

Ruthenium (III) Mediated Oxidation of Thiamine Hydrochloride by PDP in Nitric Acid Medium

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ABSTRACT: Oxidation of thiamine hydrochloride (Vit. B₁) by PDP mediated by micro amounts (10^{-6} mol dm⁻³ to 10^{-4}) of Ru (III) in aqueous nitric acid medium has been studied at 25°C. The reaction is second order in both PDP and Ru (III) concentrations. The order with respect to B₁ concentration varies first order to zero order as the vitamin B₁ concentration increases, An increase in HNO₃ concentration decrease the reaction rate. The active species of Oxidant and catalyst are [PDP] and [Ru(H₂O)₆]³⁺ A possible mechanism is proposed and reaction constants involved have been determined. Ruthenium (III) is an efficient catalyst in many redox reactions involving different complexities due to the formation of intermediate complexes, free radicals and multiple oxidation states of ruthenium PDP is a well known oxidant in acidic media PDP was act as predominant active species in the concentration range 0.30 – 2.0 mol dm⁻³ of Nitric acid, but its role has not received much attention so far the oxidation of thiamine hydrochloride with alkaline potassium ferricyanide, hypo iodide, chlorite and N-chloro benzene sulphonamide were studied. The literature survey reveals that there were no report on the oxidation of thiamine hydrochloride by PDP the mechanism may be quite complicated due to the formation of different PDP and Ru (III) Complexes in the form of active complexes in nitric acid medium. Hence, we have investigated the Ru(III) mediated oxidation of vit B₁ by PDP in order to understand the behaviour of active species of oxidant and catalyst to propose a suitable mechanism.

KEYWORDS: Kinetics, thiamine hydrochloride (vit – B₁), PDP and Ruthenium (III) catalyst.

I. INTRODUCTION

Water soluble vitamins the common feature to most of vitamin B complex have been outlined below cannot be stored in body regular supply needed most play an essential role in metabolism. Most of them can be sourced from liver and yeast. Most of them are synthesised by colonial bacteria [1-6]. Excess is excreted in urine, no danger of toxic levels, not easy to be stored in the body [7]. Regular supply needed most play an essential role in metabolism. Most of them can be sourced from liver and yeast [8]. Most of them are synthesised by colonial bacteria. Excess is excreted in urine, no danger of toxic levels, not easy to be stored in the body [9-10].

II. MATERIALS AND METHODS

Reagent grade chemicals were used double distilled water was used through for the preparation of solutions. The stock solution of the oxidant has obtained by dissolving PDP in 1.0 mol dm⁻³ H₂SO₄. The solution was standardized by a known method. A stock solution of thiamine hydrochloride was prepared by dissolving thiamine hydrochloride in distilled water. The Ruthenium (III) stock solution was prepared by dissolving RuCl₃ in 0.20 mol dm⁻³ HCl and its concentration was assayed by EDTA titration. The stock solution was diluted as required before use. KNO₃ and HNO₃ were used to provide the required ionic strength and acidity All Kinetic measurement were carried out under Pseudo first order conditions, where thiamine hydrochloride was in excess over PDP at a constant ionic strength of 1.10 mol dm⁻³. The reaction was initiated by mixing thermally equilibrated ($25 \pm 0.1^\circ\text{C}$). Solutions of PDP and thiamine hydrochloride also containing the required quantity of HNO₃ and Ru(III) catalyst.

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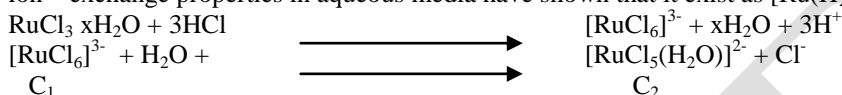
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The reaction was following by monitoring the decrease in absorbance of PDP in mixture at 264nm in a 1 cm cell placed in a thermostatted compartment of avariancary 50 Bio UV. Visible spectrophotometer as a function of time. The application of Beers law under reaction conditions had earlier been verified in the concentration range 1.0×10^{-4} to $2.0 \times 10^{-3} \text{ mol dm}^{-3}$ of PDP at 264nm in $1.0 \text{ mol dm}^{-3} \text{ HNO}_3$ and water the molar absorptivity index PDP at 264 nm was found to be $\sum = 7.9 \times 10^3 \text{ mol}^{-1} \text{ cm}^{-1}$

