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Kinetics of Oxidation of Alanine by Pyridiniumdichromate in The Presence of Perchloricacid Medium in DMSO-H2O (v/v) medium by Spectrophotometric method.

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ABSTRACT--*Kinetics of oxidation of alanine by pyridiniumdichromate (PDC) has been studiedspectrophotometrically in the presence of perchloric acid in DMSO-*H_2O *50% (v/v) medium. The reaction was first order dependence on PDC, alanine and fractional order with respect to* H^+*. The effect of solvent composition indicates that the reaction rate increases with an increase in the polarity of the medium. No significant effect was observed by added salts. The main oxidation product of L-alanine has been identified as corresponding carbonyl compound. The reaction does not induce the polymerization of acrylonitrile. The reaction has been investigated at different temperature and activation parameters were calculated.*

Keywords-- *Kinetics, Alanine, Pyridinium dichromate, Oxidation, Mechanism.*

I. INTRODUCTION

L-alanine is a non-essential amino acid and plays a crucial role as a building block of important proteins. L-alanine is easily washed away and lost in foods due to its strong hydrophilic (water soluble) properties. Foods with large amounts of L-alanine should therefore not be cooked or soaked for too long. L-alanine supplements are therefore often used in cases of h*ypoglycaemia* to prevent the organism from suffering low blood sugar or insuline shocks. The oxidation of alanine has received much attention because it support of the immune system and prevention of kidney stones. L-alanine is thus often as a remedy in orthomolecular medicine.

Sagar singh thakur and B. K. Dangarh[1-3] have reported the comparative study of oxidation of alanine and phenylalanine by pyridiniumdichromate spectrophotometrically in the presence of perchloric acid in acetic acid-aquo (v/v) medium. Shilpa Rathor *et al.*[4] reported the oxidation of alanine by PDC in the presence of perchloric acid in DMF-H20 (v/v) medium at 40ºC. S.Manivannan,[5] and K.Kaveri reported the oxidation of alanine by Trichloroisocyanuric acid in aqueous acetic acid medium. Ahmed Fawzy *et al.*[6] reported the Comparative Kinetic Study of Silver(I)-Catalyzed Oxidations of Alanine and Valine by Platinum (IV) in Perchloric and Sulfuric Acids Solutions.

Chromium compounds have been used in aqueous and nonaqueous medium for the oxidation of various organic substrates. Chromium (VI) reagents have been versatile and capable of oxidizing all the oxidizable

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organic moieties.[7] The development of Chromium (VI) reagents for the oxidation of organic substrates continues to be of interest.

Many such Cr (VI) reagents have been developed in recent years.[8-14] Pyridinium dichromate is also one such oxidant developed recently. It is a more efficient and mild oxidizing agent.[15] Few kinetic studies have been carried out on the oxidation of L-alanine using PDC in different solvent such as acetic acid and DMF but not in DMSO.

The most significant difference between DMSO and DMF is toxicity, which recommends DMSO as a safer replacement for DMF. DMSO is not hepatotoxic and does not cause reproductive problems. DMF behaves in many ways like DMSO, but it is not significantly nucleophilic. The theory of solvent polarity effects as formulated by Ingold[16], states that reactions in which charge is generated in the transition state should undergo a strong rate increase as the polarity of the medium is increased.

Literature survey reveals that no report is available on kinetics and mechanism of oxidation of L-Alanine by PDC has been studied spectrophotometrically in the presence of perchloric acid in DMSO-aquo 50% (v/v) medium. Hence we have tried to correlate the structure and reactivity in these oxidations.

II. MATERIALS AND METHODS

L-Alanine (Analar), Pyridinium dichromate (Aldrich) were used as supplied. Double distilled water was used throughout the investigation. All other reagents used were of"AnalaR" grade. The rate measurements were carried out at 300 C ± 1 ºC in 0.06M HClO4 under the condition [alanine] >> [PDC], in the solvent system of 50 % (v/v) DMSO - H2O . The progress of the reaction was followed by measuring the absorbance of PDC in one cm cell placed in the compartment of Infra instruments IR 513 C single beam spectrophotometer.

