Autocatalytic Oxidation of Thiamine Hydrochloride (Vitamin B_1) by Permanganate in Aqueous Sulfuric Acid Medium: A Kinetic and Mechanistic Study

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ABSTRACT: The reaction kinetics of autocatalytic oxidation of thiamine hydrochloride (vitamin B_1) by the permanganate ion in aqueous sulfuric acid medium has been investigated spectrophotometrically under the pseudo–first-order condition at 25°C. The observed stoichiometry is 6:5 in terms of the mole ratio of permanganate ions and thiamine hydrochloride. Formation of products was confirmed by UV–vis, IR, GC-MS, and NMR spectral data. Usually in the permanganate oxidation–reduction reactions, one of the products, Mn^{2+} autocatalyzes the reaction, but in the present investigation the autocatalytic effect is due to the (4-methyl–thiazol-5-yl) acetic acid, a product formed from the oxidation of vitamin B_1, which is a rare case. The added Mn^{2+} does not have any significant effect on the rate of reaction. The reaction is first order with respect to both permanganate and thiamine hydrochloride concentrations. An increase in the sulfuric acid concentration decreases the rate of reaction. A composite scheme and rate laws were proposed. The activation parameters with respect to the slow step and reaction constants involved in the mechanism were determined and discussed. © 2016 Wiley Periodicals, Inc. Int J Chem Kinet 48: 281–291, 2016

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INTRODUCTION

Thiamine hydrochloride, known as vitamin B_1, occurs in the outer coats of the seeds of many plants including cereal grains. Thiamine hydrochloride is fundamentally associated with carbohydrate metabolism [1]. Vitamin B_1 might also serve as a modulator of neuromuscular transmission [2]. The requirement of vitamin B_1 is related to the metabolic rate and is greater when carbohydrate is a source of energy [3]. Thiamine is synthesized in bacteria, fungi, and plants. Animals must cover all their needs from their food, and insufficient intake results in a disease called beriberi, affecting the peripheral nervous system (polyneuritis) or the cardiovascular system, with fatal outcome if not cured by thiamine administration [4]. As most feedstuffs used in poultry diets contain enough quantities of vitamins to meet the requirements in this species, deficiencies in this vitamin does not occur with commercial diets [5]. Today, there is still a lot of work devoted to elucidating the exact mechanisms by which thiamine deficiency leads to the specific symptoms observed. Finally, new thiamine phosphate derivatives have recently been discovered [6]. The oxidation kinetics and mechanism of vitamin B_1 are thus important to the process in vitro.

The permanganate ion is widely used as an oxidizing agent in synthetic as well as in analytical chemistry [7] and according to Insauti et al., it has several advantages as an analytical reagent [8]. In general, reduction of the permanganate, in acid media goes to either Mn(IV) or Mn(II) having the reduction potential [9] of the couple Mn(VII)/Mn(IV): 1.695 V and Mn(VII)/Mn(II): 1.51V. In acid medium, it exists in different forms, viz., $HMnO_4$, $H_2MnO_4^+$, $HMnO_3$, Mn_2O_7, and depending on the nature of the reductant the oxidant has been assigned both the inner sphere and outer sphere mechanism pathways in their redox reactions [10,11].

It is usual in the case of permanganate oxidation–reduction reactions, the product, Mn^{2+} autocatalyzes the reaction. But, in the present investigation one of the products (4-methyl–thiazol-5-yl) acetic acid, formed from the oxidation of vitamin B_1 by MnO_4^-, autocatalyzes the rate of reaction, which is a rare case. Owing to this, the mechanism may be quite complicated and interesting one. Permanganate in acid solution exists as MnO_4^-, $H_2MnO_4^+$, $HMnO_3$, and Mn_2O_7. Among all the species, MnO_4^- is the most active oxidizing species [12]. The literature survey indicates that there are no reports on the oxidation of vitamin B_1 by permanganate in an acid medium. Hence, we have investigated the autocatalyzed oxidation of vitamin B_1 by permanganate to arrive at suitable mechanisms.

EXPERIMENTAL

Materials and Methods

Materials. The solutions were prepared in water which had been twice distilled in an all-glass unit in the presence of potassium permanganate. Reagent-grade chemicals were used. A stock solution of vitamin B_1 was prepared by dissolving in water. Permanganate (MnO_4^-) stock solution was obtained by dissolving potassium permanganate (Glaxo; analar, India) in water and standardized by titrating against oxalic acid [13]. Always freshly prepared and standardized MnO_4^- solutions were used in the kinetics. The manganese(II) solution was made by dissolving manganese sulfate (AR) in water. The (4-methyl–thiazol-5-yl) acetic acid (CDH) solution was prepared by dissolving it in water. Na_2SO_4 (AR) and H_2SO_4 (AR) were used to provide the required ionic strength and acidity, respectively.

Kinetic Measurements. All kinetic measurements were performed under pseudo–first-order conditions with vitamin B_1 concentration greater than permanganate concentration at constant ionic strength of 1.60 mol dm^{-3} except in the variation of acid, in which $I = 3.10$ mol dm^{-3}. The reaction was initiated by mixing thermally equilibrated (25.0 ± 0.1°C) solutions of vitamin B_1 and permanganate, which has also contained the required amounts of sodium sulfate and sulfuric acid. The reaction was followed by measuring the absorbance of the permanganate concentration in the reaction mixture at 525 nm in a 1-cm cell placed in the thermostated compartment of a Varian Cary 50 Bio UV–vis spectrophotometer. Application of Beer's law was verified between 1.0×10^{-4} and 1.0×10^{-3} mol dm^{-3} of permanganate concentration at 525 nm under the reaction conditions, and the molar extinction coefficient was found to be $\varepsilon = 2200 \pm 50$ dm^3 mol^{-1} cm^{-1}. The kinetic runs were followed more than 85% completion of the reaction. Since one of the products, (4-methyl–thiazol-5-yl) acetic acid autocatalyzes the reaction, the pseudo–first-order rate constants, k_{obs}, were calculated from the plots of log (absorbance) vs. time, for about 70% completion of the reaction after which sigmoid curves were obtained (Fig. 1). The k_{obs} values were reproducible within ±5% and are the average of at least three independent kinetic runs (Table I) [14,15].

