Kinetics and mechanism of oxidation of nicotinic acid by potassium permanganate in aqueous acidic medium

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ABSTRACT

The stoichiometry and kinetics of oxidation of nicotinic acid by potassium permanganate has been investigated in aqueous acidic medium at 28 ± 1^oC, $I = 0.5$ mol dm^{-3} (Na_2SO_4), $[H^+] = 1\times10^{-1}$ mol dm^{-3}. The results obeys the rate law

$-d[C_6H_5NO_2]/dt = (a+b[H^+])[C_6H_5NO_2][MnO_4^-]$

where $a = 0.016$ $dm^3mol^{-1}s^{-1}$, $b = 1.57$ $dm^6mol^{-1}s^{-1}$

The rate of reaction decreased with increase in ionic strength. Added cations and anions catalysed the reaction. The result of spectroscopic and kinetic investigation did not indicate intermediate complex formation because there was no change in λ_{max} at 525nm. A plausible mechanism has been proposed for this reaction.

Key words: Kinetics, mechanism, oxidation, permanganate ion and nicotinic acid.
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INTRODUCTION

Nicotinic acid (vitamin B_3 or vitamin PP) is a colourless organic compound which is soluble in water and other polar solvent. It is a derivative of pyridine with a carboxyl group (COOH) at the 3-position.

Nicotinic acid is of great biological and pharmacological importance. Pharmacological doses of nicotinic acid has been proven to reverse atherosclerosis by reducing total cholesterol triglycerides, Very Low Density Lipoprotein (VLDL) and Low Density Lopoprotein (LDL) and increasing High Density Lipoprotein (HDL). It has been proposed that nicotinic acid has the ability to lower lipoprotein which is beneficial at reducing thrombotic tendency [1].

Reduction reactions of a 2-chloronicotinic acid under Finkelstein condition has been reported [2]. In this reaction, ortho-carboxyl group and a para-bromo promoted chloride displacement were involved. And the overall product was 5-bromonicotinic acid.

Though nicotinic acid has a wide range of applications, little is known about the kinetics and mechanism of its important reactions.

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Permanganate ion in acidic and alkaline medium are widely used as oxidizing agent in synthetic and analytical chemistry. It can also act as a hydroxylating agen , as reported in literature [3-7].

According to Insauti *et al.,* [8], it has several advantages as an analytical reagent e.g. it is strong, vividly coloured, serving as its own indicator.

Depending on the nature of reductant, the oxidant has been assigned both inner and outersphere pathways in their redox reactions [9]. In order for the oxidant and reductant (nicotinic acid) to be effectively utilized in industries and laboratories, we are motivated to study the kinetics and mechanism of their reactions as reported in this work. Nicotinic acid is structurally shown as
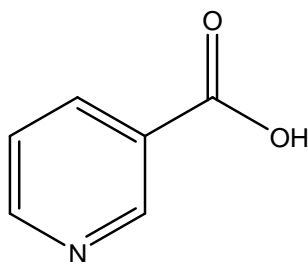
MATERIALS AND METHODS

Experimental
Standard solution of nicotinic acid (BDH) and potassium tetraoxomanganate(VII) were prepared daily with distilled water before used. But $KMnO_4$ was always standardized before used, H_2SO_4 was used as a source of hydrogen ion concentration. Na_2SO_4 was used to maintain the ionic strength (I) of the reaction constant. All reagents were of analytical grades and were used without further purification.

Stoichiometry
The stoichiometric studies was carried out by spectrophotometric titration [10,11]. Reaction mixtures containing various concentrations of nicotinic acid but constant[MnO_4^-], [H^+], and ionic strength of the reaction medium were allowed to stand until the reaction had gone to completion. The absorbances of the solutions were measured at 525nm and the stoichiometry was evaluated from the plot of absorbances versus mole ratio of the oxidant to reductant .