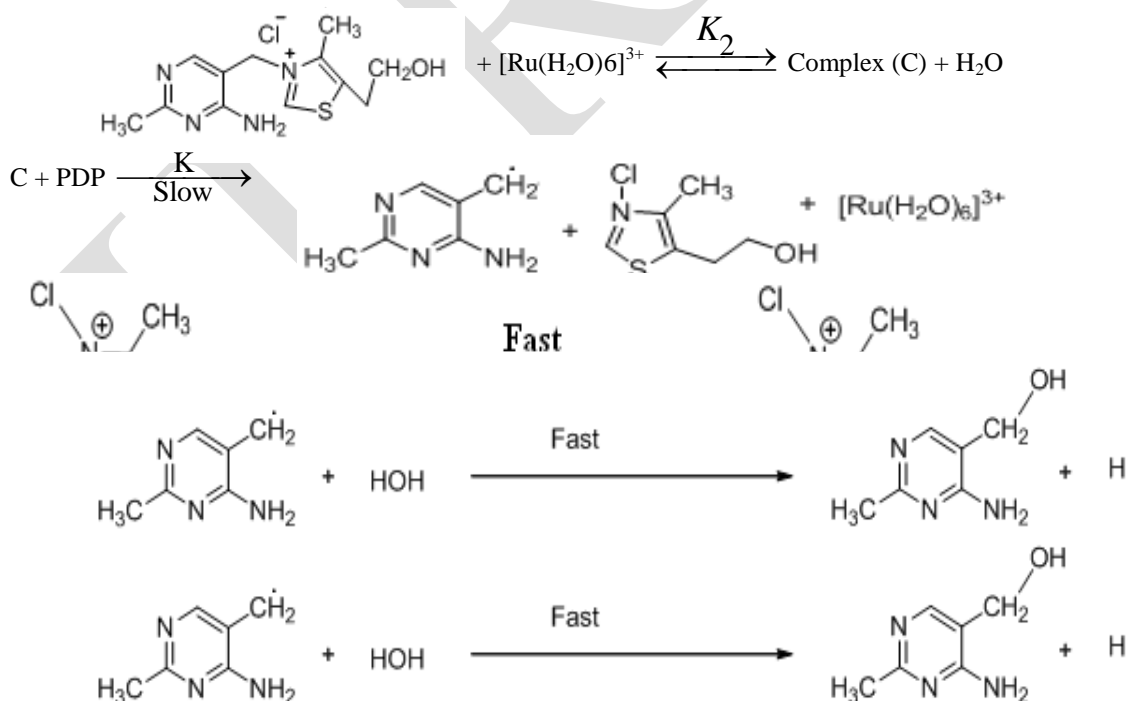
The Kinetics was followed up to more than 80% completion of the reaction and good second order kinetics were observed. The second order rate constant K_c were calculated from the slopes of plots of $\log [\text{PDP}]$ vs time. The K_c Values were reproducible within $\pm 5\%$ and are the average of at least three independent kinetic rules.

III. MECHANISM

Ruthenium (III) chloride is known exist in solution in various aqua form. Electronic and spectral studies and ion – exchange properties in aqueous media have shown that it exist as $[\text{Ru}(\text{H}_2\text{O})_6]^{3+}$



The products, 4-amino -2 methyl Pyrimidine -5- Carboldehyde and 2- (4 Methyl thia 2 ol- 5yl)- ethanol were confirmed by GC-MS spectra.



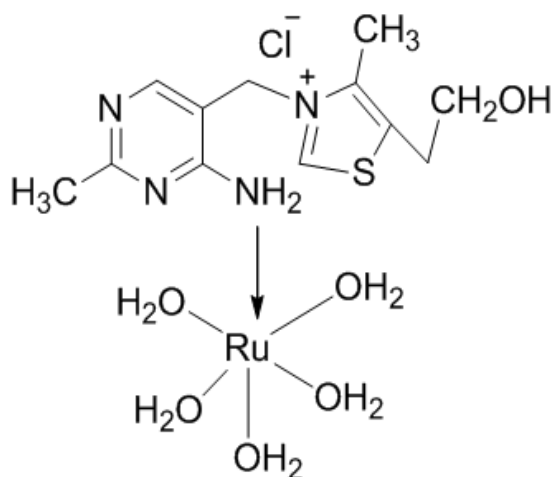
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The probable structure of the complex



