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### Kinetics And Mechanistic Oxidation Of L-Cysteine Using By –Bromo Pthalimide In Presence Of Chloro – Complex Of Pd (II) As Homogenous Cataylst In Aqueous Aectic Acid Medium

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#### Abstract

Spectrophotometric study of oxidation of Palladium(II) chloride catalyzed L- Cysteine in aqueous acetic acid medium has been studied. Present research work focus on effect of various parameters on oxidation of L- Cysteine. Parameters varies during the study of reaction is concentration of L- Cysteine, Palladium(II) chloride and effect of salts on oxidation phenomenon. As a conclusion oxidation reaction was found as first order reaction with respect to L- Cysteine, Palladium(II) chloride and Perchloric acid.

**Key words :** Oxidation of L- Cysteine, NBP, Perchloric acid (HClO<sub>4</sub>), Mercuric Acetate, Palladium(II) chloride catalyzed, Acid medium oxidation, Kinetic study.

#### Introduction

Amino acids are the essential building blocks for any living organism, it plays vital role during various metabolism and occupied unique place in various biological systems. Due to such spectacular biological importance and unavoidable necessity, study of amino acid with respect to their various chemical reactions gain huge reputation for researchers. Oxidation of various amino acids has grown its own importance

and several remarkable works has been done till date to understand oxidation mechanism of amino acids. Oxidation of various amino acids is well reported by N-halo compounds like, N-boromophthalamide<sup>1-2</sup>, N-bromosuccinimide<sup>3</sup>, benzyltrimethylammonium tribromide<sup>4</sup>, N-Chlorosaccharin<sup>5</sup>, N-iodosuccinimide<sup>6</sup>, and many other oxidants<sup>7-9</sup>. There are some most recent references of oxidation of amino acids<sup>10-13</sup>. Present study is result of our continuous efforts taken

to understand kinetics of various oxidation reactions<sup>14-25</sup>.

## Experimental

### Material and Methods

Analytical reagent grade chemicals and triple distilled water were used throughout the investigation. The solution of nbp (Lancaster, 98%) was prepared in 80% acetic acid and stored in a black-coated flask to prevent any photochemical deterioration. The prepared solution of NBP was standardized by reported method<sup>20</sup>. The Pd(II) chloride solution was prepared by dissolving a known weight of palladium (II) chloride (S.D. Fine) in HCL of known strength and stored in a black coated bottle to prevent any photochemical deterioration. Standard solution of KCl, Phthalimide were prepared with distilled water. Mercuric Acetate (Loba chem., Mumbai, India) solution was acidified with 20 % acetic acid and perchloric acid (GR) was diluted with triple distilled water for the present investigation.

Kinetic investigations were performed under pseudo first order conditions with excess of Cysteine over, the oxidant at 25°C to 45°C. Required amount of solution of substrate, Perchloric Acid were equilibrated. A measured amount of N Bromo Pthalimide was added to the reaction mixture with constant stirring. The time of initiation of the reaction was recorded when half of the content of pipette were released. The solution was taken in a cuvette and absorbance was measured at 330nm using double beam spectrophotometer SL 210. Cysteine ( $2 \times 10^{-3}$  M), NBP ( $2 \times 10^{-4}$  M) and Perchloric Acid (0.5M) and water volume 100 ml kept a side for 24hrs. The unconsumed NBP was determined spectrophotometrically and the product was verified by TLC. The stiochiometry is determined to be 2:1.

#### Product Analysis :

Product study was made under acidic condition in presence of Palladium chloride (II). Keeping concentration of NBP, mercuric acetate and acetic acid in excess over L-Cysteine. The two solutions were mixed and Perchloric Acid was also

added. The reaction mixture was set aside for about 72hr. to ensure completion of the reaction. The reaction mixture was then evaporated and extracted with ether. The ether layer was washed with water many times. The ether layer was than kept as a water bath for the evaporation of ether and cooled in ice-bath to obtain the product.

The product was identified as a mixture of nitrile, aldehyde and trace of ammonia. Nitrile, aldehyde and ammonia were identified by color reaction with hydroxylamine and iron (III) chloride<sup>1</sup>, by Schiff's reagent and by Nessler's reagent respectively. The consumption of more than two moles of NBP per mole of amino acid may be due to the reaction of ammonia with NBP and may also be due to the further oxidation of aldehyde. The product was dissolved in Acetonitrile and a TLC analysis was done. Only one spot corresponding to respective Product was obtained. Formation of Product was further confirmed by mixing the product with pure solution and noting that there was no change in the melting point.

## Results and Discussion

### Effect of variation of N Bromo Pthalimide (NBP) concentration :

The study of the effect of variation of NBP concentration, the experimental sets were prepared in which concentration of NBP varied from  $7.14 \times 10^{-6}$  to  $7.14 \times 10^{-5}$  M keeping constant concentration of L-Cysteine and Perchloric Acid ( $\text{HClO}_4$ ). As the reaction has been studied under pseudo first order condition using equation -

$$K = \frac{2.303}{t} \log \frac{a}{a-x} \quad (1)$$

Which was modified as-?

$$k = \frac{2.303}{t} \log \frac{(OD)_{\infty} - (D)_0}{(OD)_{\infty} - (OD)_t} \quad (2)$$

Pseudo first order rate constants were calculated.

When initial rate is plotted against concentration of N Bromo Pthalimide the trend line has been found to be almost straight with negative slope indicating first order reaction at low concentration of N Bromo Pthalimide. This has been

further confirmed when  $\log [\text{NBP}]$  versus  $\log [\text{FOR}]$  is plotted. Hence the reaction under pseudo first order rate depends on the concentration of oxidant. Secondly, from the obtained results, it is clear that pseudo first order rate constant decrease with increase in concentration of N Bromo Pthalimide.