Kinetic studies
All kinetic runs were carried out using a Corning Colorimeter 253 under pseudo-first order conditions with nicotinic acid concentration in at least 50 fold excess of [MnO_4^-]. The rate of the reaction was monitored by measuring the decrease in absorbance of the product at 525nm. The pseudo – first order rate constants (k_{obs}) were obtained from logarithmic plot of absorbance differences against time t, the temperature was maintained constant at 28 ± 1^oC with [H^+] = 0.1 mol dm^{-3} and I = 0.5 mol dm^{-3} (Na_2SO_4).

Effect of [H^+]
The effect of [H^+] on the rate of the reaction was studied using tetraoxosulphate(VI) acid in the range,(1.0 -16) x 10^{-2} mol dm^{-3}, while the concentration of MnO_4^- and $C_6H_5NO_2$ were kept constant at I = 0.5 mol dm^{-3} (Na_2SO_4) and T = 28 ± 1^oC, the results are presented in Table 1.

Effect of ionic strength
The effect of ionic strength on the rate of the reaction was investigated in the range I = 0.4-1.20 mol dm^{-3} (Na_2SO_4) while the concentration of the other reagents were kept constant. The result are presented in Table 1.

Absorption spectra
The absorption spectra of solution containing oxidant alone and solution of the reaction mixture under similar condition were compared between 400nm - 700nm to test for the possibility of an intermediate complex formation.

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There was no observable difference in both spectra with respect to the λ_{max}. Michealis-Menten's plot of $1/k_{obs}$ versus $1/[C_6H_5NO_2]$ were also made (Figure 4)

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RESULTS AND DISCUSSION

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Stoichiometry and product analysis: The stoichiometric measurements indicated 1:1 stoichiometry as in equation 1.

$$ \text{(nicotinic acid structure)} \quad + \quad MnO_4^- \ + \ nH^+ \ \longrightarrow \ \text{Product} \qquad (1) $$
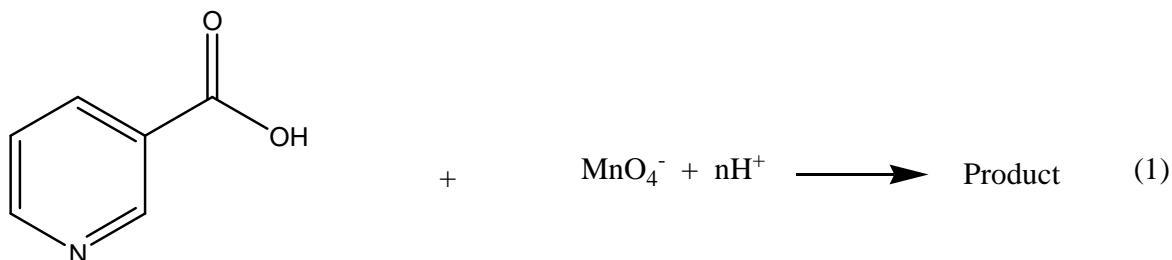
The stoichiometry of 1:1 is consistent with what has been reported for the oxidation of MnO_4^- with rosaniline hydrocholoride [12] and redox reaction of malachite green with MnO_4^- in aqueous acidic media [13].