IV. RESULTS AND DISCUSSION

λ_{max} : 264nm

E of thiamine at 264nm : $7.9 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$

[Thiamine] - 1×10^{-4M}

Stock solution concentration 2.14×10^{-3M}

0.47 ml of Thiamine + 9.5 ml of H₂O

Table 1:

Irradiation time in minutes	Absorbance
0	0.815
0.5	0.815
1.0	0.815
2.0	0.815
4.0	0.804
6.0	0.804
9.0	0.799
14.0	0.799

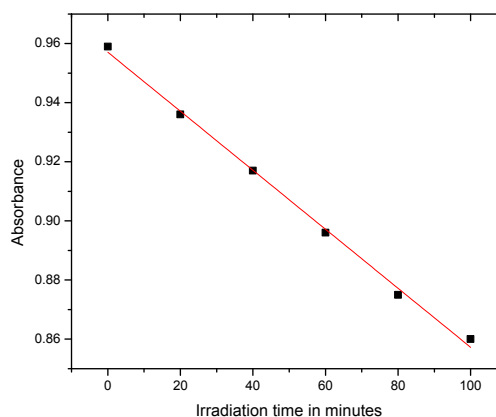
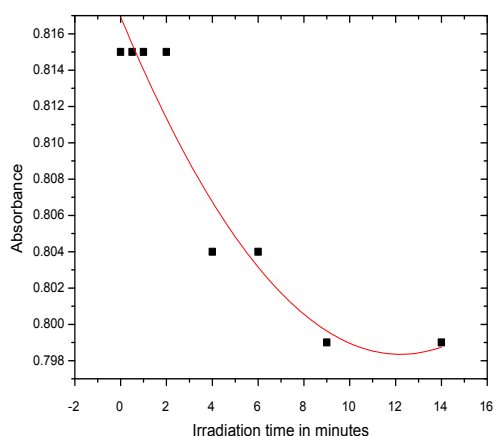
Table 2:

Irradiation time in minutes	Absorbance
0	0.959
20	0.936
40	0.917
60	0.896
80	0.875
100	0.86

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The reaction was followed by measuring the absorbance of thiamine at their respective λ_{max} by interrupting the radiation at regular interval of time. The initial rates of thiamine were calculated from the absorbance calculated from the initial rates of oxidation of thiamine and the intensity of light at 264 nm.

Set – I

Table 3: Effect of [thiamine] in Oxidation of thiamine in presence of PDP

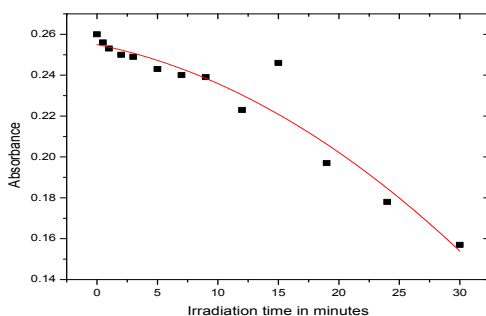
[PDP] - 2×10^{-3} M
 Distance - 14cm
 [Thiamine] - 2×10^{-5} M
 Intensity of the lamp - 4.5×10^{14}
 λ_{max} 264 nm
 E at 264nm - $7.9 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$
 [Thiamine] stock in sol⁴ - 2.116×10^{-3} M
 [PDP] stock sol⁴ - 6.6×10^{-3} M
 0.094 ml of thiamine + 3.03ml of PDP + 6.87 ml of H₂O

Irradiation time in minutes	Absorbance
0	0.26
0.5	0.256
1.0	0.253
2	0.25
3	0.249
5	0.243
7	0.24
9	0.239
12	0.223
15	0.246
19	0.197
24	0.178
30	0.157

