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THERMODYNAMIC, KINETIC, MECHANISTIC AND SPECTROSCOPIC INVESTIGATION OF THIAMINE HYDROCHLORIDE (VITAMIN B_1) OXIDATION BY VANDIUM (V), AN INSULIN MIMETIC COMPOUND AT LOW PH

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ABSTRACT

The kinetics of oxidation of Thiamine Hydrochloride (Vitamin B_1) by vanadium (v) compound have been carried out by using spectrophotometric technique over the range $2.0 \le 10^5$ [Vit B_1] mol dm-3 ≤ 5.0, $1.7 \le pH \le 2.5$ and temperature range $293\ K \le T \le 318\ K$ were run under pseudo – first order conditions. The rate of oxidation was found to be first order with respect to vitamin B_1, and vanadium (v) concentration. This reaction is pH dependent. When pH increases 1.7 to 2.5, rate constant decreases whereas with decrease of dielectric constant of the medium rate constant increases. Ionic strength has no effect on such reaction. During electron transfer process thiamine hydrochloride forms a weak coordination complex with dioxovanadium (v) ion, hence inner-electron transfer reaction is suggested. Oxidation product was isolated and identified as thiochrome and vanadium (iv) which was supported by UV visible, FTIR and ^{1}HNMR spectroscopy. Moderate values of activation parameters such as activation enthalpy $\Delta H^{\#} = 37.67 \pm 6.82$ kJmol^{-1}, $\Delta S^{\#} = 101.2 \pm 21.73$ JK mol^{-1} activation free energy $\Delta G^{\#} = 67.86$ kJmol^{-1} are favourable for electron transfer process. The negative value of $\Delta S^{\#}$ indicates that transition state is more ordered than reactants.

KEYWORDS: Kinetic, redox reaction, vitamin B_1, vanadium (v) complex, spectrophotometry, product thiochrome, activation parameters.

1. INTRODUCTION

Thiamine Hydrochloride is known as Vitamin B_1 which is the first member of Vitamin B family. It is biologically very important. Thiamine derivatives and thiamine dependent enzymes are present in all cells of the body, thus a thiamine deficiency would have adversely affect all the organ system. Nervous system is sensitive to thiamine deficiency because of dependence of an oxidative metabolism. Thiamine deficiency leads to beriberi, optical neuropathy and poly neutries.[1,2] A lack of thiamine can be caused by malnutrition. Kinetics of oxidation of thiamine by other oxidants such as chloramines-T[3], Hg(II)[4], cerium(IV)[5], micellar catalysed chloramines-T[6], hexacyanoferrate(III)[7] hypoiodide[8], N-chlorobenzene-sulfonamide[9] have been reported.

Vanadium is an interesting metal that changes colour based on its oxidation state. Vanadium plays an important role in liver of various organisms. Thus much research in the chemical, biological and physiological fields has focused on vanadium. Although the importance of vanadium is well known, its necessity as a fundamental element in human body is still unclear. Thus vanadium complex have been widely investigated. Vanadium complex can act as oxidizing agent[10-12], insulin-mimic drug.[13,14] Vanadium forms complexes with oxidation state -2 to +5. But +3, +4, +5 oxidation state of Vanadium found in living organism. The changes in oxidation state +5, +4, +3 occur because oxidation potential of these states is quite low. The redox chemistry of vanadium is interesting. The redox chemistry of vanadium(V) by inorganic and biological reducing agents, such as EDTA[15], potassium bromate[16], Chloroform[17], aromatic aldehyde[18], paracetamol[19], ascorbic acid[20] have been reported.

The literature survey reveals that there was no report on the oxidation of thiamine hydrochloride (Vitamin B_1) by vanadium(V). Hence present work deals with interaction of thiamine hydrochloride with vanadium(V) at low pH. The mechanism of the reaction was suggested by studying the kinetics of such reaction and identifying the product.

2. EXPERIMENTAL

2.1 Materials and Methods

All chemicals are of analytical grade. Ammonium metavanadate from E. Merck was used as a source of vanadium (V). Thiamine hydrochloride (Vitamin B_1) was procured from local pharmaceutical company ABC pharmaceutical, Bhubaneswar.

Aqueous solution of thiamine hydrochloride of desired strength was prepared in doubly distilled water. Sodium perchlorate stock solution was prepared by dissolving sodium perchlorate crystals. The strength of sodium perchlorate solution was estimated by exchanging a definite volume of the solution with cation exchange resin Dowex 50 w x 8 (H^+ form). It was used for maintaining ionic strength; desired pH was maintained using $HClO_4$ and NaOH.