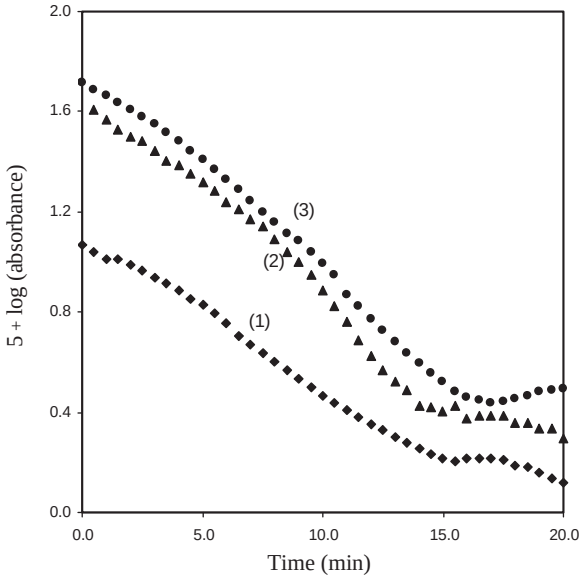


Figure 1 Plot of log (absorbance) vs. time [vitamin B_1] $= 1.0 \times 10^{-3}$; $[H_2SO_4] = 0.50$; $I = 1.60$, $[MnO_4^-] \times 10^4$/mol dm^{-3}: (1) 0.5, (2) 1.0, and (3) 2.0.

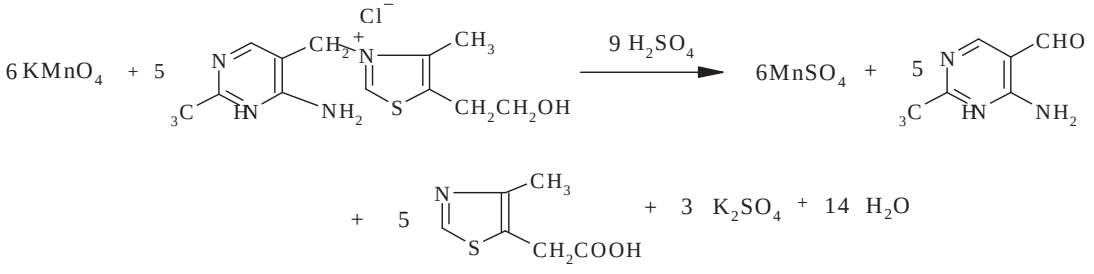
Table I Effect of Variation of MnO_4^- and Vitamin B_1 Concentrations on the Autocatalyzed Oxidation of Vitamin B_1 by MnO_4^- in Aqueous Sulfuric Acid Medium at 25°C. $[H^+] = 0.28$; $I = 1.60$/mol dm^{-3}

$[MnO_4^-] \times 10^4$ (mol dm^{-3})	[Vitamin B_1] $\times$ 10^3 (mol dm^{-3})	$k_{obs} \times 10^3$ (s^{-1})	$k_{cal} \times 10^3$ (s^{-1})
0.50	3.0	5.19	5.19
1.0	3.0	5.22	5.22
2.0	3.0	5.30	5.10
3.0	3.0	5.30	5.41
4.0	3.0	5.18	5.18
5.0	3.0	5.15	5.15
2.0	1.0	1.69	1.80
2.0	2.0	3.39	3.60
2.0	3.0	5.30	5.40
2.0	4.0	6.91	7.01
2.0	6.0	9.91	10.4
2.0	8.0	13.6	14.4
2.0	10.0	17.0	18.0

RESULTS

Stoichiometry and Product Analysis

Different sets of concentrations of reactants in 0.50 mol dm^{-3} sulfuric acid at constant ionic strength, 1.60 mol dm^{-3} were kept for over 5 h at 25°C in a closed container. When [permanganate] > [vitamin B_1], the remaining permanganate concentration was assayed by measuring the absorbance at 525 nm. The reaction products were identified as Mn^{2+}, (4-methyl–thiazol-5-yl) acetic acid, and (4-amino-2-methyl–pyrimidine-5-carbaldehyde). The results indicate that 5 mol of vitamin B_1 consumed 6 mol of permanganate according to Eq. (1).



(1)

The products were isolated by using the TLC separation technique and characterized by physicochemical spectral studies. The reaction products were confirmed by UV–vis, IR, GC-MS, and ^{1}H NMR spectral studies. Mn^{2+} was confirmed by UV–vis spectra and spot test [16]. Two hours after completion of the reaction, the reaction mixture was treated with the 5% Na_2CO_3 and then it was extracted by ether. The ether layer was separated and dried well on $CaCO_3$. On evaporation of the ether, the obtained product was found to be (4-amino- 2-methyl–pyrimidine-5-carbaldehyde), which was confirmed by GC-MS, where a molecular ion peak was observed at $m/z = 137$ (Fig. 2), and it was also confirmed by the ^{1}H NMR ($CDCl_3$) in which δ 9.80 (s, 1H, for –C–CHO), δ 9.01 singlet proton(s, 2H, NH_2), δ 8.34 singlet proton (S, 1H, Ar-H), and δ 2.33 singlet (s, 3H CH_3) (Fig. 3). The remaining aqueous layer was acidified with 5% HCl and extracted with ethyl acetate. After removing ethyl acetate, the formed residue was recrystallized by using ethyl acetate and hexane mixture to get yellow needles of (4-methyl–thiazol-5-yl) acetic acid. The (4-methyl–thiazol-5-yl) acetic acid was further confirmed by the IR (KBr) where the OH band shows stretching at 3400 cm^{-1}, for CO the broad band at 1730 cm^{-1}. In GC–MS, a molecular ion peak was observed at $m/z = 112$. (Fig. 4), where as in ^{1}H NMR, δ 11.43 singlet (s, 1H, COOH), δ 8.35 singlet (s,1H, Ar-H), δ 5.57 (s, 2H, CH_2), and 2.57 singlet (s, 3H, CH_3) (Fig. 5).