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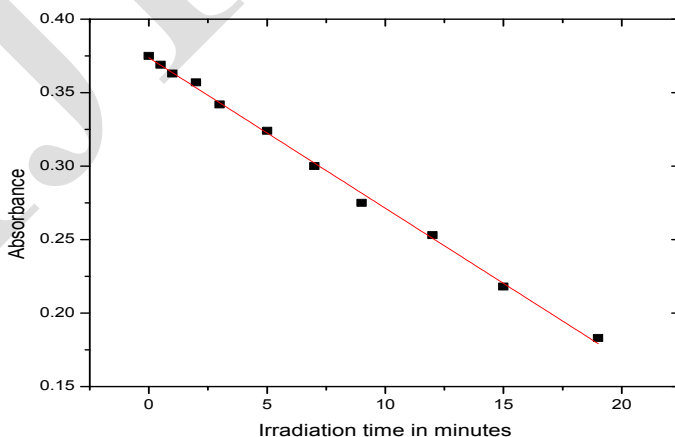
The plot of the absorbance of thiamine versus irradiation of time was found to be polynomial fit and second order reaction. It increases with increasing of reaction time.

Set – II

Table 4: Effect of [thiamine] in Oxidation of thiamine in presence of PDP

[Thiamine] - $4 \times 10^{-5}M$
 [PDP] - $2 \times 10^{-3}M$
 λ_{max} 264 nm
 0.094 ml of thiamine + 3.03ml of PDP + 6.87 ml of H₂O

Irradiation time in minutes	Absorbance
0	0.375
0.5	0.369
1	0.363
2	0.357
3	0.342
5	0.324
7	0.3
9	0.275
12	0.253
15	0.218
19	0.183



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A plot of absorbance of thiamine verses irradiation of time was found to be linear II order polynomial fit (excluding 2nd minute reading)

Slope = 0.010247

R² = 0.99998

Set – III

Table 5: Effect of [thiamine] in Oxidation of thiamine in presence of PDP

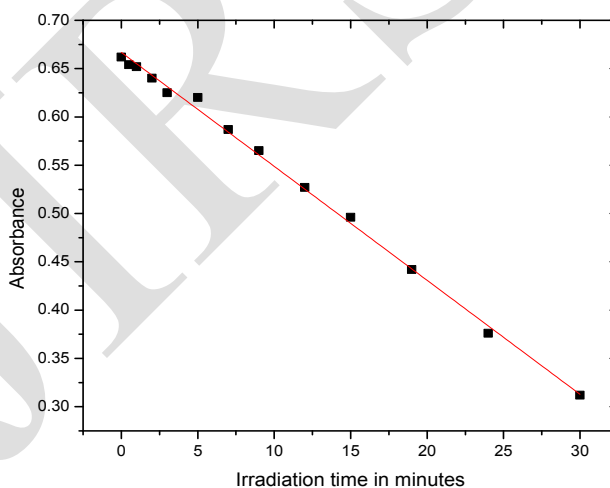
[Thiamine] - 8 x 10⁻⁵M

[PDP] - 2 x 10⁻³ M

λ_{max} 264 nm

0.38 ml of thiamine + 3.03ml of PDP + 6.6 ml of H₂O

Irradiation time in minutes	Absorbance
0	0.662
0.5	0.654
1	0.652
2	0.64
3	0.625
5	0.62
7	0.587
9	0.565
12	0.527
15	0.496
19	0.442
24	0.376
30	0.312



The initial rates and quantum yields of oxidation of thiamine were found to be increase in concentration of thiamine and PDP.

II order polynomial fit (excluding 5th minute reading)

