acids allow them to have amphiprotic properties

(Creighton, 1993). When taken up into the human body from the diet, the 22 standard amino acids are used to either synthesize proteins and other biomolecules or are oxidized to urea and carbon dioxide as a source of energy (Sakami, 1963). The oxidation pathway starts with the removal of the amino group by a transaminase; the amino group is then fed into the urea cycle. The other product of transamidation is a keto acid that enters the citric acid cycle (Brosnan, 2000). Of the 22 standard amino acids, 8 are called essential amino acids because the human body cannot synthesize them from other compounds at the level needed for normal growth, so they must be obtained from food (Young, 1994). Others are known as non-essential amino acids that can be synthesized by body.

Amino acids are used for a variety of applications in industry, but their main use is as additives to animal feed. In this industry, amino acids are also used to chelate metal cations in order to improve the absorption of minerals from supplements, which may be required to improve the health or production of these animals (Ashmead, 1993).

This prompted us to undertake the present investigation, which consists of "Acid bromate oxidation of dl-serine and dl-threonine in the presence of Palladium (II) chloride as catalyst and mercuric acetate as a scavenger" in which serine is non essential while threonine is essential amino acid. 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.

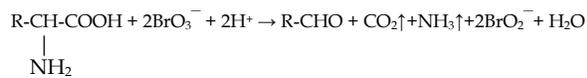
Kinetics

A thermostated water bath was used to maintain the desired temperature within $\pm 0.1^\circ\text{C}$. 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 separately 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.

RESULTS AND DISCUSSION

Reaction mixture containing excess of bromate over amino acids in different ratios was 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 the following stoichiometric equation



Where, R = CH_2OH -, for dl-serine
 R = $\text{CH}_3\text{-CH(OH)}$ -, for dl-threonine
 S = $\text{CH}_2\text{OH-CH(NH}_2\text{)-COOH}$, for dl-serine and
 $\text{CH}_3\text{-CH(OH)-CH(NH}_2\text{)-COOH}$, for dl-threonine
 Oxidation products of dl-serine and dl-threonine are $\text{CH}_2\text{OH-CHO}$ and
 $\text{CH}_3\text{-CH(OH)-CHO}$, respectively.
 (dl-serine = α -amino- β -hydroxypropionic acid and
 dl-threonine = α -amino- β hydroxy- n- butyric acid)

Further, the product analysis by spotting techniques indicates the presence of aldehyde in the reaction mixture. So the product of oxidation should be the glycolic aldehyde (2-hydroxy ethanal) and α -hydroxy propionaldehyde (3-hydroxy propanal) for dl-serine and dl-threonine, respectively.

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 versus time. It was observed that values of $(-dc/dt)$ were constant at all initial concentrations of bromate, showing thus zero-order dependence on [bromate]. The plots of $\log(-dc/dt)$ versus $\log(\text{substrate})$ are linear indicating first order dependence on substrate. 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 Table 2.

Table 1. Effect of variation of reactants on the reaction rate.

[Bromate] $\times 10^3$ M	[Substrate] $\times 10^2$ M	[HClO ₄] $\times 10^3$ M	$(-dc/dt)\times 10^7$ ML ⁻¹ s ⁻¹	
			dl-serine	dl-threonine
0.80	0.50	1.00	3.61	2.51
1.00	0.50	1.00	3.72	2.56
1.25	0.50	1.00	3.65	2.32
1.67	0.50	1.00	3.57	2.31
2.50	0.50	1.00	3.61	2.68
5.00	0.50	1.00	3.41	2.41
1.00	0.16	1.00	1.23	0.87
1.00	0.20	1.00	1.46	1.09
1.00	0.25	1.00	1.91	1.33
1.00	0.30	1.00	2.52	1.78
1.00	1.00	1.00	7.27	4.91
1.00	0.50	0.80	3.51	2.86
1.00	0.50	1.25	3.73	2.55
1.00	0.50	1.67	3.65	2.67
1.00	0.50	2.50	3.68	2.71
1.00	0.50	5.00	3.67	2.81

[Hg(OAc)₂] = 1.25×10^{-3} M; [KCl] = 1.00×10^{-3} M; [dl-serine] = 0.5×10^{-2} M; [dl-threonine] = 0.5×10^{-2} M;
 Temp. = 35°