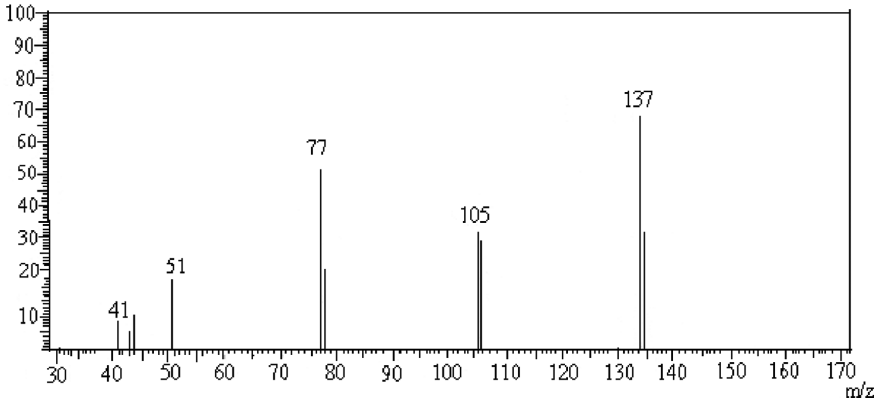


Figure 2 GC–MS spectra of the product (4-amino-2-methyl–pyrimidine-5-carbaldehyde).

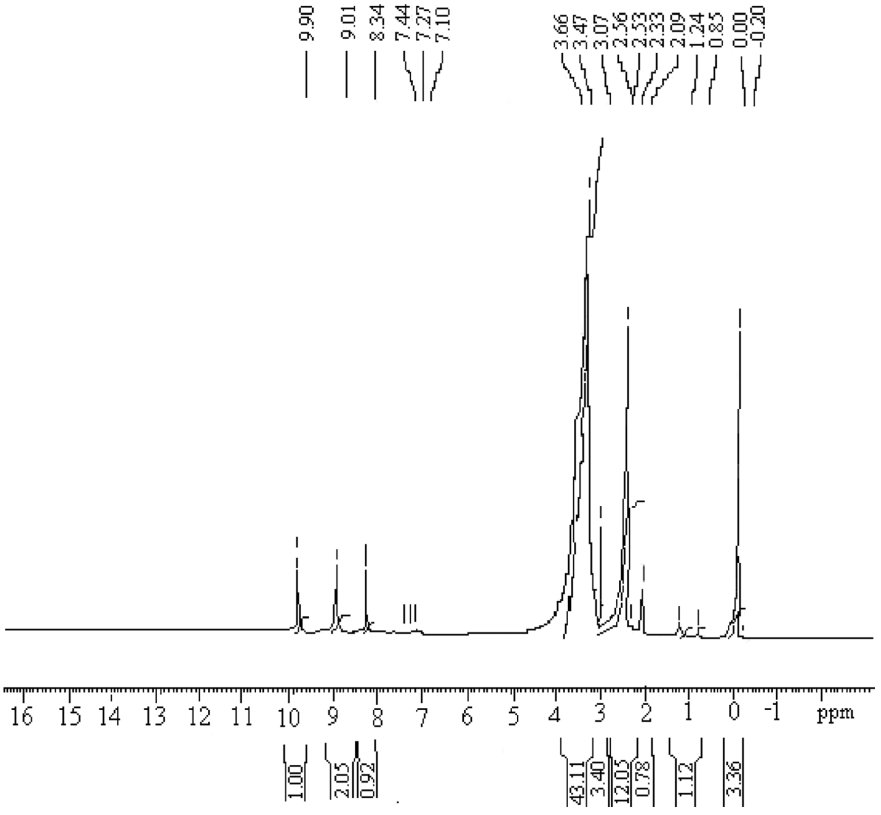


Figure 3 ^{1}H NMR of the product (4-amino-2-methyl–pyrimidine-5-carbaldehyde).

Reaction Orders

The reaction orders were determined from the slope of logk_{obs} vs. log (concentrations) plots by varying the concentration of vitamin B_1 and sulfuric acid in turn, keeping all other concentrations and conditions constant.

Effect of [Permanganate]

The oxidant, permanganate (MnO_4^-), concentration was varied in the range of 5.0×10^{-5} to 5.0×10^{-4} mol dm^{-3}. The observed pseudo–first-order rate constants, k_{obs}, were almost constant (Table I), indicating first-order dependence with respect to the permanganate concentration.

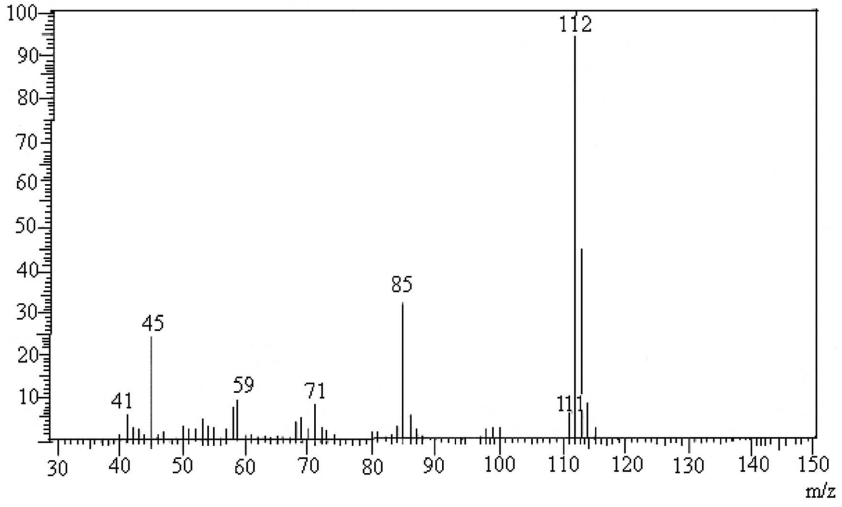


Figure 4 GC–MS spectra of the product (4-methyl–thiazol-5-yl) acetic acid.