One of the product of the reaction Mn^{2+} was qualitatively identified by reaction with indole [14,15], whereas the presence of carbonyl compound was identified by addition of 2,4-dinitrophenyl hydrazine to the product thereby forming yellow precipitates.
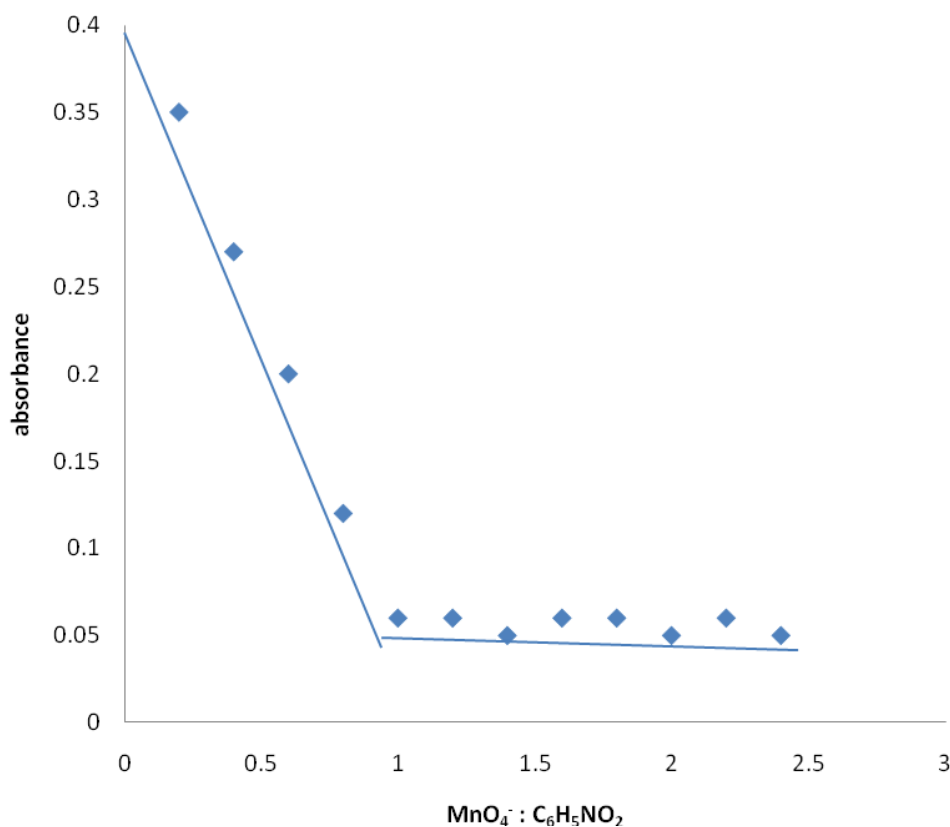

Figure 1. A plot of absorbance against mole ratio of permanganate ion to nicotinic acid

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Kinetics

The pseudo-first order plots of $\log(A_t-A_\infty)$ versus time (Figure 1) were linear to about 60% extent of reaction indicating that the reaction is first order in $[MnO_4^-]$ under the experimental condition.

The pseudo-first order rate constant was determined at different initial concentrations of $C_6H_5NO_2$. Plot of $\log k_{obs}$ versus $\log[C_6H_5NO_2]$ at $[H^+]=1\times10^{-1}$ mol dm^{-3} gave a slope of unity, this suggest a first order dependence on $[C_6H_5NO_2]$. The values of second order rate constants k_2 were fairly constant (Table 1), suggesting that the reaction is also first order in $[MnO_4^-]$ and that the reaction is second order overall. The rate equation is,

$$\frac{-d[C_6H_5NO_2]}{dt} = k_2[MnO_4^-][\,C_6H_5NO_2] \qquad\qquad\qquad (2)$$

where $k_2 = (1.72 \pm 0.015)\times10^{-1}$ $dm^3mol^{-1}s^{-1}$. This trend has been reported for the redox reaction of some oxyanions [14].