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

[Pd(II)]x10 ⁶ M	[KCl]X10 ³ M	[NaClO ₄]x10 ³ M	[Hg(OAc) ₂]x10 ³ M	(-dc/dt)x10 ⁷ ML ⁻¹ s ⁻¹	
				dl-serine	dl-threo
1.12	1.00	-	2.25	1.85	1.67
2.25	1.00	-	2.25	2.86	2.57
3.37	1.00	-	2.25	4.28	4.15
4.50	1.00	-	2.25	5.35	5.00
5.72	1.00	-	2.25	6.85	6.35
6.74	1.00	-	2.25	8.05	7.95
2.25	0.80	-	2.25	2.42	2.22
2.25	1.00	-	2.25	2.71	2.57
2.25	1.25	-	2.25	2.96	2.78
2.25	1.67	-	2.25	3.30	3.04
2.25	2.50	-	2.25	3.58	3.36
2.25	5.00	-	2.25	3.82	2.60
2.25	1.00	0.80	2.25	3.72	2.48
2.25	1.00	1.00	2.25	3.66	2.50
2.25	1.00	1.25	2.25	3.70	2.58
2.25	1.00	1.67	2.25	3.56	2.66
2.25	1.00	2.50	2.25	3.60	2.64
2.25	1.00	5.00	2.25	3.78	2.80
2.25	1.00	-	0.80	3.66	2.66
2.25	1.00	-	1.00	3.60	2.64
2.25	1.00	-	1.67	3.50	2.80
2.25	1.00	-	2.50	3.56	2.66
2.25	1.00	-	5.00	3.50	2.48

First order dependence on [Pd(II)] is evident from close resemblance between the slope values (1.88×10^{-2} at 35° for dl-serine and 2.63×10^{-2} at 35° for dl-threonine, respectively), of $(-dc/dt)$ versus [Pd(II)] plot (Fig.1) and average of

experimental k_1 values (1.95×10^{-2} at 35° for dl-serine and 2.69×10^{-2} for dl-threonine at 35° respectively). This can also be justified by Least Square method. (Fig. 2)

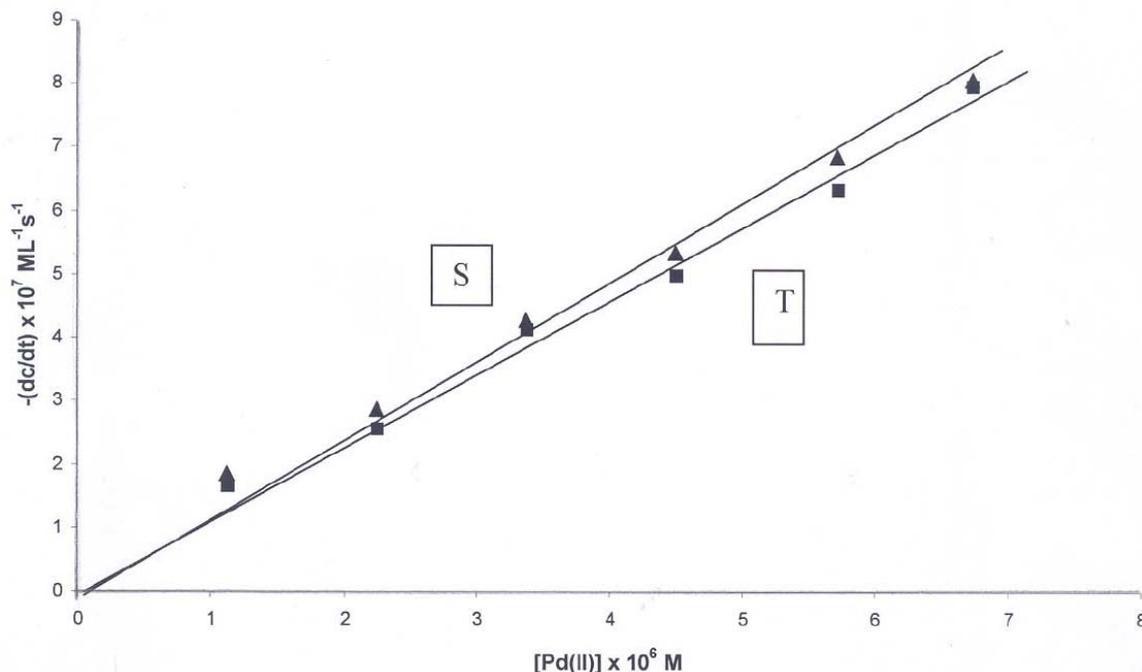


Fig. 1. Plot between [Pd(II)] x 10⁶ M and $(-dc/dt) \times 10^7 \text{ ML}^{-1} \text{ s}^{-1}$ for the oxidation of substrates (dl-serine (S) and dl-threonine (T) at 35°C, respectively).