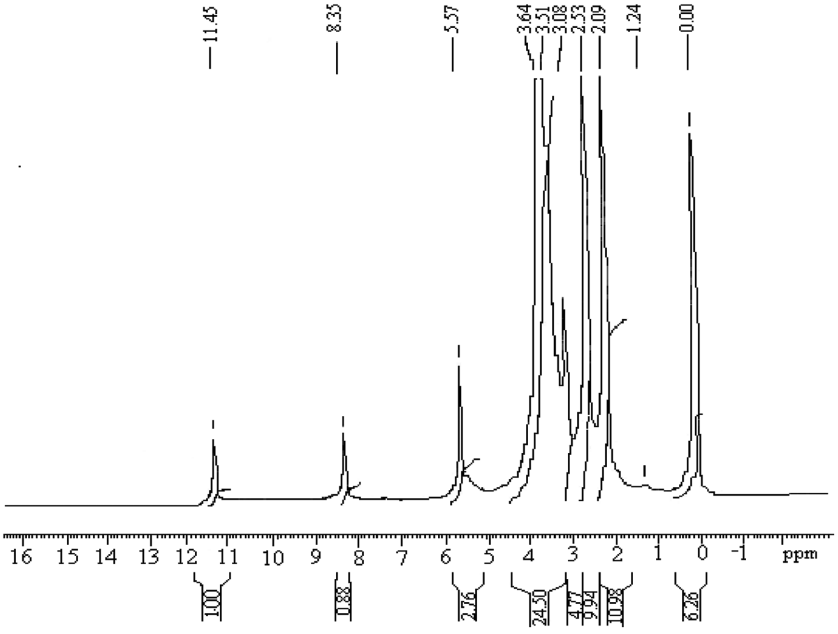


Figure 5 ^{1}H NMR spectra of the product (4-methyl–thiazol-5-yl) acetic acid.

Effect of [Vitamin B_1]

The effect of variation of vitamin B_1 on the rate of reaction was studied in the concentration range, 1.0×10^{-3} to 1.0×10^{-2} mol dm^{-3}, at constant concentrations of MnO_4^-, H_2SO_4, and constant ionic strength. It was observed that as the vitamin B_1 concentration increased, k_{obs} also increased (Table I). The value of the slope of the plot of log k_{obs} vs. log [vitamin B_1] was found to be unity, and it shows a linear relationship with the linear regression equation $y = 1.688x + 5 \times 10^{-5}$ and relative coefficient ($r = 0.9996$), which indicates first order with respect to the vitamin B_1 concentration.

Effect of [Acid]

At a fixed concentration of oxidant, $[MnO_4^-] = 2.0 \times 10^{-4}$ mol dm^{-3}, vitamin $B_1 = 3.0 \times 10^{-3}$ mol dm^{-3}, and by keeping other conditions constant, the k_{obs} was found to be decreased with increasing sulfuric acid concentration (Table II). The in situ H^+ ion concentration in the sulfuric acid–sulfate media was calculated

Table II Effect of the Sulfuric Acid Concentration on the Autocatalyzed Oxidation of Vitamin B_1 by MnO_4^- at 25°C. $[MnO_4^-] = 2.0 \times 10^{-4}$; [vitamin B_1] $= 3.0 \times 10^{-3}$, I = 3.1 mol dm^{-3}

H_2SO_4 (mol dm^{-3})	$[H^+]$ (mol dm^{-3})	$[SO_4^{2-}]$ (mol dm^{-3})	$[HSO_4^-]$ (mol dm^{-3})	$k_{obs} \times 10^3$ (s^{-1})	$k_{calcd} \times 10^3$ (s^{-1})
0.10	0.025	0.855	0.175	7.93	7.25
0.20	0.059	0.689	0.340	7.03	6.93
0.30	0.126	0.556	0.474	6.53	6.38
0.40	0.182	0.412	0.618	6.07	5.96
0.50	0.280	0.310	0.720	5.30	5.40
0.60	0.414	0.244	0.786	4.30	4.70
0.80	0.719	0.149	0.881	3.66	3.75
1.00	1.074	0.101	0.926	3.00	2.99

Table III Effect of Initially Added Product, (4-Methyl–thiazol-5-yl) acetic acid, on the Oxidation of Vitamin B_1 in Aqueous Sulfuric Acid Medium at 25°C. $[MnO_4^-] = 2.0 \times 10^{-4}$; [vitamin B_1] $= 3.0 \times 10^{-3}$; $[H^+] = 0.28$, I = 1.60 /mol dm^{-3}

[4-Methyl–thiazol-5-yl) acetic acid] $\times 10^4$ (mol dm^{-3})	$k_{obs} \times 10^3$ (s^{-1})
0.25	5.21
0.50	8.31
1.00	22.9
1.50	38.0
2.00	44.0
2.50	51.0