*Effect of Variation of concentration of N Bromo Pthalimide on initial rate and rate constant of L-Cysteine:*

The effect of temperature was studied keeping constant concentration of all reactants such

as  $[\text{NBP}] = 2 \times 10^{-4} \text{ M}$ ,  $[\text{L-Cysteine}] = 2 \times 10^{-3} \text{ M}$  and  $[\text{HClO}_4] = 0.5 \text{ M}$ . The temperature variation was done in the range of 25 to 45° C. The energy of activation was calculated by plotting graph between  $\log k$  verses  $1/T$ , a straight line was obtained. The temperature dependence on a number of reactions can be depicted by an equation. The modest enthalpy of activation and higher rate constant of slow step indicate that the oxidation presumably occurs by an inner sphere mechanism.

Table-1: Effect of Variation of concentration of N Bromo Pthalimide on initial rate and rate constant of L-Cysteine

Sr. No	Conc. of [NBP] ( $1 \times 10^{-5}$ )M	Initial Rate	$\log (\text{for})$	Rate constant (k)( $\text{sec}^{-1}$ )
1	$0.714 \times 10^{-5}$	3.296	1.322	0.05140
2	$1.42 \times 10^{-5}$	3.456	1.325	0.05130
3	$2.14 \times 10^{-5}$	3.757	1.328	0.05122
4	$2.85 \times 10^{-5}$	4.366	1.326	0.05128
5	$3.57 \times 10^{-5}$	4.766	1.329	0.05120
6	$3.57 \times 10^{-5}$	4.910	1.331	0.05116
7	$5 \times 10^{-5}$	5.207	1.333	0.05112
8	$5.71 \times 10^{-5}$	5.458	1.334	0.05108
9	$6.42 \times 10^{-5}$	5.710	1.336	0.05103
10	$7.14 \times 10^{-5}$	5.982	1.341	0.05090

Table-2: Average rate determination of oxidation of L-Cysteine

Time(s)	O.D.	$10^{-5}$ Conc. ( $\text{mole}/\text{dm}^3$ )	$10^{-5} < c >$	$10^{-5} D c$	D t	$10^{-8} < \text{rate} >$ $\text{mole}/\text{dm}^3/\text{s}$	$\log < c >$	$\log < \text{rate} >$
0	0.4348	21.3874						
3	0.4347	21.3824	21.3849	0.0049	3	1.6386	1.3301	0.2145
6	0.4345	21.3732	21.3778	0.0092	3	3.0697	1.3300	0.4871
9	0.4342	21.3576	21.3654	0.0156	3	5.2080	1.3297	0.7167
12	0.4340	21.3483	21.3530	0.0093	3	3.0931	1.3295	0.4904
15	0.4337	21.3334	21.3409	0.0149	3	4.9703	1.3292	0.6964
18	0.4335	21.3247	21.3291	0.0087	3	2.8921	1.3290	0.4612
21	0.4331	21.3036	21.3142	0.0211	3	7.0486	1.3287	0.8481
24	0.4329	21.2938	21.2987	0.0098	3	3.2505	1.3284	0.5120
27	0.4326	21.2784	21.2861	0.0154	3	5.1495	1.3281	0.7118
30	0.4324	21.2670	21.2727	0.0114	3	3.7855	1.3278	0.5781