(a) Spectrophotometric Investigation

1. UV-visible spectroscopy: UV- visible spectral measurements were recorded on SIMAZU 1800 UV- visible double beam spectrophotometer using 10 mm matched quartz cell with peltier system.

(b) FTIR Spectra

Infrared spectra (FT mode) were recorded on samples prepared as KBr pellets. The spectra were recorded on FTIR spectrophotometer, Thermo fisher model No. Nicolet iS – 5.

(c) ^{1}H NMR spectra of the complex was recorded by 400 MH_Z (Bruker) in D_2O medium.

(d) pH measurement

The pH measurements were made with a pH meter model LI 120 (Elico, India) with a combined glass Ag/AgCl, Cl^- (3.0 mol dm^{-3}NaCl) electrode Cl- 51. The pH meter was standardized against NBS buffers of pH 4.01, 6.86 and 9.20 prepared from potassium hydrogen phthalate, Na_2HPO_4/KH_2PO_4 and $Na_2B_4O_710H_2O$ respectively were used to calibrate pH meter.

2.2 Kinetic Study

The kinetics of the reaction between thiamine hydrochloride and ammonium metavanadate at pH range 1.7 to 2.5 have been studied under pseudo-first order condition where vanadium(V) taken excess over thiamine hydrochloride by measuring decrease of absorbance at λ_{max} = 242 nm using UV-visible spectrophotometer. The reaction was studied varying the [thiamine hydrochloride] = 2 x 10^{-5} to 5 x 10^{-5}mol dm^{-3}, temperature range 293 K $\leq$ T $\leq$ 318 K, pH = 1.7 to 2.5 at constant ionic strength I= 0.5 mol dm^{-3}. Since the reaction was comparatively fast and completed within 5 minutes, experiments were carried out inside the cell of path length 1 mm. The pH of the solution was adjusted to desired value by using $HClO_4$ or NaOH. pH was measured before and after the kinetic study. No significant change was observed. Pseudo-first order rate constant have been calculated using non-linear least square method in equation (1).

$$\ln (A_t-A_\infty) = \ln(A_0-A_\infty)-k_{obs}xt \qquad (1)$$

Where A_0, A_t, A_∞ denotes optical density of the reaction mixture at zero time, time t and infinite time respectively. The rate constants were reproducible to within 5%. The correlation coefficient were found to be 0.99 in most of the cases. All calculation were made on Microsoft 2003 Excel programme.

2.3 Stoichiometry and product analysis

To find the stoichiometric co-efficient between vanadium (V) and Vitamin B_1 at various concentration of ammonium metavanadate (V) and thiamine hydrochloride in a molar ratio of 1:10 was taken. Solution was maintained at pH = 2.0 and I=0.5 mol dm^{-3}. The unreacted vanadium(V) concentration was estimated spectrophotometrically.[21]

From the above experiment, it was observed that 1 mole of thiamine hydrochloride reacted with one mole of vanadium to generate product. The stoichiometry was found to be 1:1 as depicted in equation (2)

$$TAH + VO_2^+ (aq) + 2H^+ = \underset{(Product)}{Thiochrome} + [V(H_2O)_6]^{4+} \qquad (2)$$

In order to get the reaction product, ammonium metavanadate (0.2 mol) and thiamine hydrochloride (0.2 mol) was dissolved in 20 ml of water at pH = 2.0 and were warmed and allowed to complete the reaction. From the solution metal ion was removed through cation exchange resin (Dowex 50WX8). The solution was slowly evaporated to concentrate the solution, then it was kept overnight, a brown coloured crystalline product was separated. It was washed with ethanol and dried in desiccator containing silica gel. The yield of product was 75%. UV-visible spectra of product shows λ_{max}=390nm (Fig. 1c) which corresponds to thiochrome. The product was further confirmed by FTIR spectra and ^{1}HNMR spectra as thiochrome as shown in Fig. S-1, S-2 and Fig. S-3, S-4 respectively.

FTIR spectra of thiamine hydrochloride (Fig. S-1) shows two sharp peaks at 3492 cm^{-1} and 3424 cm^{-1} due to N-H stretching in free amine, 3049 cm^{-1} is due to C-H stretching in aromatic group, 1667 cm^{-1} and 1614 cm^{-1} are due to N-H bending and C-N stretching, 1000-1381 cm^{-1} is due to C=N stretching and C-N bending, 1423-1614 is due to C=C aromatic stretching, 643-800 is due to C-H out plane bending and C-S stretching.