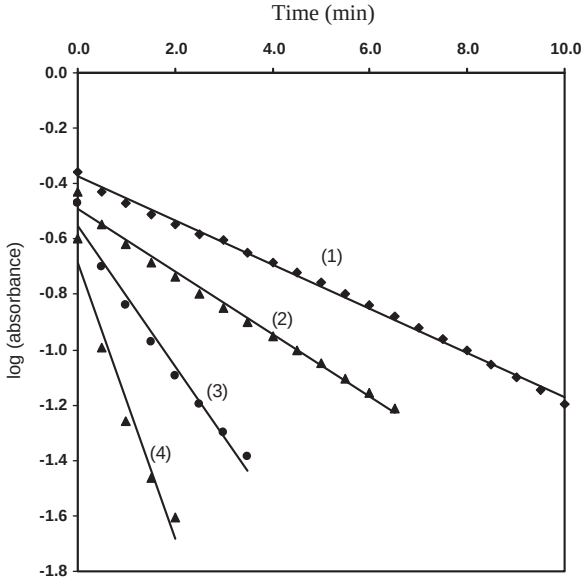


Figure 6 Effect of the added product, (4-methyl–thiazol-5-yl acetic acid), on the oxidation of vitamin B_1 by MnO_4^-. [4-methyl–thiazol-5-yl) acetic acid]: (1) 0.25×10^{-4}, (2) 0.50×10^{-4}, (3) 1.0×10^{-4}, and (4) 1.5×10^{-4} mol dm^{-3}.

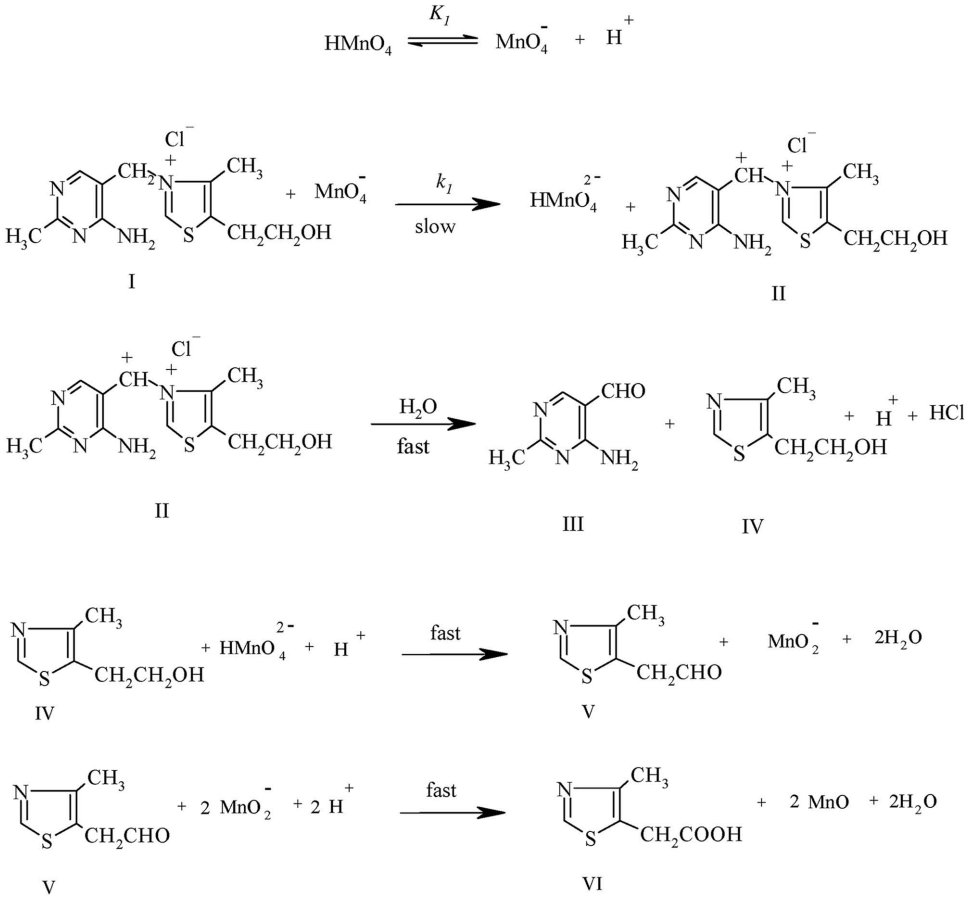
by using the known ionization constant [17] of acid sulfate as in the earlier study [18]. The value of the slope of the plot of log k_{obs} vs. log [acid] was found to be order with respect to the H^+ ion concentration was negative and less than unity, and it shows a linear relationship with the linear regression equation, $y = -5.577x + 8.196$ and relative coefficient ($r = -0.9863$).

Effect of Initially Added Products

The initially added products, manganese(II), (4-amino-2-methyl–pyrimidine-5-carbaldehyde), and (4-methyl–thiazol-5-yl) acetic acid, were studied in the concentration range, 5.0×10^{-5} to 5.0×10^{-4} mol dm^{-3} and 2.5×10^{-5} to 2.5×10^{-4} mol dm^{-3} concentration ranges, respectively, while keeping the reactant concentrations and all other conditions constant. It was observed that added (4-methyl–thiazol-5-yl) acetic acid enhances the rate of reaction (Table III) with an unit order, whereas the added manganese(II) and (4-amino-2-methyl–pyrimidine-5-carbaldehyde) did not change the rate of reaction appreciably. The results indicate the autocatalytic nature of the product, (4-methyl–thiazol-5-yl) acetic acid. The plots of log (absorbance) vs. time for initially added product, (4-methyl–thiazol-5-yl) acetic acid at different concentrations, showed almost linearity up to 70% completion of the reaction (Fig. 6), after which sigmoid curves were obtained (not shown).

Effect of Ionic Strength and Dielectric Constant

At constant concentrations of reactants and at other conditions kept constant, the ionic strength was varied



Scheme 1

between 1.6 and 3.1 mol dm^{-3} by varying the concentrations of sodium sulfate. At constant acidity and other constant conditions, the dielectric constant of the medium was varied by varying acetic acid–water (v/v) content in the reaction mixture from 0 to 50%. Both ionic strength and dielectric constant did not have any significant effect on the rate of reaction.