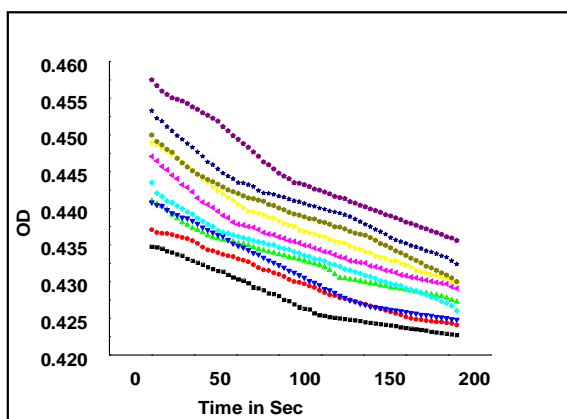


Fig -1 Variation of concentration of N Bromo Pthalimide Vs L-Cysteine

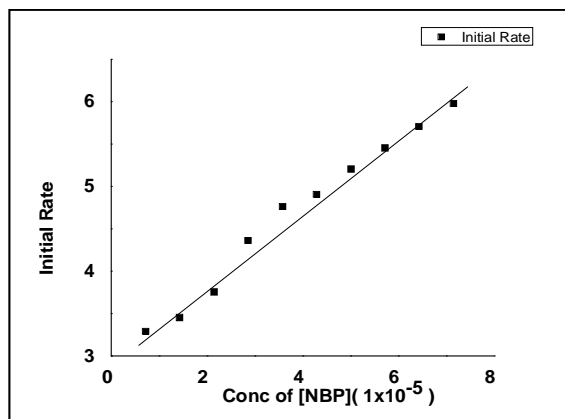


Fig - 2. Variation of concentration of N Pthalimide Vs log for of Cysteine

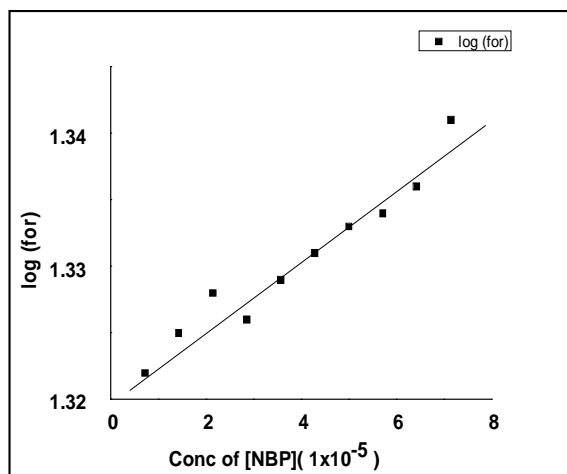


Fig -3. Variation of concentration of N Bromo Pthalimide Vs log for of Cysteine

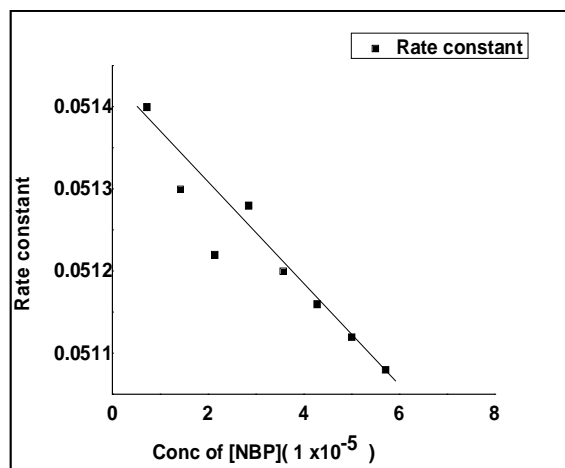


Fig -4. Variation of concentration of N Bromo Pthalimide Vs rate constant

*Effect of variation of L-Cysteine concentration (Substrate) :*

To study the effect of variation of concentration of substrate, the sets were prepared in which the concentration of L-Cysteine was varied from  $7.14 \times 10^{-6}$  to  $7.14 \times 10^{-5}$  M, keeping constant concentration of  $[NBP] = 2 \times 10^{-4}$  M,  $[Perchloric\ Acid] = 0.5$  M. As the reaction has been studied under pseudo first order condition pseudo first order rate constants were

calculated. It is clear that pseudo first order rate constants were found decrease with increases with concentration of [Cysteine] in irregular way. When initial rate is plotted against concentration of L-Cysteine, the trend line is linear with positive slope. When log [FOR] versus log [L-Cysteine] is plotted it confirms the fractional order of reaction. Hence the reaction under pseudo first order rate depends on the concentration of substrate.

Table-3: Effect of Variation in concentration of L-Cysteine on initial rate and rate constant

Sr. No.	Cystein conc. $1 \times 10^{-5} \text{M}$	Initial Rate (mole / lit / sec)	log (for)	Rate constant (k) ( $\text{sec}^{-1}$ ) L-Cysteine.
1	$0.714 \times 10^{-5}$	3.3904	1.0379	0.05924
2	$1.42 \times 10^{-5}$	3.7248	1.049	0.05891
3	$2.14 \times 10^{-5}$	4.1981	1.0489	0.0589
4	$2.85 \times 10^{-5}$	4.6726	1.0548	0.05874
5	$3.57 \times 10^{-5}$	5.0464	1.0641	0.05846
6	$4.28 \times 10^{-5}$	5.3975	1.0702	0.05829
7	$5 \times 10^{-5}$	5.6084	1.0811	0.05798
8	$5.71 \times 10^{-5}$	5.9719	1.0923	0.05767
9	$6.42 \times 10^{-5}$	6.2874	1.056	0.05729
10	$7.14 \times 10^{-5}$	6.9484	1.1123	0.05712

Table-4: Average rate determination of oxidation of L-Cysteine

Time(s)	O.D.	$10^{-5}$ Conc. (mole/ $\text{dm}^3$ )	$10^{-5} < c >$	$10^{-5} D c$	D t	$10^{-8} < \text{rate} >$ mole/ $\text{dm}^3/\text{s}$	log $< c >$	log $< \text{rate} >$
0	0.2287	11.2498						
3	0.2286	11.2449	11.2473	0.0050	3	1.6592	1.0510	0.2199
6	0.2284	11.2349	11.2399	0.0100	3	3.3184	1.0508	0.5209
9	0.2282	11.2251	11.2300	0.0098	3	3.2698	1.0504	0.5145
12	0.2281	11.2184	11.2217	0.0067	3	2.2306	1.0501	0.3484
15	0.2275	11.1920	11.2052	0.0264	3	8.7890	1.0494	0.9439
18	0.2273	11.1804	11.1862	0.0116	3	3.8702	1.0487	0.5877
21	0.2271	11.1688	11.1746	0.0116	3	3.8702	1.0482	0.5877
24	0.2269	11.1621	11.1655	0.0067	3	2.2306	1.0479	0.3484
27	0.2265	11.1407	11.1514	0.0214	3	7.1494	1.0473	0.8543
30	0.2263	11.1291	11.1349	0.0116	3	3.8702	1.0467	0.5877