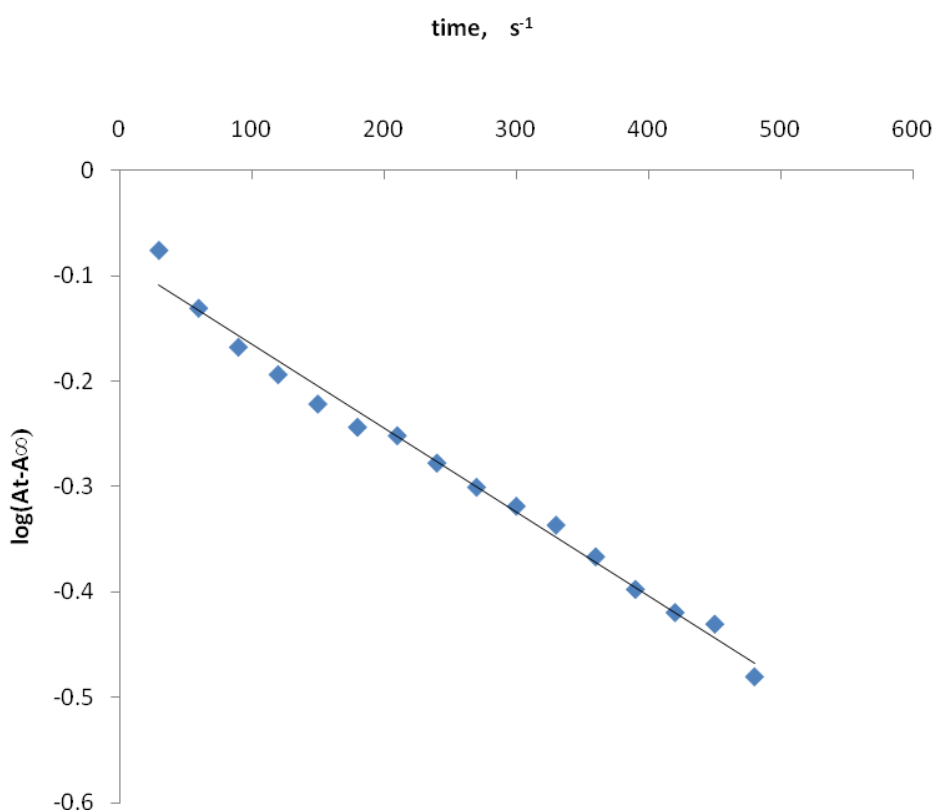**Figure 2: A typical pseudo first order plot for the redox reaction of nicotinic acid with permanganate ion at $[MnO_4^-] = 1.10\times10^{-2}$mol dm^{-3}, $[C_6H_5NO_2]=8.4\times10^{-2}$mol dm^{-3}, $[H^+] = 0.1$mol dm^{-3}, $\lambda_{max} = 525$nm and $T = 28\pm1°C$**

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Table 1: Pseudo first and second order rate constants for the reaction of nicotinic acid and MnO_4^- at $[MnO_4^-] = 1.75 \times 10^{-4}$ mol dm^{-3}, $\lambda_{max} = 525$nm and T = 28 ± 1^oC

$10^2[C_6H_5NO_2]$, mol dm^{-3}	$10[H^+]$, mol dm^{-3}	$10[I]$, mol dm^{-3}	$10^3 k_{obs}$, s^{-1}	$10k_2$, dm^3·mol^{-1}s^{-1}
0.90	1.0	5.0	1.55	1.72
1.10	1.0	5.0	1.81	1.74
1.20	1.0	5.0	2.10	1.71
1.60	1.0	5.0	2.58	1.70
1.90	1.0	5.0	3.34	1.73
2.10	1.0	5.0	3.64	1.73
3.15	1.0	5.0	5.34	1.70
5.25	1.0	5.0	9.00	1.71
6.30	1.0	5.0	11.00	1.74
8.40	1.0	5.0	14.40	1.71
17.50	1.0	5.0	29.70	1.70
8.40	0.1	5.0	3.19	0.38
8.40	0.3	5.0	4.79	0.57
8.40	0.6	5.0	9.40	1.12
8.40	0.8	5.0	12.00	1.43
8.40	1.0	5.0	14.50	1.73
8.40	1.2	5.0	16.80	2.00
8.40	1.4	5.0	19.99	2.38
8.40	1.6	5.0	22.68	2.70
8.40	1.0	4.0	16.10	1.92
8.40	1.0	5.0	14.50	1.73
8.40	1.0	6.0	12.40	1.48
8.40	1.0	7.0	11.00	1.31
8.40	1.0	8.0	9.40	1.12
8.40	1.0	9.0	8.30	0.99
8.40	1.0	10.0	7.40	0.88
8.40	1.0	12.0	4.96	0.59

Effect of hydrogen ion concentration on the rate of the reaction:
It was observed that the rate of reaction increased with increase in acid concentration (Table 1).