Slope = 0.01247

R² = 0.99998

Set – IV

Table 6: Effect of [thiamine] in Oxidation of thiamine in presence of PDP

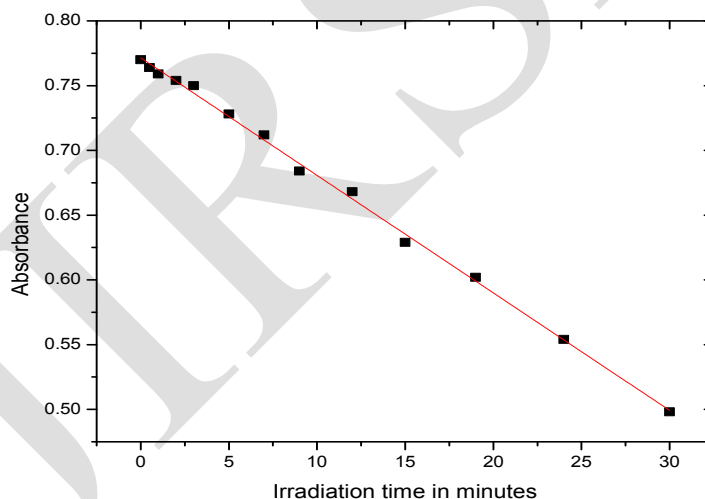
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[Thiamine] - $1 \times 10^{-4} \text{M}$
 [PDP] - $2 \times 10^{-3} \text{M}$
 λ_{max} - 264 nm
 [PDP] stock sol⁴ - $6.6 \times 10^{-3} \text{M}$
 [Thiamine] stock in sol⁴ - $2.116 \times 10^{-3} \text{M}$
 0.47 ml of thiamine + 3.03ml of PDP + 6.87 ml of H₂O

Irradiation time in minutes	Absorbance
0	0.770
0.5	0.764
1	0.759
2	0.754
3	0.750
5	0.728
7	0.712
9	0.684
12	0.668
15	0.629
19	0.602
24	0.554
30	0.498



The graph plotted between absorbance of thiamine and irradiation of time in the presence of PDP was found to be linear

II order polynomial fit (excluding 3rd minute reading)

Slope = 0.00815

R² = 0.997

Set – V

Table 7: Effect of [thiamine] in Oxidation of thiamine in presence of PDP

[Thiamine] - $1.2 \times 10^{-4} \text{M}$
 [PDP] - $2 \times 10^{-3} \text{M}$

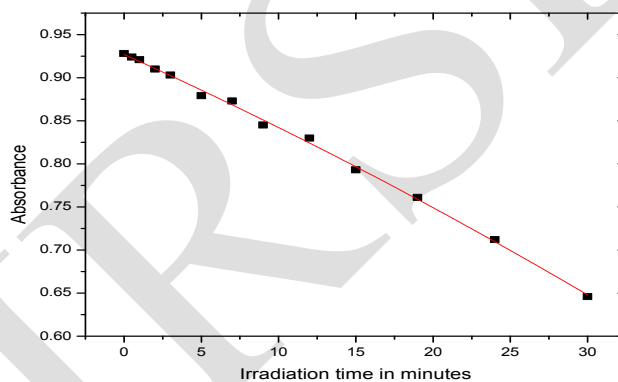
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λ_{max} - 264 nm
0.57 ml of thiamine + 3.03ml of PDP + 6.4 ml of H₂O

Irradiation time in minutes	Absorbance
0	0.928
0.5	0.924
1	0.921
2	0.910
3	0.903
5	0.879
7	0.873
9	0.845
12	0.830
15	0.793
19	0.761
24	0.712
30	0.646



The graph plotted between absorbance of thiamine and irradiation of time in the presence of PDP was found to be linear. The rates of oxidation of thiamine decreases with increasing concentration of thiamine at constant [PDP].

II order polynomial fit

Slope = 0.0098

R² = 0.98995

Set – I

Table 8: Effect of [PDP] in Oxidation of thiamine in presence of PDP

[Thiamine] - 1 x 10⁻⁴M

[PDP] - 1 x 10⁻³ M

λ_{max} - 264 nm

0.47 ml of thiamine + 1.51ml of PDP + 8.02 ml of H₂O

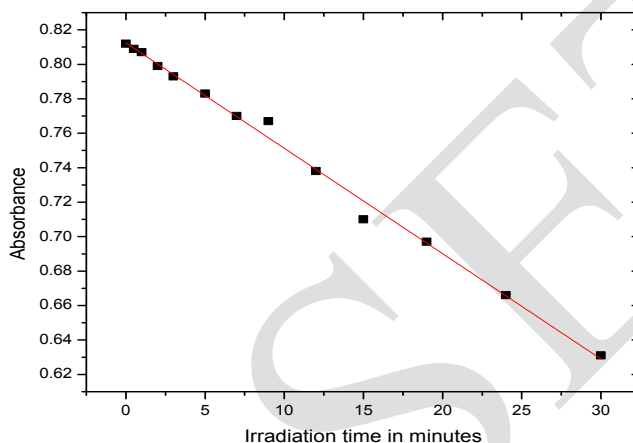
Irradiation time in minutes	Absorbance
0	0.812
0.5	0.809
1	0.807
2	0.799

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3	0.793
5	0.783
7	0.770
9	0.767
12	0.738
15	0.71
19	0.697
24	0.666
30	0.631



The effect of PDP concentration on the oxidation of thiamine increases with increasing of [PDP] at constant thiamine concentration.