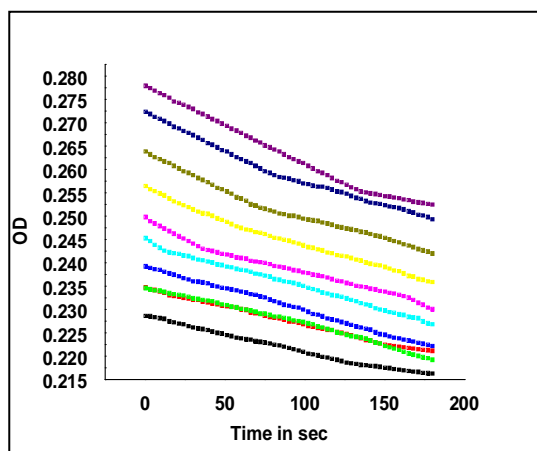


Fig -5 Effect of Variation of Amino Acid (substrate) Cysteine

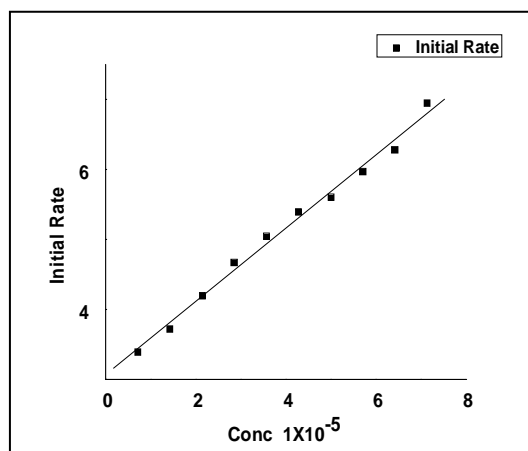


Fig. 6: Variation of conc. of L-Cysteine Vs Initial rate

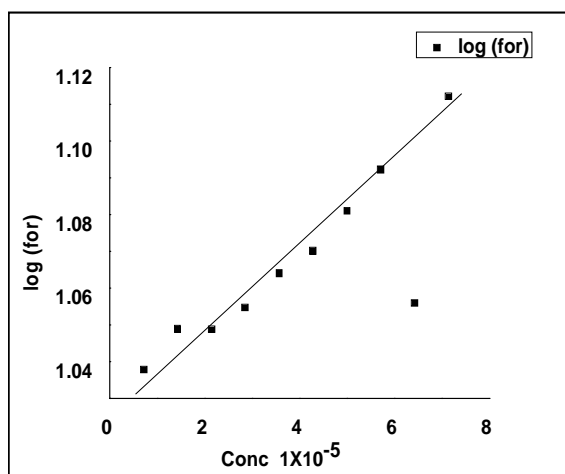


Fig -7. Variation of concentration of L-Cysteine Vs (Log For)

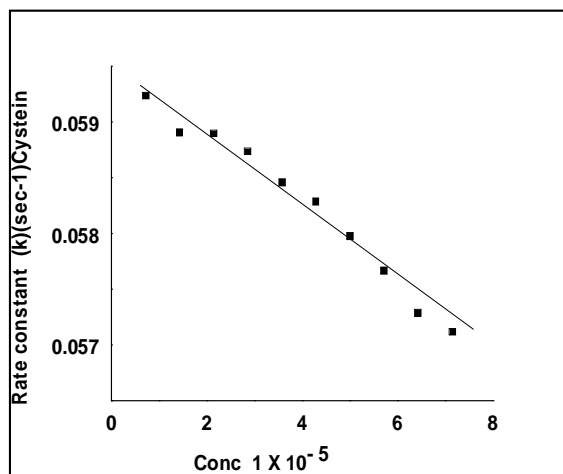


Fig -8. Variation of concentration of L-Cysteine Vs rate constant

*Effect of variation of Perchloric Acid concentration:*

The study of the effect of variation of concentration of Perchloric Acid ( $\text{HClO}_4$ ), in the experimental sets the concentration of  $\text{HClO}_4$  is varied from  $0.714 \times 10^{-5}$  to  $7.14 \times 10^{-5}$  M, keeping constant concentration i.e.  $[\text{L-Cysteine}] = 2 \times 10^{-3}$  M and  $[\text{NBP}] = 2 \times 10^{-4}$  M. As the reaction has been studied under pseudo first order condition for varying  $[\text{HClO}_4]$  was

made and pseudo first order rate constants were calculated. It is clear from that pseudo first order rate constants decreases with change in concentration of  $\text{HClO}_4$  confirming the first order dependence with respect to acid. Hence the reaction under pseudo order rate depends on the concentration of acid. The average rate determination data confirm that the order with respect to acid concentration is unity.

Table-5: Effect of Variation in concentration of Perchloric Acid ( $\text{HClO}_4$ ) on initial rate and rate constant of [L-Cysteine] oxidation

[NBP] = $2 \times 10^{-4}$ M      [L-Cysteine] = $2 \times 10^{-3}$ M      [ $\text{HClO}_4$ ] = 0.5M				
Sr. No	Conc of Perchloric Acid ( $1 \times 10^{-5}$ ) M	Initial Rate (mole/lit/sec)	log (for)	Rate constant (k)(sec <sup>-1</sup> ).
1	$0.714 \times 10^{-5}$	6.3605	0.9269	0.06297
2	$1.42 \times 10^{-5}$	5.1581	0.9398	0.06246
3	$2.14 \times 10^{-5}$	5.3499	0.9385	0.06254
4	$2.85 \times 10^{-5}$	5.2679	0.9506	0.06211
5	$3.57 \times 10^{-5}$	4.94	0.9581	0.06183
6	$4.28 \times 10^{-5}$	4.5891	0.9656	0.06159
7	$5 \times 10^{-5}$	4.3796	0.9753	0.06126
8	$5.71 \times 10^{-5}$	4.0919	0.9739	0.0613
9	$6.42 \times 10^{-5}$	3.8151	0.9768	0.06121
10	$7.14 \times 10^{-5}$	4.0355	0.9831	0.061

Table-6: Average rate determination of oxidation of L-Cysteine

Time(s)	$10^{-5}$ Conc. (mole/dm <sup>3</sup> )	$10^{-5} < c >$	$10^{-5} \Delta c$	$\Delta t$	$10^{-8} < \text{rate} >$ mole/dm <sup>3</sup> /s	$\log < c >$	$\log < \text{rate} >$
0	9.0932						
3	9.0574	9.0753	0.0359	3	11.9591	0.9579	1.0777
6	9.0306	9.0440	0.0268	3	8.9323	0.9564	0.9510
9	9.0031	9.0168	0.0275	3	9.1723	0.9551	0.9625
12	8.9645	8.9838	0.0386	3	12.8686	0.9535	1.1095
15	8.9480	8.9562	0.0164	3	5.4760	0.9521	0.7385
18	8.9205	8.9343	0.0275	3	9.1723	0.9511	0.9625
21	8.8972	8.9088	0.0233	3	7.7788	0.9498	0.8909
24	8.8655	8.8813	0.0317	3	10.5657	0.9485	1.0239
27	8.8380	8.8517	0.0275	3	9.1723	0.9470	0.9625