Test for Free Radicals

The intervention of free radicals was examined as follows: To a 10-cm^3 of reaction mixture, 2 cm^3 of acrylonitrile scavenger was added and kept in the inert atmosphere for 5 h. Diluting with methanol, no precipitate resulted, indicating the absence of free radical intervention.

Effect of Temperature

The rate of reaction was studied at four different temperatures 15, 25, 35, and 45°C by varying the sulfuric acid concentration. The rate of reaction increased with an increase in temperature. The rate constant, k_1, of the slow step of Scheme 1 was obtained from the intercept of the plots of [vitamin B_1]/k_{obs} vs. [H^+] at four different temperatures (Table IV). The energy of activation, E_a, was evaluated from the slope of the plot of log k vs. $1/T$ and the value is 54 ± 1 k J mol^{-1}. The enthalpy of activation, $\Delta H^{\neq}$, and the entropy of activation, $\Delta S^{\neq}$, were obtained by the Eyring equation [19].

$$k = \frac{k_B T}{h} e^{(-\Delta G^{\#}/RT)} = \frac{k_B T}{h} e^{-(\Delta H^{\#} + T\Delta S^{\#})/RT} \quad (2)$$

where k is the second-order rate constant, k_B is the Boltzmann's constant, R is the gas constant, T is the absolute temperature, and $\Delta G^{\neq}$ is the free energy of activation. The linear form of Eq. (2) is

$$\ln\frac{k}{T} = -\frac{\Delta H^{\#}}{RT} + \frac{\Delta S^{\#}}{R} + \ln\frac{k_B}{h} \quad (3)$$

Table IV Effect of Temperature on the Autocatalyzed Oxidation of Vitamin B_1 by MnO_4^-, in Aqueous Sulfuric Acid Medium and with Respect to the Slow Step of Scheme 1 Temperature (K) k_1 ($dm^3\ mol^{-1}\ s^{-1}$) and Effect of Temperature on the First Equilibrium Step of Scheme 1

Temperature (K)	K_1 (mol dm^{-3})
Effect of temperature on the autocatalyzed oxidation of vitamin B1 by MnO_4^-	
288	0.97
298	2.53
308	5.78
313	8.23
Activation parameter	
Parameter	Values*
E_a	54 ± 1 kJ mol^{-1}
$\Delta H^{\#}$	52 ± 1 kJ mol^{-1}
$\Delta S^{\#}$	−48 ± 2 J $K^{-1}mol^{-1}$
$\Delta G^{\#}$	52 ± 2 kJ mol^{-1}
log A	9.9 ± 0.2
Effect of temperature on the first equilibrium step of Scheme 1	
Temperature (K)	K_1 (mol dm^{-3})
288	0.74
298	0.67
308	0.60
313	0.55
Thermodynamic quantities with respect to K_1	
ΔH (kJ mol^{-1})	−7 ± 2
ΔS (J K^{-1} mol^{-1})	−28 ± 5
ΔG (kJ mol^{-1})	1.0 ± 0.02

*Error against each parameter is average of three independent kinetic measurements.

The slope of the plot of $\log k/T$ *vs.* $1/T$ gives the value of enthalpy of activation, $\Delta H^{\neq} = 52 \pm$ k J mol^{-1}. By using this value $\Delta H^{\neq}$, and the rate constant at a particular temperature T, the value of $\Delta S^{\neq}$ was obtained by simple rearrangement of Eq. (2) and the value is $\Delta S^{\neq} = -48.8 \pm 2$ J K^{-1} mol^{-1}. Using these values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$, the obtained free energy of activation, $\Delta G_{298}{}^{\neq}$ is 52 ± 2 k J mol^{-1}.

DISCUSSION

In the present investigation as the sulfuric acid concentration increased the rate of reaction decreased. It indicates that as the H^+ concentration increased the formation of MnO_4^- species decreased in the reaction mixture. The reaction between vitamin B_1 and permanganate in sulfuric acid has a stoichiometry 5:6 with first order each in permanganate and vitamin B_1 concentrations. The oxidation products were manganese(II), (4-methyl–thiazol-5-yl) acetic acid, and (4-amino-2-methyl–pyrimidine-5-carbaldehyde). It was observed that, one of the products, (4-methyl–thiazol-5-yl) acetic acid, autocatalyzed the reaction rate, where as other products, manganese(II) and (4-amino-2-methyl–pyrimidine-5-carbaldehyde), did not have any significant effect on the rate of reaction. In view of the decreasing rate with increasing H^+ ion, $HMnO_4$ decomposes to give MnO_4^- and H^+ ion. Such a type of active species of MnO_4^- is evidenced by the literature [12]. Furthermore, MnO_4^- species reacts with vitamin B_1 in a rate-determining step to give the intermediate $HMnO_4{}^{2-}$ and carbocation(II). In a fast step, intermediate(II) hydrolyzes to give (4-amino-2-methyl–pyrimidine-5-carbaldehyde)(III) and (4-methyl–thiazol-5-yl)-ethanol(IV). In further fast step, (4-methyl–thiazol-5-yl) ethanol(IV) reacts with 1 mol of $HMnO_4{}^{2-}$ to give (4-methyl–thiazol-5-yl) acetaldehyde(V) and $MnO_2{}^-$. The formed intermediate (V) which in turn reacts with two moles of $MnO_2{}^-$ to give the final product (4-methyl–thiazol-5-yl) acetic acid(VI) and Mn^{2+}. The results are accommodated in the following mechanism (Scheme 1).