II order polynomial fit (excluding thiamine)

Slope = 0.00703

$R^2 = 0.99857$

Set – II

Table 9: Effect of [PDP] in Oxidation of thiamine in presence of PDP

[Thiamine] - $1 \times 10^{-4} M$

[PDP] - $2 \times 10^{-3} M$

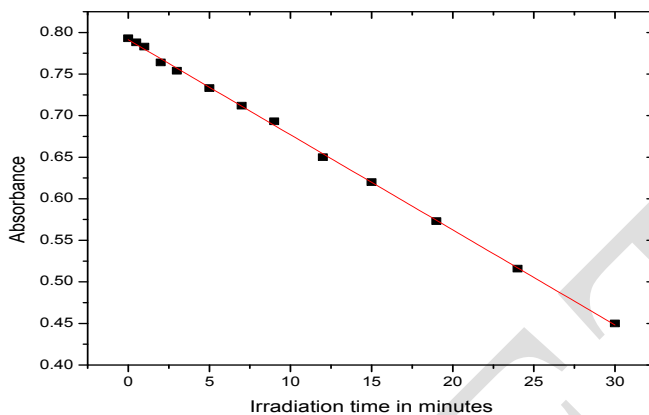
0.47 ml of thiamine + 3.03ml of PDP + 6.5 ml of H₂O

Irradiation time in minutes	Absorbance
0	0.793
0.5	0.788
1	0.783
2	0.764
3	0.754
5	0.733
7	0.712
9	0.693
12	0.650
15	0.620
19	0.573
24	0.516
30	0.450

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The effect of PDP concentration on the oxidation of thiamine increases with increasing of [PDP] at constant thiamine concentration.

IInd order polynomial fit

Slope = 0.014

R² = 0.99628

Set – III

Table 10: Effect of [PDP] in Oxidation of thiamine in presence of PDP

[Thiamine] - 1 x 10⁻⁴M

[PDP] - 2 x 10⁻³ M

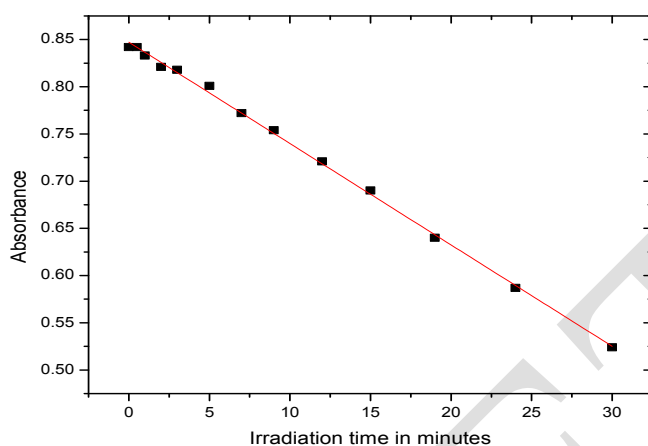
0.47 ml of thiamine + 3.03ml of PDP + 6.5 ml of H₂O

Irradiation time in minutes	Absorbance
0	0.842
0.5	0.842
1	0.833
2	0.821
3	0.818
5	0.801
7	0.772
9	0.754
12	0.721
15	0.69
19	0.64
24	0.587
30	0.524

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The effect of PDP concentration on the oxidation of thiamine increases with increasing of [PDP] at constant thiamine concentration.