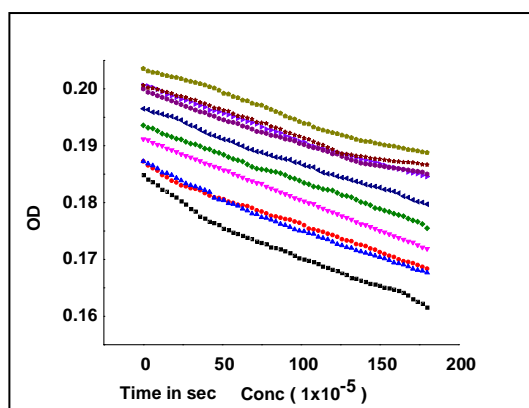


Fig -9 Effect of Variation of Perchloric Acid Vs Cysteine

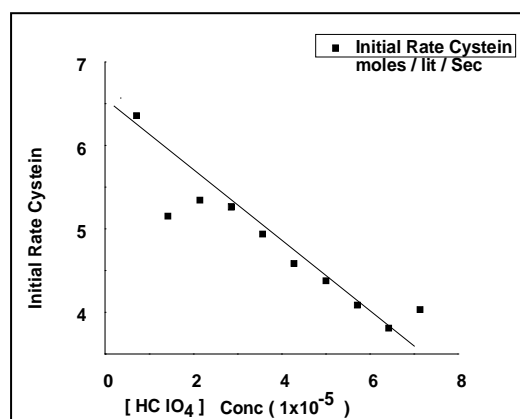


Fig -10. Variation of concentration Perchloric Acid Vs Initial rate

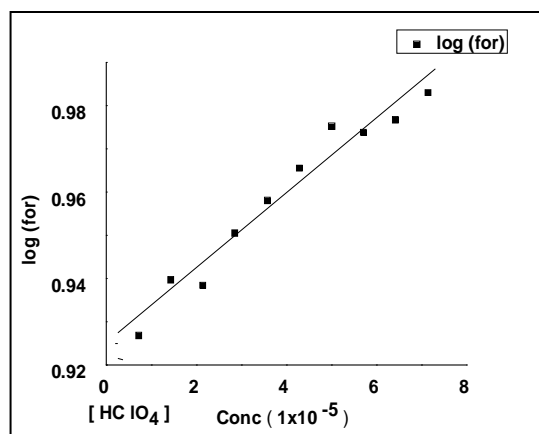


Fig -11. Effect of Variation of Perchloric Acid Vs (Log For)

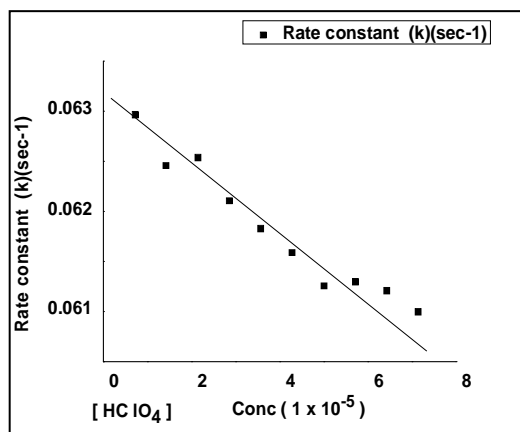


Fig -12. Variation of concentration of Perchloric Acid Vs Rate constant

To study the effect of variation of concentration of  $\text{PdCl}_2$ , in the experimental sets the concentration of Pd (II) is varied from  $0.714 \times 10^{-6}$  to  $7.14 \times 10^{-6}$  M, keeping constant concentration i.e.  $[\text{L-Cysteine}] = 2 \times 10^{-3}\text{M}$  and  $[\text{NBP}] = 2 \times 10^{-4}\text{M}$ . As the reaction has been studied under pseudo first order condition for varying  $\text{PdCl}_2$  was made and pseudo first

order rate constants were calculated. It is clear from that pseudo first order rate constants decreases with change in concentration of  $\text{PdCl}_2$  confirming the first order dependence with respect to acid. Hence the reaction under pseudo order rate depends on the concentration of acid. The average rate determination data confirm that the order with respect to salt concentration is unity.

Table-7: Effect of Variation in concentration of Palladium chloride (II) Pd (II) on initial rate and rate constant of [L-Cysteine] oxidation and

Table-8: Effect of Variation in concentration of catalyst  $\text{PdCl}_2$  on initial rate and rate constant of [L-Cysteine] oxidation

Sr. No.	Conc of Pd (II) ( $1 \times 10^{-6}$ ) M	Initial Rate (mole/lit/sec)	log (for)	Rate constant (k)( $\text{sec}^{-1}$ )
1	$0.714 \times 10^{-6}$	3.8467	0.7563	0.07004
2	$1.42 \times 10^{-6}$	4.0323	0.7602	0.06977
3	$2.85 \times 10^{-6}$	4.3336	0.7663	0.06952
4	$3.2 \times 10^{-6}$	4.6254	0.7527	0.07022
5	$3.57 \times 10^{-6}$	4.8934	0.78	0.06884
6	$4.28 \times 10^{-6}$	4.9061	0.7911	0.06884
7	$5 \times 10^{-6}$	5.1401	0.7968	0.06828
8	$5.71 \times 10^{-6}$	5.36151	0.8096	0.06814
9	$6.42 \times 10^{-6}$	5.7118	0.8163	0.06273
10	$7.14 \times 10^{-6}$	6.1014	0.829	0.06668