A plot of $\log k_{obs}$ against $\log[H^+]$ gave a slope of 0.74 using least square analysis.

Also a plot of k_2 against $[H^+]$ was linear with a positive intercept; fitted into equation below:

$$k_2 = a + b[H^+] \qquad\qquad\qquad (3)$$

Least square analysis of the plot gave a = 0.016dm^{3}mol^{-1}s^{-1} and b = 1.57dm^{6}mol^{-2}s^{-1} at 28 ± 1^oC.

Therefore the rate equation of the reaction as a function of $[H^+]$ can now be written as

$$\frac{-d[C_6H_5NO_2]}{dt} = (a+b[H^+])[C_6H_5NO_2][MnO_4^-] \qquad\qquad (4)$$

The nature of acid dependence observed depicted that there are two pathways, one which depends on acid and the other which does not depend on acid. This result shows that both the protonated and unprotonated forms of the reactant are reactive [13,15,16].

Effect of ionic strength
The rate of reaction was found to decrease with increase in ionic strength. A plot of $\log k_2$ versus $I^{1/2}$ gave negative slope of -1.07 from least square method.

The negative salt effect observed indicated that the rate determining step involved the reaction of cationic and anionic specie [17,18].
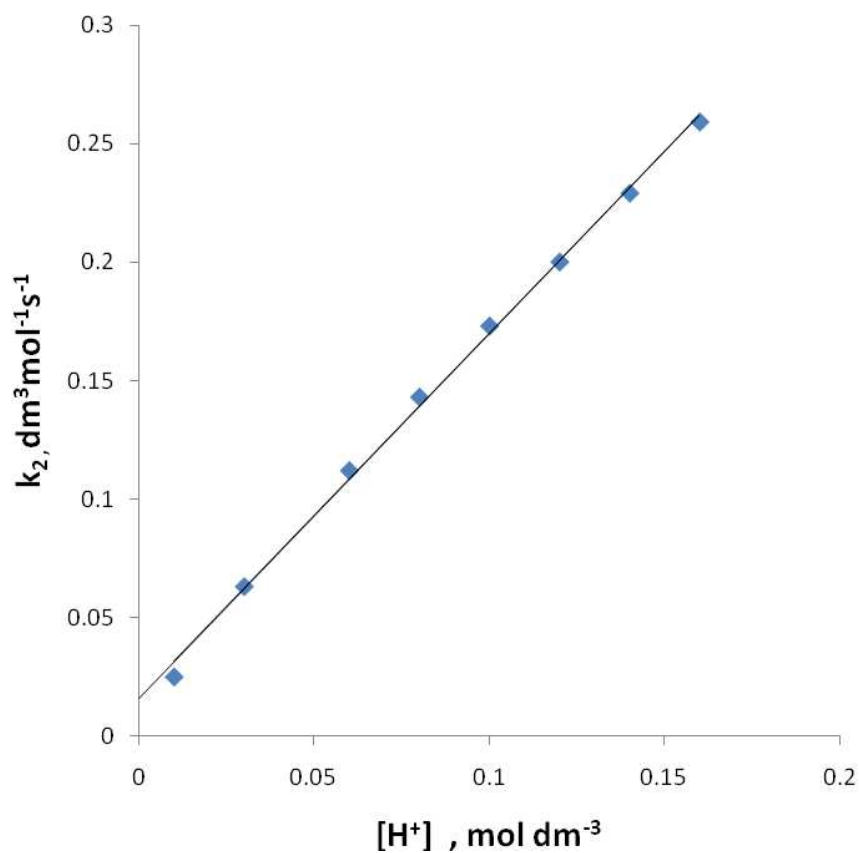
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Figure 3: Plot of k_2 versus [H$^+$] at [MnO$_4^-$] = 1.75x10^{-4}mol dm^{-3}, [C$_6$H$_5$NO$_2$]=8.4x10^{-2} mol dm^{-3}, I = 0.5 mol dm^{-3}