FTIR spectra of oxidation product of thiamine hydrochloride (Fig. S-2) show a broad peak at 3372 cm^{-1} corresponds to combination of co-ordinated water and O-H stretching. There is no peak for NH_2 and NH group, 1632 cm^{-1} and 1683 cm^{-1} are due to C=N stretching in the ring, 1414 cm^{-1}, 1476 cm^{-1} and 1583 cm^{-1} are due to C=C aromatic and 600-736 cm^{-1} due to C-H out plane bending and C-S stretching. All these peaks correspond to thiochrome. Assignment of peaks is from literature.[22] It is further confirmed by ^{1}H NMR of spectra of thiamine hydrochloride and its oxidation product. Fig. S-3 shows the following ^{1}H NMR of thiamine hydrochloride: δ 2.44 (S, 3H, CH_3), δ 2.74 (t, 2H, CH_2), δ 2.91 (S, 3H, CH_3), δ 3.66 (t, 2H, CH_2), δ 4.58 (S, 1H, OH), and δ 5.96 (S, 2H, CH_2). ^{1}H NMR of the oxidation product of thiamine hydrochloride (Fig. S-4) shows no peak at δ 6.13 as NH_2 group is absent in the product. The remaining peaks are present δ 2.44 (S, 3H, CH_3), δ 2.26 (S, 3H, CH_3), δ 2.15 (t, 2H, CH_2), δ 3.57 (t, 3H, CH_3), δ 3.8 (d, 2H, CH_2), δ 3.76 (d, 2H, CH_2), δ 4.8 (S, 1H, CH), δ 4.78 (S, 1H, OH), δ 8.09 (S, 1H, CH). All these chemical shift values correspond to the structure of thiochrome. Assignment of ^{1}H NMR peaks are from the literature.[23] It is further supported by characteristic peak at λ_{max} = 390 nm in UV-Visible spectra. Similar product have been reported by others using hydroxyl[24], peroxyl radical[25], peroxidase[26] as oxidants.

3. RESULTS AND DISCUSSION

The aqueous solution of NH_4VO_3 was yellow in colour due to formation of active species VO_2^+ (dioxo vanadium) which shows a peak at λ_{max}= 262 nm. Thiamine hydrochloride, show two peaks in UV-visible spectra, 232 nm and 264 nm. When these two solutions were mixed at pH = 2.0, yellow colour slowly changed to green colour indicated by spectral change (Fig. 1a) Time scan spectra (Fig. 1a) shows decrease of absorbance at λ_{max} = 242 nm with time. After a long interval of time (24 h) these peaks disappeared and new peak appeared at 373 nm corresponding to $[V(H_2O)_6]^{4+}$(Fig. 1b).