Table-9: Average rate determination of oxidation of L-Cysteine

Time(s)	O.D.	$10^{-5}$ Conc. (mole/ $\text{dm}^3$ )	$10^{-5} < c >$	$10^{-5} \text{D c}$	D t	$10^{-8} < \text{rate} >$ mole/ $\text{dm}^3/\text{s}$	log <c>	log <rate>
0	0.1244	6.1169						
3	0.1240	6.1000	6.1085	0.0170	3	5.6560	0.7859	0.7525
6	0.1239	6.0941	6.0970	0.0059	3	1.9584	0.7851	0.2919
9	0.1237	6.0827	6.0884	0.0114	3	3.8072	0.7845	0.5806
12	0.1235	6.0750	6.0788	0.0077	3	2.5676	0.7838	0.4095
15	0.1232	6.0598	6.0674	0.0151	3	5.0467	0.7830	0.7030
18	0.1230	6.0484	6.0541	0.0114	3	3.8072	0.7821	0.5806
21	0.1226	6.0309	6.0396	0.0176	3	5.8528	0.7810	0.7674
24	0.1225	6.0256	6.0282	0.0053	3	1.7616	0.7802	0.2459
27	0.1221	6.0060	6.0158	0.0195	3	6.5127	0.7793	0.8138
30	0.1220	6.0027	6.0044	0.0033	3	1.1017	0.7785	0.0421



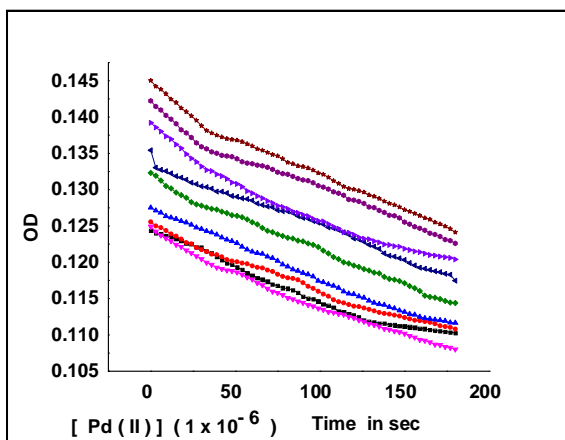


Fig -13. Effect of Variation of catalyst Pd (II) on

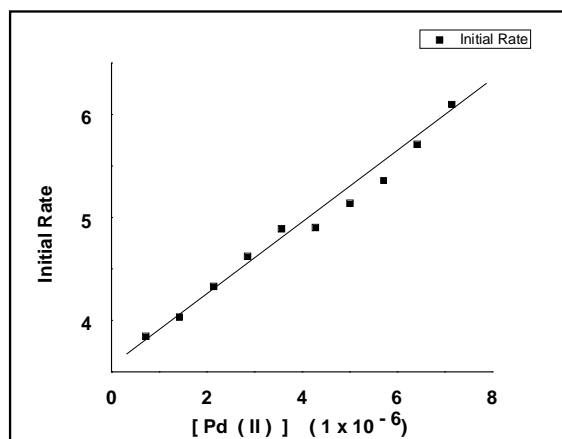


Fig -14. Variation of conce Cysteine catalyst Pd (II) Vs Initial rate

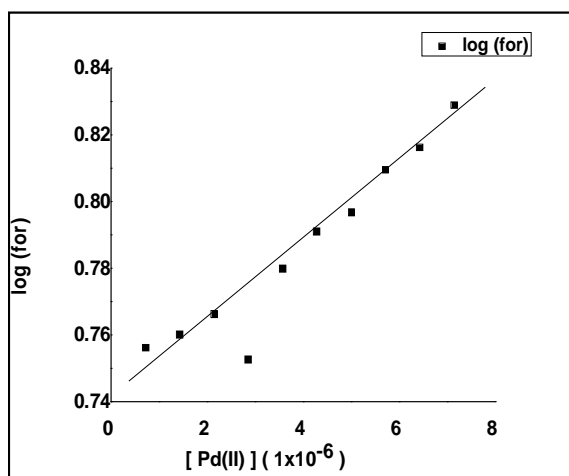


Fig -15. Effect of Variation of catalyst Pd (II) Vs concentration (Log For)

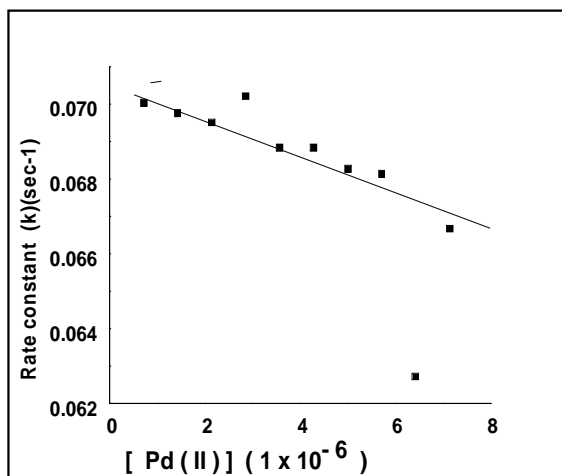


Fig -16. Variation of of catalyst Pd (II) Vs Rate constant

*Effect of variation of Salt concentration on Cysteine:*

The study of the effect of variation of salts, the concentration of salt was varied from  $0.714 \times 10^{-6}$  to  $7.14 \times 10^{-6}$  M, keeping constant concentration of reactants such as  $[NBP] = 2 \times 10^{-4}$  M,  $[L\text{-Cysteine}] = 2 \times 10^{-3}$  M,  $[HClO_4] = 3 \times 10^{-4}$  M. These results are given in the table..... From the obtained results, it is clear that pseudo first order rate constant  $k_{obs}$

increases with the increase in concentration of salts. A plot of  $\log k_{obs}$  vs  $\sqrt{\mu}$ , according to extended Bronsted Debye-Huckel equation was found to be linear with positive slope of salt effect. On the other hand pseudo first order rate constant decreased with increase in concentration of salts. A plot of  $\log k_{obs}$  versus  $\sqrt{\mu}$  was found to be linear with negative slopes (KCl), indicating negative salt effect.