1.1. *Kinetic procedure*

The reactions were followed under pseudo first-order conditions by keeping large excess (x 10) of the alanine over PDC. The reactions were followed at constant temperatures (303K), by monitoring the decrease in [PDC] spectrophotometrically at 535 nm the pseudo first-order rate constant k_{obs}, was evaluated from the linear (r = 0.990-0.999) plots of log [PDC] against time for up to 80% completion of the reaction.

1.2. *Data analysis:*

Correlation analysis **was carried out using OriginPro 8.5 computer software. The goodness of the fit is discussed using the correlation coefficients and standard deviations.**

III. RESULTS AND DISCUSSION:

The results of oxidation of alanine by PDC are represented in table 1-6.

Effect of variation of concentration of alanine on the rate of reaction:

The oxidation of alanine with PDC in DMSO in presence of perchloric acid yields Acetaldehyde, by keeping constant [PDC] and [HClO4], the increase in concentration of Alanine(1.5x10-2 to 3.0x10-2) increases the rate

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of reaction (Table-1). The plot of the log of kobs versus log [alanine] for the different initial concentration of alanine is linear demonstrates that first order dependence of rate on alanine (Fig. 1).

Table 1: Effect of varying [alanine] on the rate of oxidation by PDC:

[PDC] = $1x10^{-3}$ $mol.dm^{-3}$ [$HClO_4$] = 6 x 10^{-3} $mol.dm^{-3}$

DMSO – H_2O = 50 % (v/v) Temperature = 308k

S.No	10^2[Alanine] mol.dm^{-3}	1.0	1.5	2.0	2.5	3.0
	Time (mins)	1+log[alanine]				
1	5	0.48996	0.45332	0.42651	0.41330	0.344392
2	10	0.47857	0.43297	0.41330	0.38739	0.330414
3	15	0.46538	0.41497	0.39967	0.37291	0.285557
4	20	0.45332	0.40140	0.38739	0.35984	0.271842
5	25	0.43933	0.39270	0.37107	0.33041	0.255273
6	30	0.42975	0.37658	0.35025	0.31597	0.238046
7	35	0.41330	0.36361	0.32222	0.30103	0.222716
Kobs x $10^4/S^{-1}$		0.9711	1.1093	1.2820	1.4315	1.5902

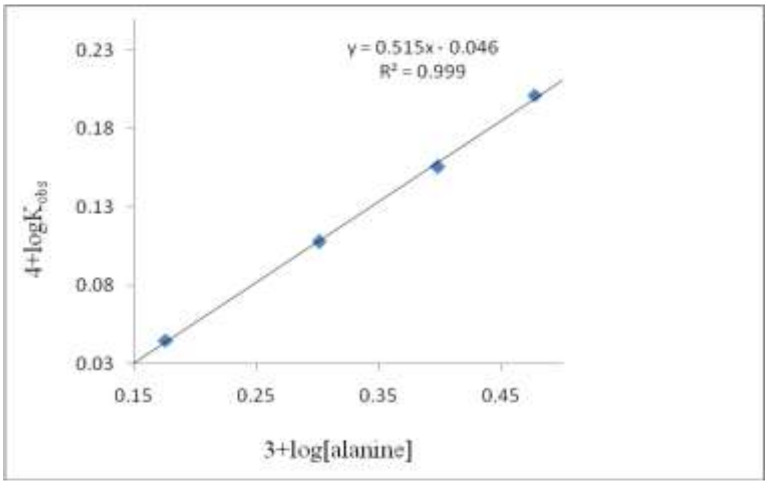

Fig.1: 4+log [Kobs] Vs 3+log [alanine]

Effect of varying [PDC] on the rate of oxidation of alanine:-

At constant [alanine] and [HClO4] by varying the concentration of [PDC] from 1.5 x 10^{-3} to 3.5 x 10^{-3} mol dm-3 rate of reaction is increases Table-2. The plot of log kobs versus log [PDC] for the different initial concentration of PDC is linear with positive slope presents the first order dependence of rate on PDC (Fig. 2).