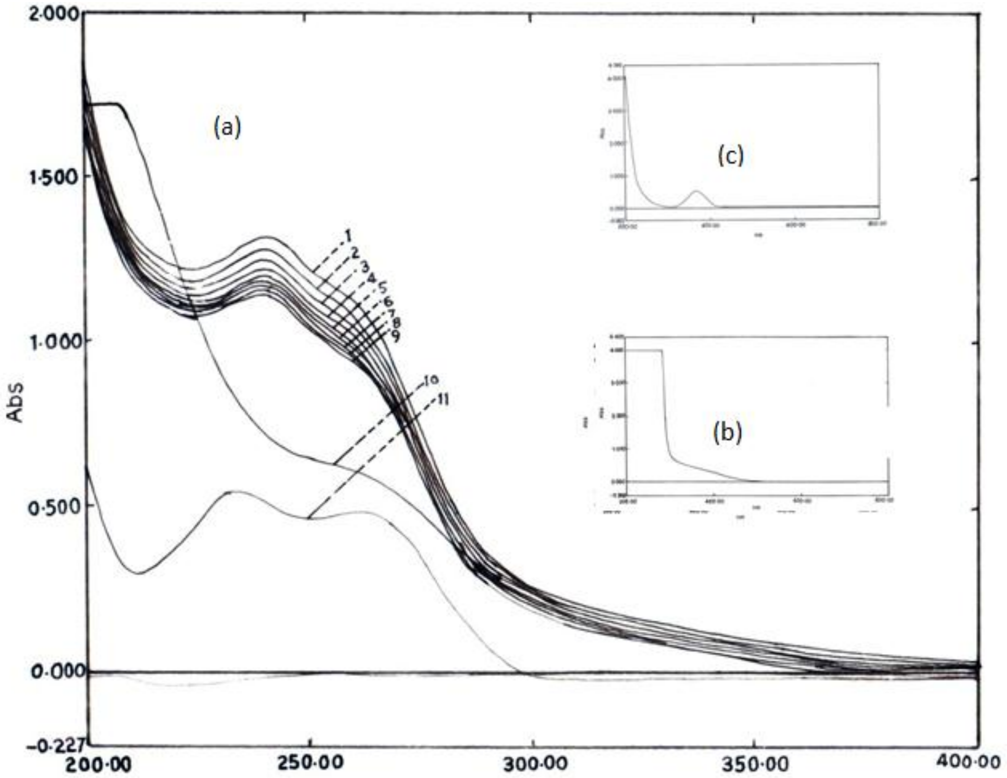


Figure 1: (a) UV-visible spectral scan, Thiamine Hydrochloride = 2 ×10^{-5}mol dm^{-3} (11), $[VO^+_2]$ = 2×10^{-4}mol dm^{-3} (10), immediately after mixing at pH = 2.1 (1), curves (2- 9), Δt = 15 (s) (b) $[VO_2^+]$ after 24h (c) Product, Thiochrome.

The redox reaction between thiamine hydrochloride and Vanadium(V) was studied over the range $2.0 \leq 10^5 [TAH] \leq 5.0$, $1.7 \leq pH \leq 2.5$, $293 K \leq T \leq 313$ K and I = 0.5 mol dm^{-3}. Pseudo-first order rate constant (k_{obs}) of the above reaction were measured at four different temperatures 293 K - 313 K presented in Table -1. The plot of k_{obs} *versus* [THA] was linear (Fig. 2) with a significant intercept indicating first order dependence on thiamine hydrochloride.

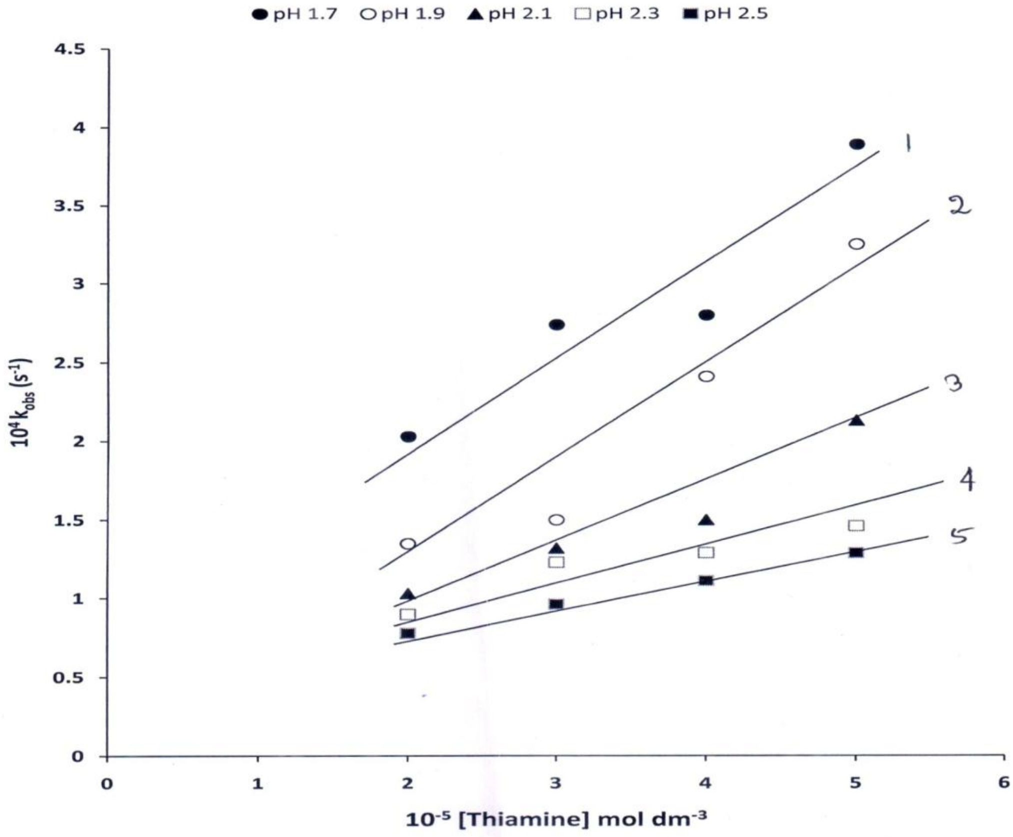


Fig. 2: Variation of $k_{obs}(s^{-1})$ with substrate (THA) at different pH, 293K at PH=1.7(1) 1.9(2) 2.1(3)2.3 (4) 2.5(5).