From Scheme 1, the following rate law (6) can be derived as follows:

$$\text{Rate} = \frac{-\text{d}[MnO_4^-]}{\text{dt}} = k_1[MnO_4^-]\ [\text{vit. B}_1]$$

$$= \frac{k_1 K_1 [HMnO_4]_f\ [\text{vit. B}_1]}{H^+} \qquad (4)$$

The total concentration of permanganate ion is given by

$$[MnO_4^-]_t = [HMnO_4]_f + [MnO_4^-]$$

$$= [HMnO_4]_f \left(1 + \frac{K_1}{[H^+]}\right)$$

$$\therefore \quad [HMnO_4]_f = \frac{[MnO_4^-]_t\ [H^+]}{K_1 + [H^+]} \qquad (5)$$

Substituting Eq. (5) in Eq. (4) and omitting the subscripts,

$$\frac{\text{Rate}}{[MnO_4^-]} = k_{obs} = \frac{k_1 K_1\ [\text{vit B}_1]}{K_1 + [H^+]} \qquad (6)$$

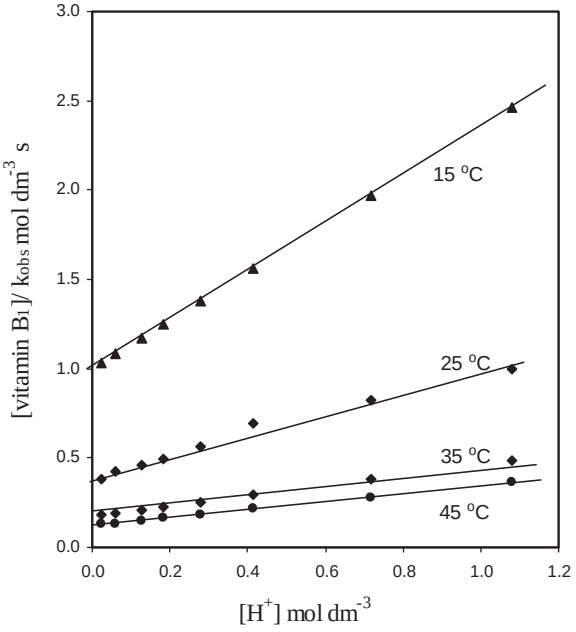


Figure 7 Verification rate law (6) in the form of Eq. (7) (conditions are as in Table II).

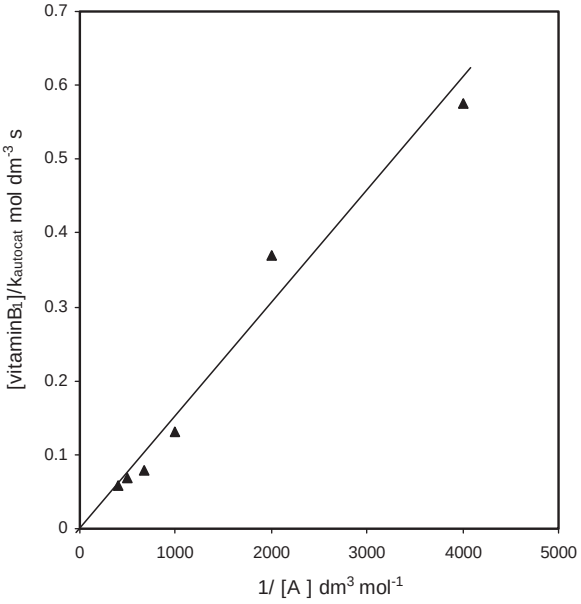


Figure 8 Verification rate law (13) (conditions are as in Table III).

The rate law (6) accommodates all the experimental results except the autocatalytic effect of (4-methyl–thiazol-5-yl) acetic acid. The rate law (6) may be rearranged to Eq. (7), which is suitable for verification.

$$\frac{[\text{vit. B}_1]}{k_{\text{obs}}} = \frac{[\text{H}^+]}{K_1\, k_1} + \frac{1}{k_1} \tag{7}$$

According to Eq. (7), a plot of $[\text{vit B}_1]/k_{\text{obs}}$ vs. $[\text{H}^+]$ should be linear and is found to be so at different temperatures (Fig. 7). The intercept of the plot gave $k_1 = 2.53 \pm 0.10\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ at 25°C. From the values of slope and k_1, K_1 was calculated, $K_1 = 0.67 \pm 0.05$ mol dm^{-3} at 25°C. The obtained value of K_1 agrees reasonably well with the literature [10]. Using these values, the rates under different experimental conditions were calculated and compared with experimental data. The experimental and calculated values agreed reasonably well (Tables I and II) which confirms Scheme 1.

Autocatalysis

Autocatalysis by one of the products (4-methyl –thiazol-5-yl) acetic acid [A] is interesting. The order of unity in [(4-methyl–thiazol-5-yl) acetic acid] may be attributed to the weak complex formation between the product, (4-methyl–thiazol-5-yl) acetic acid, and oxidant, MnO_4^-. This is followed by the interaction of weak complex with vitamin B_1 as shown in Scheme 2. The steps shown in Scheme 2 will form the part of Scheme 1.

The evidence for adduct formation was obtained from UV–vis spectra of both MnO_4^- and (4-methyl–thiazol-5-yl) acetic acid and permanganate mixture, in which a hypsochromic shift of 6 nm from 236 to 230 nm and hyperchromicity at 230 nm, occurred. This was also confirmed from the Michaelis–Menten plot (Fig. 8). The zero intercept of the plot indicates the weak complex formed between MnO_4^- and product, A. Thus formed weak complex is short lived and reactive. Hence, it may be considered as an adduct. Such adduct formation is observed in the literature [20].