Table 2: Rate constants for the effect of cations and anions in redox reaction between MnO$_4^-$ and nicotinic acid at [C$_6$H$_5$NO$_2$]=8.4x10^{-2}mol dm^{-3}, [MnO$_4^-$] = 1.75x10^{-4} mol dm^{-3}, [H$^+$] = 0.1 mol dm^{-3}, I = 0.5 mol dm^{-3}

10^4[NO$_3^-$], mol dm^{-3}	$10^2 k_{obs}$, s^{-1}	$10 k_2$, dm^{3}mol^{-1}s^{-1}
5	1.51	1.79
50	2.00	2.38
75	2.07	2.48
100	2.24	2.67
10^3[Cl$^-$]		
5	1.52	1.81
50	1.95	2.32
75	2.13	2.54
100	2.44	2.91
10^4[Li$^+$]		
5	1.34	1.60
50	1.22	1.45
75	1.13	1.35
100	0.97	1.15
10^4[Mg^{2+}]		
5	1.32	1.57
50	1.07	1.28
75	0.85	1.01
100	0.52	0.62

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Effect of added anion and cation
The effect of added anions (NO_3^- and Cl^-) and cations (Li^+ and Mg^{2+}) were investigated by varying the concentrations of these anions and cations while keeping $[MnO_4^-]$, $[C_6H_5NO_2]$, $[H^+]$ and ionic strength constant at 28 ± 1^oC. There was enhancement of the rate by the added anions within the concentrations range studied. While in the other hand there was inhibition of the rate by the added cations within the concentration range studied (Table 2). The catalysis of the rate by added ions have been reported by earlier resarchers to be an evidence of reaction that occur through an outer-sphere mechanistic pathway [19,20].

Free radical test:
Acrylamide was added to a partially oxidized reaction mixture of MnO_4^- and $C_6H_5NO_2$. Then followed by a large excess of methanol, there was no gel formation. This probably suggest that no free radical is formed in the reaction. There was no change in λ_{max} from 525nm when the absorbance of the reaction mixture was monitored using Corning Colorimeter 253 between 400 – 700nm.

Michaelis Menten's plot of $1/k_{obs}$ versus $1/[C_6H_5NO_2]$ was linear without intercept. This also indicates that intermediate with appreciable equilibrium concentration are unlikely implicated in this reaction [13,14].
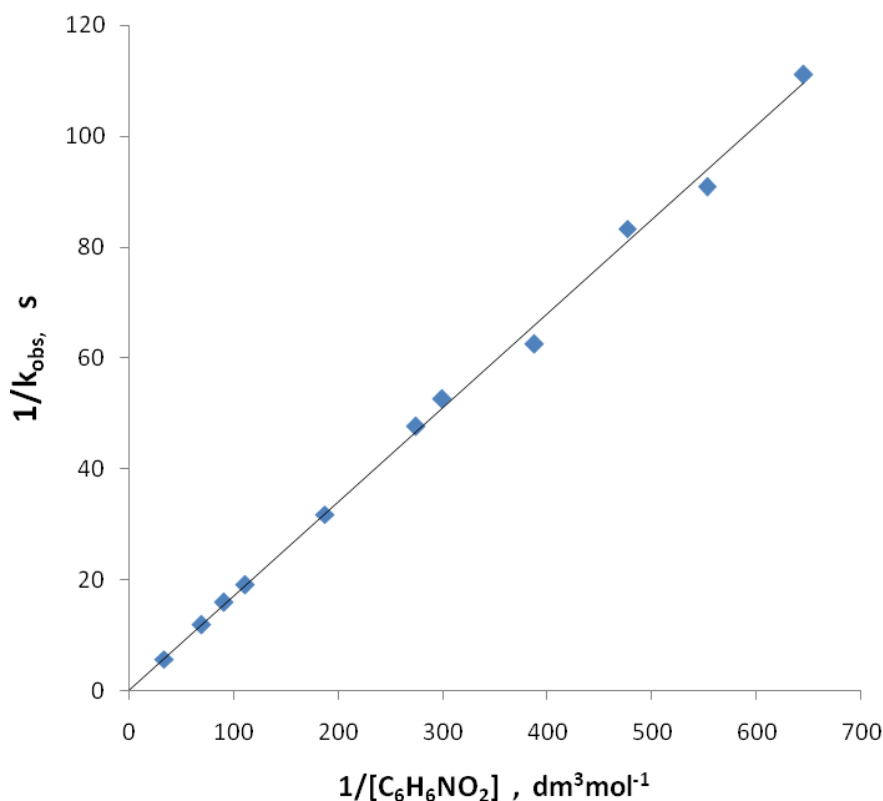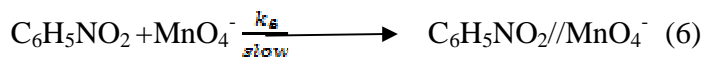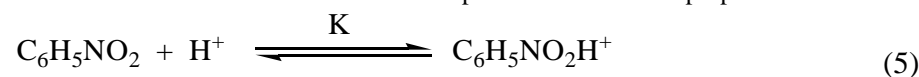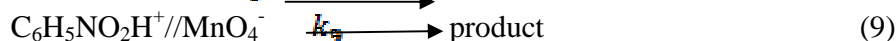