Table 1: Effect of variation of $[\mathrm{Vit\ B_1}]$ pH, temperature on the pseudo-first order rate constant (Kobs) in Oxidation of thiamin hydrochloride $[Vit\ B_1]$ by vanadium (v) in low pH at $\mathrm{I = 0.5mol\ dm^{-3}}$.

10^5[Vit B_1] mol dm^{-3}	pH	$10^4 k_{obs}$ (s^{-1})			
		293K	298K	313 K	318K
2.0	1.7	2.03	3.59	4.51	5.93
	1.9	1.35	2.43	3.35	4.90
	2.1	1.03	1.60	2.33	3.56
	2.3	0.91	1.24	1.83	2.88
	2.5	0.779	1.16	1.76	2.48
3.0	1.7	2.74	3.85	5.00	8.01
	1.9	1.50	2.53	3.83	6.11
	2.1	1.32	2.29	3.20	4.71
	2.3	1.21	1.99	2.96	4.57
	2.5	0.961	1.71	2.68	4.52
4.0	1.7	2.80	4.57	5.50	8.08
	1.9	2.41	3.28	4.86	7.77
	2.1	1.50	2.31	4.21	7.57
	2.3	1.29	2.24	3.61	6.62
	2.5	1.11	2.09	3.42	6.29
5.0	1.7	5.0	6.11	7.16	8.58
	1.9	3.25	4.43	6.83	8.00
	2.1	2.13	3.38	4.96	7.69
	2.3	1.46	3.12	4.16	7.46
	2.5	1.29	2.30	3.91	7.03

Experimental error $\pm 5\%$

3.1 pH effect

When the pH of the reaction solution varied from 1.7 to 2.5, pseudo-first order rate constant (k_{obs}) decreased indicating the reaction was pH dependent (Fig. 3). Above pH > 3.0, the kinetic study was prevented, hence rate measurements were restricted to pH<3.0.