Table-10: Effect of Variation in concentration of salt ( KCl ) on initial rate and rate constant of [L-Cysteine] oxidation

Sr. No	Conc. of KCl ( $1 \times 10^{-6}$ )	Initial Rate (mole/lit/sec)	log (for)	Rate constant (k) ( $\text{sec}^{-1}$ )	Log K	$\sqrt{\mu} \times 10^{-6}$
1	$0.714 \times 10^{-6}$	3.7853	0.7042	0.07288	-1.1373	0.8449
2	$1.42 \times 10^{-6}$	4.2837	0.6909	0.07381	-1.1388	1.1916
3	$2.14 \times 10^{-6}$	4.4005	0.7026	0.073	-1.136673	1.4628
4	$2.85 \times 10^{-6}$	4.549	0.7129	0.07235	-1.1405	1.6881
5	$3.57 \times 10^{-6}$	4.3797	0.7125	0.07235	-1.1405	1.8894
6	$4.28 \times 10^{-6}$	4.5132	0.72	0.07202	-1.1425	2.0688
7	$4.99 \times 10^{-6}$	4.6591	0.7291	0.07147	-1.1458	2.2338
8	$5.712 \times 10^{-6}$	4.6468	0.7442	0.07056	-1.1514	2.3899
9	$6.42 \times 10^{-6}$	4.5626	0.7561	0.07003	-1.1547	2.5337
10	$7.14 \times 10^{-6}$	4.6718	0.7595	0.06984	-1.174	2.6721

Table-11: Average rate determination of oxidation of L-Cysteine

Time(s)	O.D.	$10^{-5}$ Conc. (mole/dm <sup>3</sup> )	$10^{-5} < c >$	$10^{-5} D c$	D t	$10^{-8} < \text{rate} >$ mole/dm <sup>3</sup> /s	log < c >	log < rate >
0	0.1105	5.4351						
3	0.1101	5.4168	5.4260	0.0183	3	6.0994	0.7345	0.7853
6	0.1100	5.4105	5.4137	0.0064	3	2.1310	0.7335	0.3286
9	0.1097	5.3981	5.4043	0.0123	3	4.1152	0.7327	0.6144
12	0.1095	5.3886	5.3933	0.0096	3	3.1864	0.7319	0.5033
15	0.1092	5.3734	5.3810	0.0151	3	5.0440	0.7309	0.7028
18	0.1090	5.3611	5.3672	0.0123	3	4.1152	0.7298	0.6144
21	0.1086	5.3422	5.3516	0.0189	3	6.2837	0.7285	0.7982
24	0.1085	5.3364	5.3393	0.0058	3	1.9468	0.7275	0.2893
27	0.1084	5.3339	5.3351	0.0025	3	0.8360	0.7271	-0.0778
30	0.1083	5.3264	5.3302	0.0074	3	2.4756	0.7267	0.3937

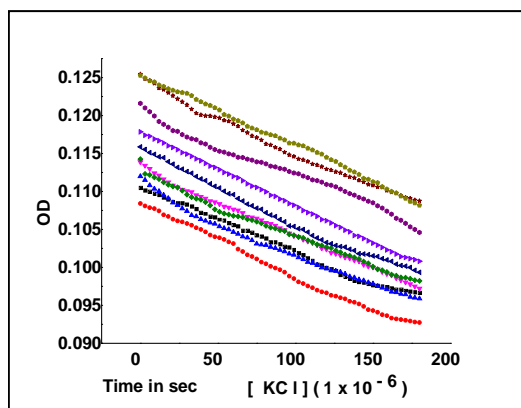


Fig -17. Effect of Variation of KCl on Cysteine

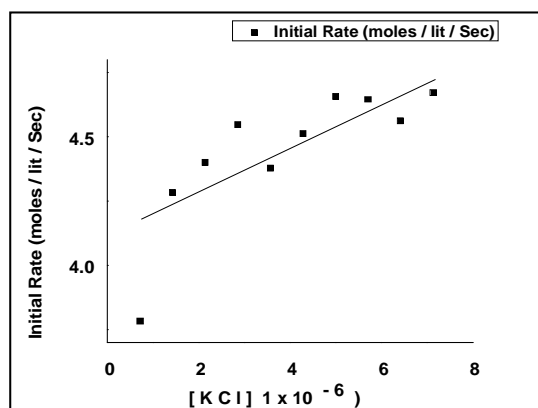


Fig -18. Variation of oncentration KCl Vs Initial rate

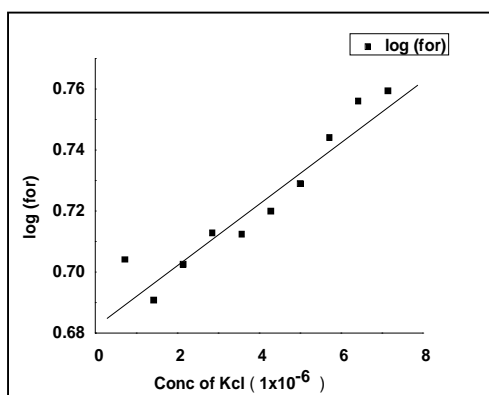


Fig -19 Effect of Variation of KCl Vs (Log For)