IInd order polynomial fit

Slope = 0.107

R² = 0.99971

Set – I

Table 11: Effect of light intensity on Oxidation of thiamine in presence of PDP

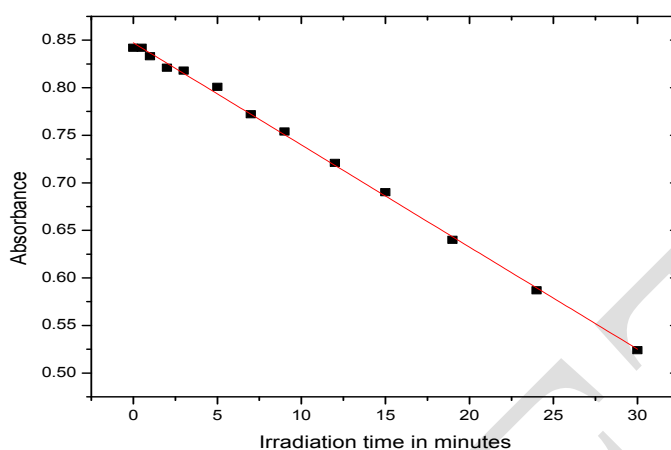
[Thiamine] - 1×10^{-4} M
 [PDP] - 2×10^{-3} M
 Distance - 14cm
 Intensity - 4.5×10^4 q/s
 0.47 ml of thiamine + 3.03ml of PDP + 6.5 ml of H₂O

Irradiation time in minutes	Absorbance
0	0.842
0.5	0.842
1	0.833
2	0.821
3	0.818
5	0.801
7	0.772
9	0.754
12	0.721
15	0.69
19	0.64
24	0.587
30	0.524

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The effect of light intensity on the oxidation of thiamine was studied at constant thiamine concentration and constant PDP concentration and it was found the rates of oxidation of thiamine increases with increase in light intensity. While quantum yields of thiamine were independent of light intensity.

IInd order polynomial fit

Slope = 0.0107

R² = 0.99971

Set – II

Table 12: Effect of light intensity on Oxidation of thiamine in presence of PDP

[Thiamine] - 1 x 10⁻⁴M

[PDP] - 2 x 10⁻³ M

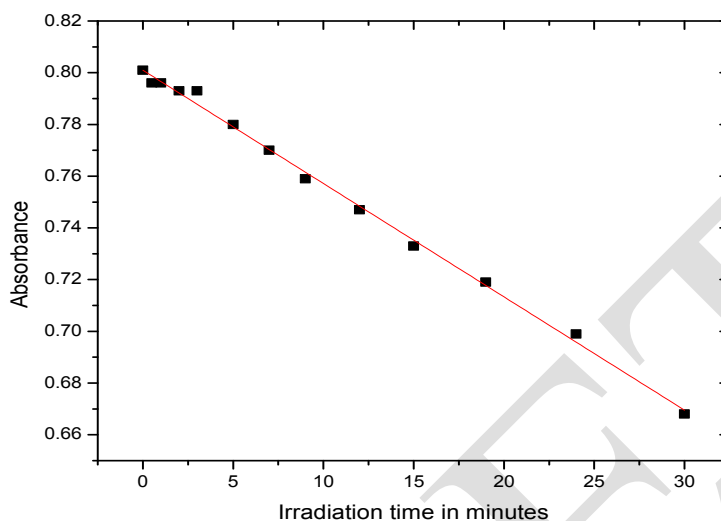
Distance - 21cm

Irradiation time in minutes	Absorbance
0	0.801
0.5	0.796
1	0.796
2	0.793
3	0.793
5	0.78
7	0.77
9	0.759
12	0.747
15	0.733
19	0.719
24	0.699
30	0.668

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The effect of light intensity on the oxidation of thiamine was studied at constant thiamine concentration and constant PDP concentration and it was found the rates of oxidation of thiamine increases with increase in light intensity. While quantum yields of thiamine were independent of light intensity.

II order polynomial fit

Slope = 0.00491

$R^2 = 0.99828$

Set – II

Table 13: Effect of light intensity on Oxidation of thiamine in presence of PDP

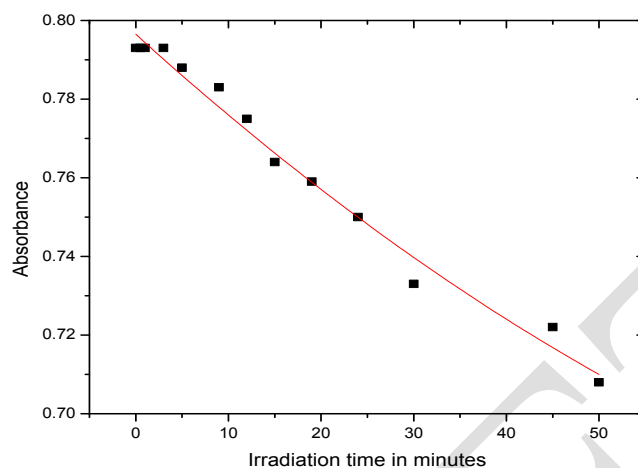
[Thiamine] - $1 \times 10^{-4}M$
 [PDP] - $2 \times 10^{-3} M$
 Distance - 28cm