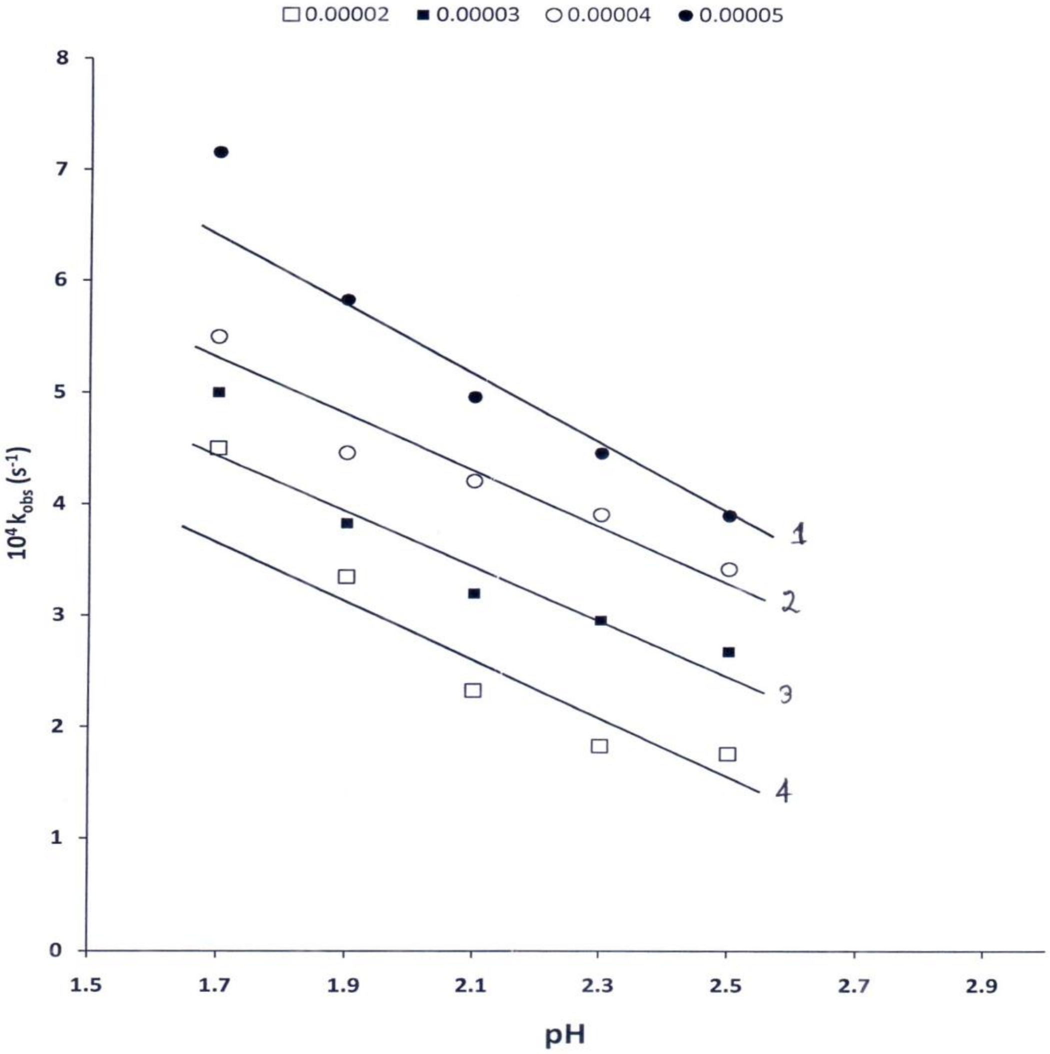


Fig. 3: Variation of k_{obs}(s^{-1}) with pH at different concentration of substrate. (1) [THA] = 2×10^{-5} mol dm^{-3} (2) 3×10^{-5} mol dm^{-3} (3) 4×10^{-5} mol dm^{-3} (4) 5×10^{-5}mol dm^{-3}

3.2 Ionic strength effect

The effect of ionic strength (I) was studied by varying $NaClO_4$ from 0.5 mol dm^{-3} to 2.0 mol dm^{-3} at pH = 2.0, keeping all other conditions constant. Plot of k_{obs}*versus*$\sqrt{I}$ was almost constant hence the reaction was independent of ionic strength.

3.3 Solvent polarity effect

The effect of dielectric constant of the solvent was studied at 303K by varying acetic acid from 20% to 60% (v/v) keeping all other conditions constant. $10^4 k_{obs}$ (s^{-1}) changed from 0.33 to 2.3 when the dielectric constant varied from 81.50 to 45.50 (Table 2). Plot of log k_{obs}*versus* D^{-1} is a straight line with a positive slope (R^2 = 0.99) indicating ion dipolar interaction in the rate determining step following Amies concept.[27]

Table 2: Pseudo-first order rate constants with variation of dielectric constants for the oxidation of Thiamine Hydrochloride.

Percentage of Acetic acid	Dielectric Constant	$10^4 k_{obs}$ (s^{-1})
20	81.50	0.33
30	72.00	0.83
40	63.30	1.4
50	56.00	1.72
60	45.50	2.3

3.4 Free radical test

The intervention of free radical was examined by adding acrylonitrile monomer to the reaction mixture in inert atmosphere and kept for 2h at room temperature. Upon dilution with methanol, the reaction mixture did not show any precipitate polymer indicating no intervention of free radicals during the reaction.

3.5 Temperature effect

The rate of the reaction was measured at four different temperatures 293K, 298K, 308K and 313K at constant concentration of the reactants and ionic strength. There action rate was increased with increasing temperature. The temperature variation data are presented in Table 1.

3.6 Mechanism and rate law

Basing on the above experimental facts, stoichiometry, identification of product, the probable mechanism may be delineated as in Scheme I.