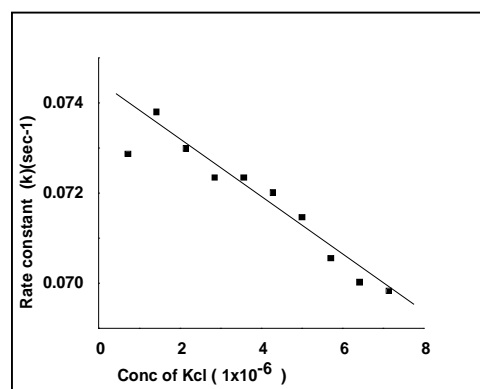


Fig -20. Variation of concentration KCl Vs Initial rate

Table-12: Effect of Temperature on Kinetics of pthalamide Oxidation of Cysteine in acedic media

Cysteine =  $(7.14 \times 10^{-5})$  M

Perchloric acid = 0.5 M

NBP =  $7.14 \times 10^{-5}$  M

Sr. No.	Time sec.	Temperature				
		R.T o	30o	35o	40o	45o
1	0	0.2287	0.2269	0.2256	0.2218	0.2164
2	3	0.2286	0.2265	0.2252	0.2215	0.2158
3	6	0.2284	0.2263	0.2251	0.2212	0.2156
4	9	0.2282	0.2260	0.2247	0.2208	0.2151
5	12	0.2281	0.2259	0.2245	0.2205	0.2146
6	15	0.2275	0.2256	0.2243	0.2202	0.2143
7	18	0.2273	0.2253	0.2240	0.2199	0.2139
8	21	0.2271	0.2251	0.2237	0.2194	0.2134
9	24	0.2269	0.2249	0.2235	0.2192	0.2131
10	27	0.2265	0.2246	0.2233	0.2189	0.2127
11	30	0.2263	0.2244	0.2229	0.2186	0.2122
20	57	0.2240	0.2222	0.2207	0.2157	0.2087

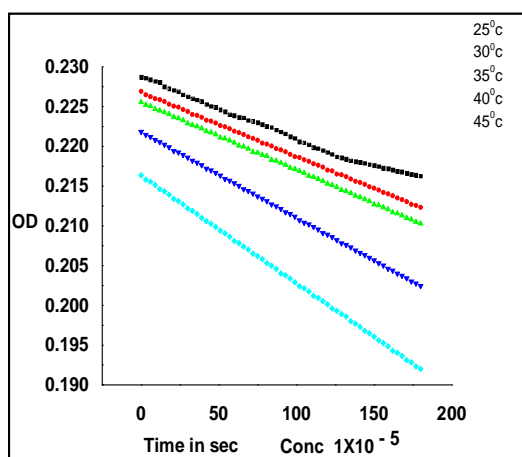


Fig -21 Effect of Variation of Temp on Cysteine

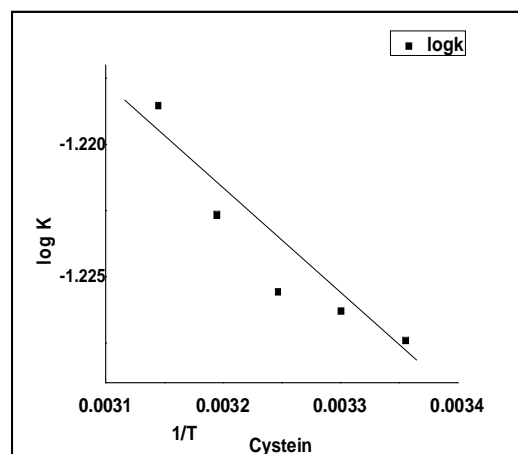


Fig -22 Effect of Variation of temp on cysteine

Effect of Temp on Cystein					
Cystein = $(0.714 \times 10^{-5})$ M			Perchloric acid = 0.5 M		NBP = $0.714 \times 10^{-5}$ M
Rate k	t °C	T °K	1/T	logk	3+logk
0.05924	25	298	0.0033557	-1.22738495	1.77261505
0.05939	30	303	0.00330033	-1.22628667	1.773713325
0.05949	35	308	0.00324675	-1.22555603	1.774443969
0.05989	40	313	0.00319489	-1.22264569	1.777354313
0.06046	45	318	0.00314465	-1.21853186	1.781468143

Effect of Temp. on Cystein

Energy of activation is = Calculated plotting graph between log k vs 1/T

$E_a = \text{Slope} \times 2.303 \times R$ ,  $E_a = \text{Slope} \times 2.303 \times R$ ,  $R = 8.314$

$$DH = DE - RT$$

Cystein =  $(0.714 \times 10^{-5})$  M

Perchloric acid = 0.5M

NBP =  $0.714 \times 10^{-5}$  M

$E_a^\# = -869.234237 \text{ Jmole}^{-1}$

Slope =  $-45.3976 \text{ kJ/Jmole}^{-1}$

Temp	T	K	DH <sup>#</sup> (J mole <sup>-1</sup> )	DS <sup>#</sup> (J mole <sup>-1</sup> )	DG <sup>#</sup> (J mole <sup>-1</sup> )
25°C	298	0.05924	-3346.8063	-121.4430	32843.2000
30°C	303	0.05939	-3388.3763	-121.4730	33417.9488
35°C	308	0.05949	-3429.9463	-121.5058	33993.8457
40°C	313	0.05989	-3471.5163	-121.5202	34564.3027
45°C	318	0.06046	-3513.0863	-121.5242	35131.6243
Average			-3429.9463	-121.4932	33990.1843

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