Irradiation time in minutes	Absorbance
0	0.793
0.5	0.793
1	0.793
3	0.793
5	0.788
9	0.783
12	0.775
15	0.764
19	0.759
24	0.75
30	0.733
45	0.722
50	0.708

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The quantum yields of oxidation of thiamine in the presence PDP were calculated from the initial rates and light intensity at 264 nm and were found to decrease with increase in [thiamine] at constant [PDP] and [Ru].

II order polynomial fit

Slope = 0.00220

$R^2 = 0.97728$

V. CONCLUSION

Different reaction mixtures with different sets of concentrations of reactants, where PDP was in excess over thiamine hydrochloride (Vit. B₁) at constant ionic strength acidity and concentration of catalyst was kept for 8h at room temperature in an inert atmosphere. The unreacted PDP concentration was assayed by measuring the absorbance at 264 nm the products were identified and confirmed by UV – Vis, I.R, G.C – Ms and NMR Spectra. The reaction orders were determined from the slopes of irradiation of time vs absorbance plots by varying the concentration of PDP and thiamine hydrochloride. The rate of reactions was measured at different temperatures, 25^o, 30^o, 35^o, 45^oC under varying acid and thiamine hydrochloride concentration. The rates were found to increase with increasing temperature. The rates and quantum yields of oxidation of thiamine increased with increase in concentration of Thiamine. Effect of light intensity on oxidation of thiamine in presence of PDP observed the graph plotted between irradiation of time and absorbance.

REFERENCES

- [1] Charitha, Lingareddy; Adinarayana, Mundra, Kinetics of oxidation of thymine by *t*-butoxyl radical — Protection and repair by caffeic acid, IJC-A, Vol.45,11, 2006, .
- [2] Stepuro, A. Yu. Oparin, V. I. Stsiapura, S. A. Maskevich, V. Yu. Titov, Oxidation of thiamine on reaction with nitrogen dioxide generated by ferric myoglobin and hemoglobin in the presence of nitrite and hydrogen peroxide Biochemistry (Moscow), Vol. 77, No. 1, pp. 4155 2012.
- [3] Davis, K. L., Martin, E., Turko, I. V., and Murad, F. Annu. Rev. Pharmacol. Toxicol., 41, 203236, 2001.
- [4] Schopfer, F. J., Baker, P. R., and Freeman, B. A. Trends Biochem Sci., 28, 646654, 2003.
- [5] Kaur, H., and Halliwell, B. FEBS Lett., 350, 912. Torre, D., Ferrario, G., Speranza, F., Orani, A., Fiori, G.P., and Zeroli, C. (1996) J. Clin. Pathol., 49, 574576, 1994.
- [6] Qury, T. D., Tatro, L., Ghio, A. J., and Piantadosi, C. A. Free Radical Res., 23, 537547, 1995.
- [7] Sampson, M. B., Ye, Y.Z., Rosen, H., and Beckman, J. S. Arch. Biochem. Biophys., 356, 207213, 1998.
- [8] Zweier, J., Wang, P., Samouilov, A., and Kuppasamy, P. Nature Med., 1, 804809, 1995.
- [9] Stepuro, I. I., Chaikovskaya, N. A., Solodunov, A. A., and Artsukevich, A. N. Biochemistry (Moscow), 62, 960, 966, 1997.
- [10] Gladwin, M. T., Shelhamer, J. H., Schechter, A. N., Pease, Fye, M. E., Waclawiw, M. A., Panza, J. A., Ognibene, F. P., Cannon III, R. O. Proc. Natl. Acad. Sci. USA, 97, 1148211487, 2000.