$$VO_2^+ + H_3O^+ \overset{K_H}{\rightleftharpoons} [V(OH)_3]^{2+} \qquad (3)$$

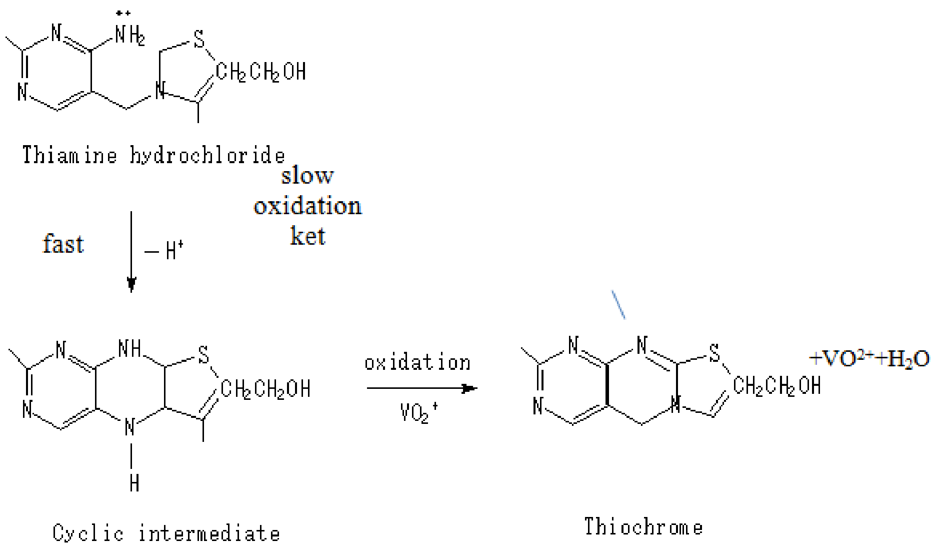
$$K_H = \frac{V(OH)_3^{2+}}{[VO_2^+]_e[H^+]_e} \qquad (4)$$

$$TAH + V(OH)_3^{2+} \overset{K_{eq}}{\rightleftharpoons} \underset{\text{Intermediate}}{[TAH.V(OH)_3^{2+}]} \qquad (5)$$

$$\begin{tikzcd}
{[TAH.V(OH)_3^{2+}]} \arrow[r, "-H^+", "fast"'] & \text{Cyclic intermediate compound} \arrow[d, "k_{et}", "slow"'] \\
 & VO^{2+} + \text{Thiochrome}
\end{tikzcd} \qquad (6)$$

Scheme – I

The rapid formation of the intermediate was followed by a slower step intramolecular electron transfer to produce vanadium(IV) and thiochrome. Formation of thiochrome was shown in Scheme II.



Scheme – II

Rate law was derived from scheme- 1

$$\text{Rate} = k_{et}[\text{Intermediate}]_e$$

$$K_{eq} = \frac{[\text{Intermediate}]_e}{[TAH]_e[V(OH)_3^{2+}]_e}$$

$$\text{Rate} = k_{et}K_{eq}\,[TAH]_e[V(OH)_3^{2+}]_e$$

$$= k_{et}K_{eq}\,K_H\,[TAH]_e[VO_2^+]_T[H^+]_e$$

$$[VO_2^+]_T = [VO_2^+]_e + [V(OH)_3^{2+}] + [\text{Intermediate}]_e$$

$$= [VO_2^+]_e + K_H[VO_2^+][H^+] + K_{eq}[TAH][V(OH)_3^{2+}]$$

$$= [VO_2^+]_e + K_H[VO_2^+][H^+] + K_HK_{eq}[TAH][VO_2^+][H^+]$$

$$= [VO_2^+]_e[1 + K_H[H^+] + K_HK_{eq}[TAH][H^+]\,]$$

$$[VO_2^+]_e = \frac{[VO_2^+]_T}{1 + K_H[H^+] + K_HK_{eq}[TAH][H^+]}$$

$$\text{Rate} = \frac{k_{et}K_{eq}K_H[TAH]_e[H^+][VO_2^+]_T}{1+ K_H[H^+] + K_HK_{eq}[TAH][H^+]}$$

$$\text{Rate} = k_{obs}\,[VO_2^+]_T$$

$$k_{obs} = \frac{k_{et}K_{eq}K_H[TAH]_T[H^+]}{1+ K_HK_{eq}[TAH][H^+]+K_H[H^+]}$$

$$\frac{k_{obs}}{[TAH]_T} = \frac{k_{et}K_{eq}K_H[H^+]}{1+ K_HK_{eq}[TAH][H^+]+K_H[H^+]}$$

$K_HK_{eq}[TAH][H^+] + K_H[H^+] << 1$ neglected,

$$\frac{k_{obs}}{[TAH]_T} = \frac{k_{et}K_{eq}K_H[H^+]}{1+K_H[H^+]}$$

$$k_2 = \frac{k_{et}K_{eq}K_H[H^+]}{1+K_H[H^+]}$$

$$\left(Let\,\frac{k_{obs}}{[TAH]_T}=k_2\right)$$

$$\frac{1}{k_2} = \frac{1}{k_{et}K_{eq}} + \frac{1}{k_{et}K_{eq}K_H[H^+]}$$

Plot of k_2^{-1} *versus* $[H^+]^{-1}$ produces a good straight line with a significant intercept. Inverse of the intercept produces composite rate constant ($k_{et}K_{eq}= k$). Slope gives the value of 1 / $k_{et}K_{eq}$ K_H. Intercept to slope ratio gives the value of K_H. Composite rate constant and equilibrium constant K_H are calculated and collected in Table - 3. Final products of the oxidation reaction are thiochrome and vanadium (IV). Our results are in good agreement with the observation of other investigators.[28-30]