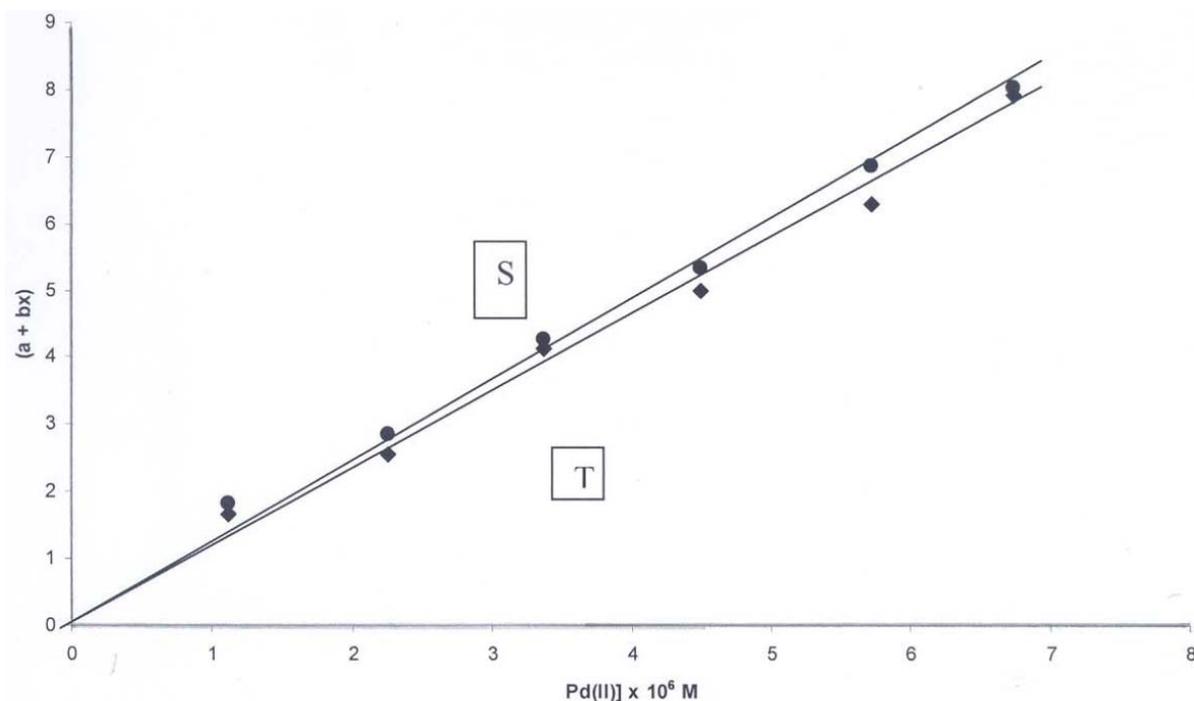


Fig. 2. Plot between $[\text{Pd(II)}] \times 10^6 \text{ M}$ and $(a + bx)$ for the oxidation of substrates (dl-serine (S) and dl-threonine (T) at 35°C , respectively). $[\text{KBrO}_3] = 1.00 \times 10^{-3} \text{ M}$; $[\text{dl-serine}] = 0.5 \times 10^{-2} \text{ M}$; $[\text{dl-threonine}] = 0.5 \times 10^{-2} \text{ M}$; $[\text{HClO}_4] = 1.00 \times 10^{-3} \text{ M}$; $[\text{Hg(OAc)}_2] = 1.25 \times 10^{-3} \text{ M}$; $[\text{Pd(II)}] = 2.25 \times 10^{-6} \text{ M}$.

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 $[\text{H}^+]$ concentrations.

The rate measurements were taken at $30^\circ\text{--}45^\circ\text{C}$ and specific rate constant was used to draw a plot of $\log(-dc/dt)$ versus $1/T$, which was linear.

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° and 45°C , and these values have been recorded in Table 3.

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

Rate constant $(-dc/dt) \times 10^7 \text{ ML}^{-1} \text{ s}^{-1}$ at different T ($^\circ\text{C}$)	dl-serine	dl-threonine
30 $^\circ$	1.99	1.89
35 $^\circ$	2.86	2.58
40 $^\circ$	5.15	3.83
45 $^\circ$	7.59	5.15
Arrhenius parameters		
ΔE^* , kJ mol $^{-1}$	54.70	52.20
log A	9.84	9.27
ΔS^* , JK $^{-1}$ mol $^{-1}$	-14.37	-17.04
ΔG^* , kJ mol $^{-1}$	73.30	74.25
ΔH^* , kJ mol $^{-1}$	68.90	69.02
At 35 $^\circ\text{C}$		

$[\text{HClO}_4] = 1.00 \times 10^{-3} \text{ M}$; $[\text{KBrO}_3] = 1.00 \times 10^{-3} \text{ M}$; $[\text{KCl}] = 1.00 \times 10^{-3} \text{ M}$;
 $[\text{dl-serine}] = 0.5 \times 10^{-2} \text{ M}$; $[\text{dl-threonine}] = 0.5 \times 10^{-2} \text{ M}$; $[\text{Pd(II)}] = 2.25 \times 10^{-6}$

The rate law is in agreement with all observed kinetics. The proposed mechanism is consistent with the activation parameters given in Table 3. The high positive values of free energy of activation (ΔG^*) indicate highly solvated transition state, while fairly high negative values of entropy of activation (ΔS^*) suggest the formation of an activated complex with reduction in degree of freedom of molecules.

CONCLUSION

The experimental results, as shown above, reveal that the reaction rate doubles when concentration of the catalyst Pd(II) 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 the present investigation, it is concluded that HBrO_3 and $[\text{PdCl}_2]$ are reactive species of KBrO_3 and Palladium (II) chloride, respectively, in acidic media.

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