From Scheme 2, the following rate law (10) can be obtained as follows:

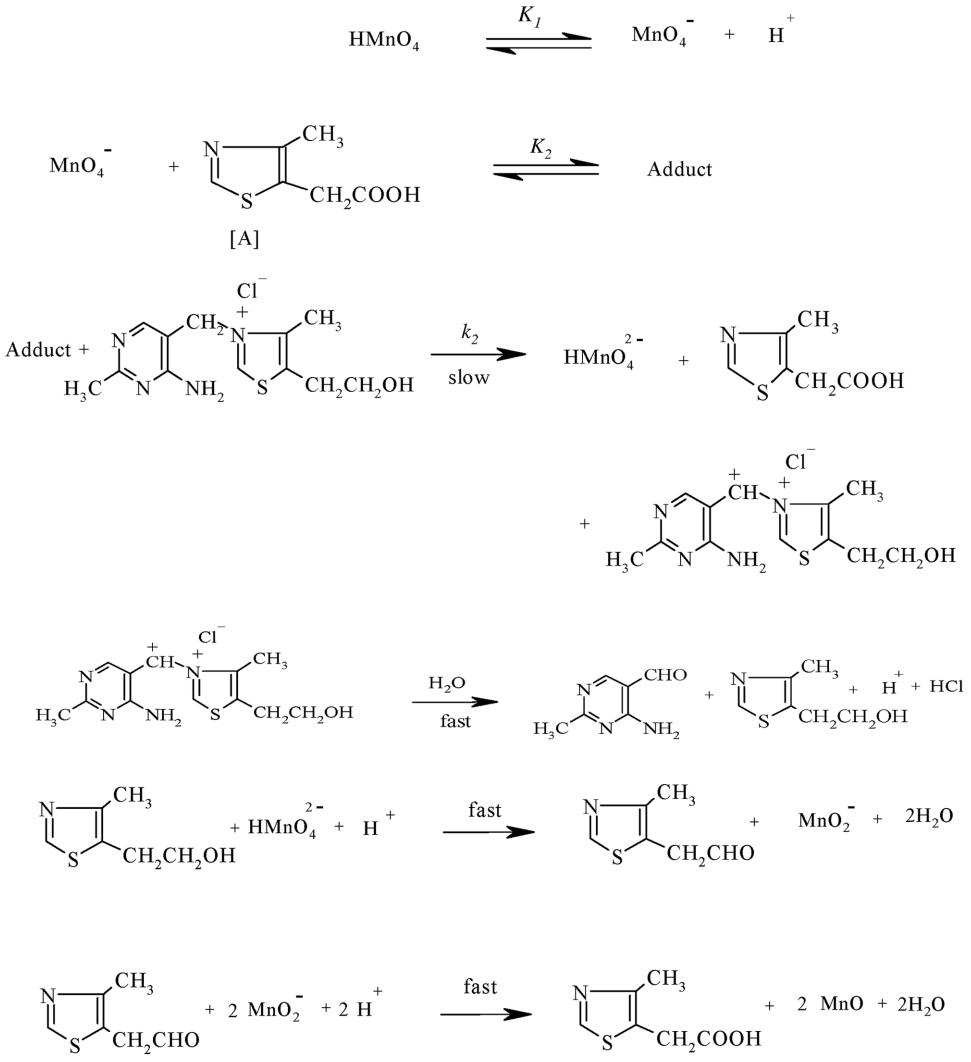
$$\text{Rate} = \frac{\text{d}[\text{MnO}_4^-]}{\text{dt}} = k_2\,[\text{adduct}]\,[\text{vit. B}_1]$$

$$= \frac{k_2 K_1 K_2\,[\text{HMnO}_4]\,[\text{A}]\,[\text{vit. B}_1]}{[\text{H}^+]} \tag{8}$$

But, the total concentration of permanganate ion is given

$$[\text{MnO}_4^-]_{\text{t}} = [\text{HMnO}_4]_{\text{f}} + [\text{MnO}_4^-]$$

$$= [\text{HMnO}_4]_{\text{f}} \left(1 + \frac{K_1}{[\text{H}^+]}\right)$$



Scheme 2

$$\therefore \quad [HMnO_4]_f = \frac{[MnO_4^-]\,[H^+]}{[H^+] + K_1} \tag{9}$$

By substituting Eq. (9) in Eq. (10) and omitting the subscripts, we get

$$\frac{\text{Rate}}{[MnO_4^-]} = k_{autocat} = \frac{k_2 K_1 K_2\,[A]\,[\text{vit } B_1]}{[H^+] + K_1} \tag{10}$$

Thus, when (4-methyl–thiazol-5-yl) acetic acid is present initially, a composite scheme involving all the steps of Schemes 1 and 2 operates and the rate law is given by

$$k_{gross} = k_{obs} + k_{autocat} \tag{11}$$

$$k_{gross} = \frac{k_1\,K_1\,[\text{vit. } B_1]}{(K_1 + [H^+])} + \frac{k_2\,K_1\,K_2\,[A]\,[\text{vit. } B_1]}{(K_1 + [H^+])} \tag{12}$$

$$\frac{[\text{vit. } B_1]}{k_{autocat}} = \frac{1}{[A]}\left(\frac{[H^+]}{k_2\,K_1\,K_2} + \frac{1}{k_2\,K_2}\right) \tag{13}$$

At constant concentration of reductant, a plot of LHS (Left hand side) vs.1/[4-methyl-thiazol-5-yl acetic acid] (A) of equation [13] should be linear and was found to be so (Fig. 8).

The effect of ionic strength and solvent polarity suggests the reaction between anion and a neutral molecule, which is in the right direction as given in Scheme 1. The negative value of $\Delta S^{\neq}$ indicates the adduct formed is more ordered than reactants [21].

The observed modest entropy of activation and higher rate constant of the slow step indicates that the oxidation presumably occurs by an inner-sphere mechanism. This conclusion is supported by the literature [22].

CONCLUSION

The reaction between permanganate and thiamine hydrochloride, (vitamin B_1) is an autocatalytic reaction in sulfuric acid at room temperature. The autocatalytic reaction is due to one of the products, (4-methyl –thiazol-5-yl) acetic acid, formed in the reaction from the vitamin B_1. The main active species of permanganate is MnO_4^-. The role of hydrogen ion is crucial to the reaction. The proposed mechanism is consistent with all the experimental evidences.

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