TABLE 2: Effect of varying [PDC] on the rate of oxidation of [Alanine]

[Alanine] = 1×10^{-2} mol.dm^{-3} [$HClO_4$] = 6 x 10^{-3} mol.dm^{-3}
DMSO – H_2O = 50 % (v/v) Temperature = 303k

.No	10^3[QCC] mol.dm^{-3}	1.5	2	2.5	3	3.5
	Time (mins)	1+log[PDC]				
1	5	0.4133	0.49969	0.54283	0.60746	0.66932
2	10	0.38739	0.47857	0.52763	0.57287	0.64246
3	15	0.37291	0.43933	0.51188	0.54531	0.60959
4	20	0.35984	0.4133	0.48287	0.51983	0.57519
5	25	0.33041	0.39967	0.45025	0.49693	0.5563
6	30	0.31597	0.38739	0.42975	0.47422	0.53908
7	35	0.30103	0.37291	0.40824	0.45637	0.51983
Kobs x 10^4/S^{-1}		1.432	1.651	1.812	1.915	1.942

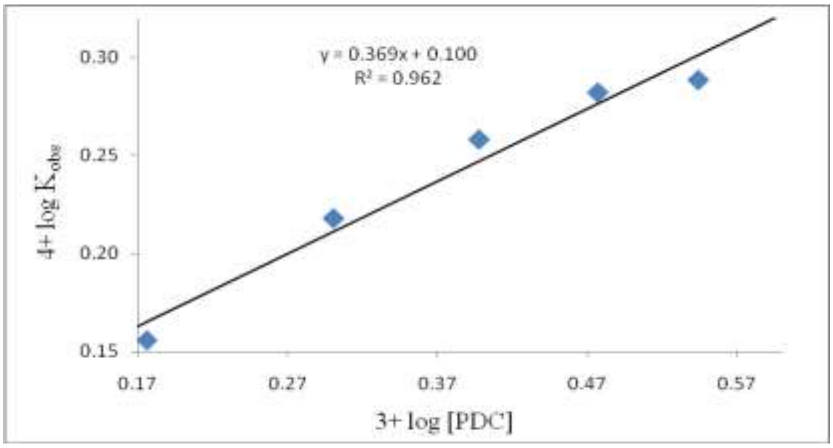

Fig.2: 4+ Logs (Kobs) Verses 3+Log [PDC]

Effect of varying [$HClO_4$] on reaction rate:

The rate of reaction was studied by varying perchloric acid concentration. The rate of reaction increased with increasing the concentration of perchloric acid and a plot of log [$HClO_4$] vs. log (K_{obs}) was linear with a less than unit slope indicate the fractional order dependence of rate on [H^+] Table-3, (Fig. 3).

Table – 3: Effect of varying [$HClO_4$] on the rate of oxidation of [alanine]

[PDC] = $1x10^{-3}$ mol.dm^{-3} [alanine] = 1 x 10^{-2} mol.dm^{-3}

DMSO – H_2O = 50 % (v/v) Temperature = 303k

S.No	10^3 [$HClO_4$] mol.dm^{-3}	6.0	9.0	12.0	15.0	18.0
	Time (mins)	1+ log(Absorbance)				
1	5	0.41330	0.43775	0.50106	0.55145	0.597695
2	10	0.38739	0.41497	0.47857	0.53275	0.585461
3	15	0.37291	0.40993	0.43933	0.51720	0.569374
4	20	0.35984	0.37840	0.41330	0.49276	0.550228
5	25	0.35025	0.35218	0.39967	0.47276	0.527630
6	30	0.31597	0.33846	0.38739	0.45332	0.492760
7	35	0.28780	0.31597	0.37291	0.40824	0.454845
Kobs x 10^4/S^{-1}		1.49	1.58	1.66	1.74	1.79