The activation parameters are calculated from the slope of the plot of log k *versus* 1/T. The enthalpy of activation $\Delta H^{\neq}$, entropy of activation $\Delta S^{\neq}$ and free energy of activation $\Delta G^{\neq}$ are calculated by using Erying equation (7).[29]

$$k = \frac{k_B\,T\left(-\frac{\Delta G^{\neq}}{RT}\right)}{h} = \frac{k_B\,T}{h}e^{(\Delta H^{\neq}+\,T\Delta S^{\neq})/RT} \qquad (7)$$

k = electron transfer rate constant
k_B = Boltzmann’s constant
R = Gas constant
T = Absolute temperature
$\Delta G^{\neq}$ = Free energy of activation.

The linear form of eq. (7) is

$$\ln\left(\frac{k}{T}\right) = \frac{-\Delta H^{\neq}}{RT} + \frac{\Delta S^{\neq}}{R} + \ln\left(\frac{k_B}{h}\right)$$

$$= \frac{-\Delta H^{\neq}}{RT} + (\frac{\Delta S^{\neq}}{R} + 10.38)$$

The slope of the plot of log (k/T) versus 1/T gives the value of enthalpy of activation and intercept ($\frac{\Delta S^{\neq}}{R}$+ 10.38) gives the entropy of activation, calculated $\Delta H^{\neq}$ = 37.67±6.82 kJ mol^{-1} and $\Delta S^{\neq}$ = -101.2 ± 21.73 JK^{-1} mol^{-1}. Using the values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$, the free energy of activation is calculated as $\Delta G^{\neq}_{(298)}$= 67.86 kJ mol^{-1} (Table 3). Moderate value of activation parameters are favourable for electron transfer process. Positive value of $\Delta H^{\neq}$ and $\Delta G^{\neq}$ indicate the endothermic formation of adduct and its non-spontaneity respectively. The large negative value of activation entropy shows the compact transition.

Table 3: Composite rate constant (k) equilibrium constant (K_H) at different temperatures and activation parameters of composite rate constant is oxidation of vitamin B, by Vanadium (v) in low pH at $I = 0.5 mol\ dm^{-3}$

	293K	298K	313K	318K	
$10^4 k$ (s^{-1})	3.92	9.25	16.6	22.7	
K_H	0.528	0.935	1.10	1.17	
$\Delta S^{\pm}, J\,K^{-1}\,mol^{-1}$	$\Delta H^{\pm}, kJ\,mol^{-1}$	$\Delta G^{\pm}_{298}, kJ\,mol^{-1}$	$\Delta H^{0}, kJ\,mol^{-1}$	$\Delta S^{0}, JK^{-1}\,mol^{-1}$	$\Delta G^{0}, kJ\,mol^{-1}$
-101.2 ± 21.73	37.67 ± 6.82	67.88	20.53 ± 8.2	66.3 ± 27.1	0.2219

4. CONCLUSION

The oxidation reaction between thiamine hydrochloride (Vitamin B_1) and Vanadium(V) compound at low pH (1.7 to 2.5) has been studied spectrophotometrically in temperature range 293 -313K and 1.7 ≤ pH ≤ 2.0. The reaction is first order in both Vitamin B_1 and Vanadium(V) concentrations. As the pH increases from 1.7 to 2.5, the pseudo-first order rate constant decreasesbut with decrease of dielectric constant of the medium, rate of the reaction increases. Ionic strength has no effect on such reaction. Thiamine hydrochloride forms a weak coordination complex with dioxovanadium(V) ion during electron transfer reaction, inner-electron transfer reaction is suggested. No outer-sphere reduction pathway was observed in these systems. Oxidation product was identified as thiochrome and vanadium(IV) aqueous ion which supports the mechanism. The overall mechanism is consistent with experimental results and product analysis. Moderate values of $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta G^{\neq}$ are favourable for electron transfer processes. The large negative value of $\Delta S^{\neq}$ indicates that the transition state is more order than reactants due to loss of degree of freedom. The above mechanism shows the way of interaction of Vitamin B_1 with Vanadium(V) ion in biological systems.

Supplementary information (SI)

The spectroscopic information of the substrate and the product (FTIR S1-S3) and (^{1}H-NMR S3, S4) are presented in supplementary information available at www.ias.ac.in/chemsci.

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