Figure 4: Michaelis Menten's plot of $1/k_{obs}$ versus $1/[C_6H_6NO_2]$

Reaction mechanism
Based on the experimental conditions employed in this study and the kinetic data obtained, a plausible reaction mechanism which is consistent with the empirical kinetic data is proposed as follows.

$$C_6H_5NO_2 + H^+ \xrightleftharpoons{K} C_6H_5NO_2H^+ \qquad (5)$$

$$C_6H_5NO_2 + MnO_4^- \xrightarrow[slow]{k_6} C_6H_5NO_2//MnO_4^- \quad (6)$$

$$C_6H_5NO_2H^+ + MnO_4^- \xrightarrow[slow]{k_7} C_6H_5NO_2H^+//MnO_4^- \qquad (7)$$

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$C_6H_5NO_2//MnO_4^- \xrightarrow{k_6}$ product   (8)

$C_6H_5NO_2H^+//MnO_4^- \xrightarrow{k_7}$ product   (9)

Equation 6 and 7 are rate determining steps.

Rate = $k_6[C_6H_5NO_2][MnO_4^-]$ + $k_7[C_6H_5NO_2H^+][MnO_4^-]$ (10)

From (1), $[C_6H_5NO_2H^+] = K[C_6H_5NO_2][H^+]$ (11)

Substitute for $[C_6H_5NO_2H^+]$ in equation 10

Therefore

Rate = $k_6[C_6H_5NO_2][MnO_4^-]$ $+k_7K[C_6H_5NO_2][MnO_4^-][H^+]$ (12)

Rate = $(k_6 + k_7K[H^+])[C_6H_5NO_2][MnO_4^+]$ (13)

Equation 13 is similar to equation 4

k_6 = a and k_7K = b

where a = 0.016 $dm^3mol^{-1}s^{-1}$ b = 1.57 $dm^6mol^{-1}s^{-1}$

Equation 6 confirmed the fact that the empirical kinetic data displayed negative salt effect, in that the two reacting species are positively and negatively charged. Similar mechanism was proposed in the reaction involving MnO_4^- and malachite green [13]

CONCLUSION

The absence of kinetic and spectrophotometric evidence for the intermediate complex formation in this reaction confirms an earlier suggestion that the reaction points towards outer-sphere pathway. These views are further buttressed by the fact that Michaelis Menten's plot was linear with no intercept. The catalysis of the rate by added anions and cations species also confirms the presence of outer-sphere mechanism. Outer-sphere mechanistic pathway has also been proposed for reactions between MnO_4^- and L-ascorbic acid and malachite green [13,15].

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