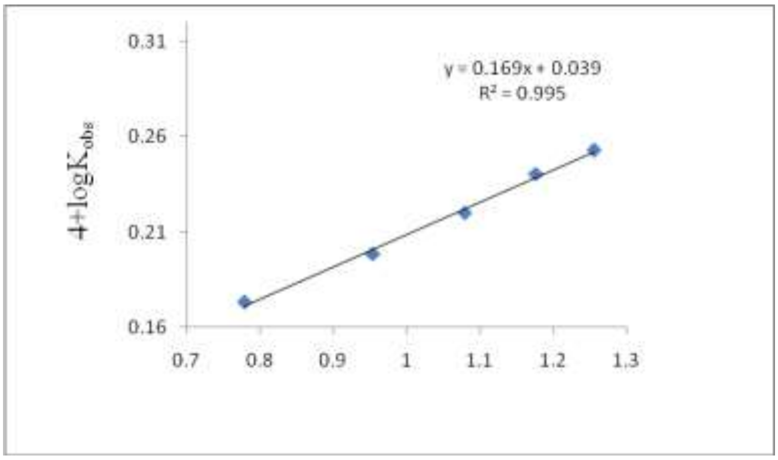

Fig.3: 4+Log (Kobs) Verses 3+Log [$HClO_4$]

Effect of Salts:

The effect of added salts on the reaction rate was studied by adding 0.001 mol dm^{-3} of the salts, by keeping the concentrations of alanine, $HClO_4$ and PDC constant. It was observed that the rate of oxidation does not alter by the addition of salts Table-4

Table 4: Effect of variation of [salts] on reaction rate

[PDC] = $1x10^{-3}$ mol.dm^{-3} [Alanine] = 1 x 10^{-2} mol.dm^{-3}
DMSO – H_2O = 50 % (v/v) Temperature = 303k
[$HClO_4$] = 6 x 10^{-3} mol.dm^{-3}

S.No	10^3[salts] mol.dm^{-3}	Kobs x $10^3/S^{-1}$
1	$MnSO_4$	0.0622
2	KCl	0.0635
3	NaCl	0.0622
4	$AgNO_3$	0.0631

Effect of dielectric constant (solvent composition):

Effect of solvent was studied by changing the proportion of DMSO and water (v/v), varied from 10 to 50%. Plots of log[absorbance] Vs time gave straight lines. From the slopes of these lines Kobs values were found out. [table-5]. As the rate of oxidation decreased, charged species are involved in the slow step.

Table 5: Effect of dielectric constant on reaction rate

[PDC] = $1x10^{-3}$ mol.dm^{-3} [Alanine] = 1 x 10^{-2} mol.dm^{-3}
[$HClO_4$] = 6 x 10^{-3} mol.dm^{-3} Temperature = 303k

S.No	[DMSO]	D	Kobs x 10^4 / S^{-1}	D^{-1}	log k_2
1	30%	69.02	2.36	0.0145	-1.627
2	35%	67.52	2.28	0.0148	-1.642
3	40%	65.98	2.05	0.0152	-1.688
4	45%	64.44	1.97	0.0155	-1.706
5	50%	62.9	1.65	0.0159	-1.783

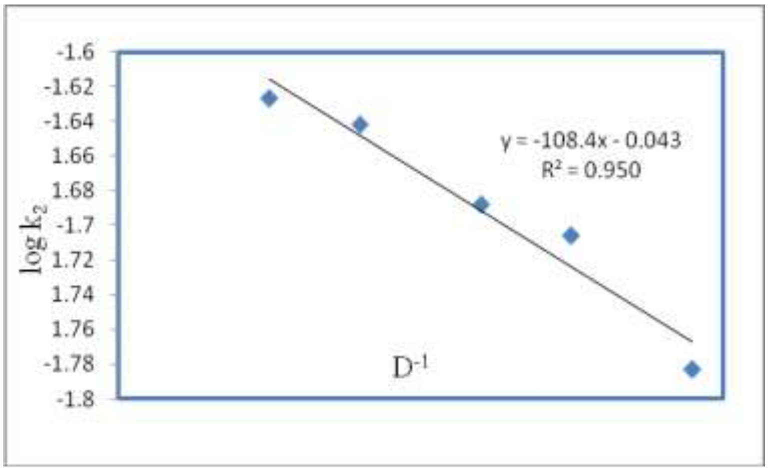

Fig.4: Log K_2 Verses D^{-1}

Effect of Temperature:

To study the effect of temperature on the rate of oxidation of alanine by PDC has been investigated at 308-323K by keeping the concentration of alanine, PDC & $HClO_4$ constant. Rate constants are given in Table-5. The Arrhenius plots of log k vs. 1/T were found to be linear (Fig. 4)**.**The activation energy (Ea) was calculated from the slope of the plots. From this value, the thermodynamic parameters $\Delta H^{\#}$, $\Delta S^{\#}$, $\Delta G^{\#}$ was evaluated Tabel-7.

Table-6: Effect of variation of Temperatures on reaction rate

[PDC] = $1x10^{-3}$ mol.dm^{-3} [alanine] = 1×10^{-2} mol.dm^{-3}

[$HClO_4$] = 6×10^{-3} mol.dm^{-3} DMSO-H_2O=50%(V/V)

S.No	Temp(K)	308	313	318	323
	Time (mins)	2+log [absorbance]			
1	5	0.098	0.090	0.086	0.080
2	10	0.084	0.080	0.080	0.075
3	15	0.079	0.070	0.070	0.068
4	20	0.071	0.060	0.060	0.059
5	25	0.070	0.050	0.055	0.048
6	30	0.058	0.055	0.049	0.041
Kobs x $10^4/S^{-1}$		3.1206	3.8345	3.8959	4.5945

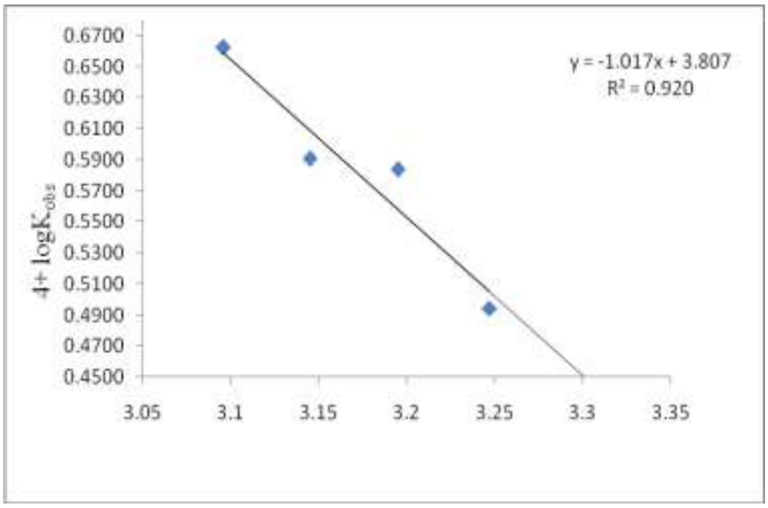

Fig.5: 4+log k_{obs} VS 1000/T

Table-7: Activation Parameters

Activation Parameters	
Ea kJ mol^{-1}	19.47
$\Delta H^{\#}$ KJ mol^{-1}	38.64
$\Delta S^{\#} JK^{-1}$ mol^{-1}	-250.27
$\Delta G^{\#}$ KJ mol^{-1}	117.6

Effect of acrylonitrile as free radical detector:

The addition of acrylonitrile to the reaction mixture at 35^0C and 45^0C did not alter the reaction rate and there was absolutely no polymer or change in the viscosity was detected, showing the absence of free radicals in the reaction mechanism.

IV. CONCLUSION

Perchloric acid catalyzed the oxidation of alanine by Pyridinium dichromate was studied in an DMSO-H_2O 50% (v/v) medium at 303 K. It shows the first-order dependence of rate with respect to PDC, Alanine and fractional order on perchloric acid. Alanine was oxidized into corresponding carbonyl compound. An added salt does not alter the rate of reaction and also the addition of acrylonitrile did not polymerize the reaction. The thermodynamic parameters have been evaluated. In the temperature range of 308-323K, Arrhenius equation is valid. The negative value of entropy indicates that the complex is more ordered than reactant.

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