A Study of the Kinetics and Mechanism of Oxidation of L -Ascorbic Acid by Permanganate Ion in Acidic Medium

O.A. Babatunde

Department of Chemistry, Nigerian Defence Academy, Kaduna, Nigeria

Abstract: The kinetics and mechanism of oxidation of L –Ascorbic acid by permanganate ion in acidic medium have been studied at 25±1°C, I = 1.0 mol dm^{-3} (NaClO$_4$), [H$^+$] =1x10^{-2} mol dm^{-3}.The stoichiometry was observed to be 2:5 in terms of mole ratio of permanganate ions and ascorbic acid consumed. The reaction shows dependence on acid concentrations and is first order in both the oxidant and the reductant. The proposed rate law is $-d[\dfrac{MnO_4^-}{dt}]=(a+b[H^+])\,[MnO_4^-][H_2A]$ where a = 0.27 x 10^{-2} dm^{-3} mol^{-1} s^{-1} and b = 0.38 dm^6 mol^{-2} s^{-1}.

The result of spectroscopic investigations and kinetic studies did not implicate the formation of intermediate complex. An outersphere reaction pathway is proposed for this reaction.

Key words: Ascorbic acid · Permanganate ions

INTRODUCTION

Ascorbic acid (H$_2$A) is found naturally in a wide variety of plants and animals [1]. It is an organic acid with anti-oxidant properties in chemical and biological systems. [2]. The L-enantiomer of ascorbic acid is commonly known as vitamin C in nutritional context and it also encompasses the oxidation product of dehydroascorbic acid [HA] with different oxidizing agents [3].

Ascorbic acid has been known to have a wide range of applications. It is used extensively in medicine, (cure and prevention of scurvy), in agriculture, in food industry, flour industry, in metallurgy and also by the chemist but little is known about the kinetics and mechanism of many of its important reactions [3].

Permanganate ions are widely used as oxidizing agent in synthetic and analytical chemistry [4]. According to Insauti *et al*. [5], it has several advantages as an analytical reagent e.g. it is strong, vividly coloured serving as its own indicator. In acidic medium it exists in different forms as HMnO$_4$, H$_2$MnO$_4^+$, HMnO$_3$, Mn$_2$O$_7$ and depending on the nature of the reductant, the oxidant has been assigned both inner sphere and outersphere pathways in their redox reactions [6, 7]. For effective use and application of both the reductant and the oxidant in industries and laboratories, the kinetics and mechanisms of their reactions is therefore reported in this paper.

Experimental: Standard solution of Ascorbic acid (BDH) was prepared with distilled water. Perchloric acid (Analar grade) was used as a source of hydrogen ions while the ionic strength of the medium was maintained constant at 1.0 mol dm^{-3} using sodium perchlorate.

Standard salt solutions were made by dissolving known amounts of the solute in a given volume of distilled water and the exact concentration determined by standard methods [8].

Stoichiometry: The stoichiometries of the reactions were determined by spectrophotometric titration using mole ratio method. The absorbances of the solution containing various concentrations of the reductant in 1.0-5.5 x10^{-5} mol dm^{-3} range and a constant concentration of the oxidant 1.0 x 10^{-4} mol dm^{-3} at [H$^+$] =1 x 10^{-2} mol dm^{-3} and T = 25±1°C were measured at 540nm after the reaction had gone to completion. The stoichiometries of the reaction were then evaluated from absorbance versus volume of the reductant plots.

Kinetic studies: The kinetics of the reaction was studied by following the decrease in the absorbance due to [MnO$_4$] at λ_{max} 540nm on Colorimeter Model 252 Spectrophotometer under the pseudo-first order conditions with [H$_2$A] in large excess over [MnO$_4$] at 25±1°C, [H$^+$] = 1x10^{-3} mol dm^{-3} and 1.0 mol dm^{-3} (NaClO$_4$) ionic strength.

Corresponding Author: Dr. O.A. Babatunde, Department of Chemistry, Nigerian Defence Academy, Kaduna, Nigeria

The pseudo-first order plots of the log (A_t-A_∞) versus time were made (where A_∞ and A_t are the absorbance at the end of the reaction and at time t) and from the slope of the plots, the pseudo- first order rate constant (k_o) was determined. The second order rate constant (k_2) was obtained from k_o as $k_o/[H_2A]$.

Effect of ionic strength: The effect of ionic strength in the rate of the reaction was investigated in the range $I = 0.2$ -1.5 mol dm $^{-3}$ [NaClO$_4$] while the concentration of the other reagents were kept constant. The results are presented in Table 1.

**Effect of [H$^+$]:** The effect of [H$^+$] on the rate of the reaction was studied using perchloric acid in the range 0.2 x 10^{-2} -3.0 x 10^{-2} mol dm^{-3} while the concentration of MnO$_4^-$ and H$_2$A were constant at $I =1.0$ mol dm^{-3} (NaClO$_4$) and T=25±1°C. The results are presented in Table 1.

Test for intermediate complex formation: Spectroscopic test was carried out by comparing the electronic spectrum of the reaction mixture one minute after the start of the reaction with that of the final product within a wavelength of 450-600 nm.

Michaelis-Menten's plots of $1/k_{obs}$ versus $1/$ [H$_2$A] were also made (Fig. 2).

RESULTS AND DISCUSSION

Stoichiometry and product analysis: The stoichiometric measurements with an excess of the reductant indicated a 2:5 stoichiometry as in equation

$$2MnO_4^- + 5H_2A + 6H^+ \rightarrow 2Mn^{2+} + 5A + 8H_2O \qquad (1)$$
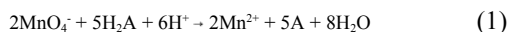
This is consistent with what has been reported for the oxidation of MnO$_4^-$ with some aldehyde [9] and some amino acids [5, 10].

Mn^{2+} was qualitatively identified by reaction with indole [11, 12].

Kinetics: Plots of log A_t -A_8 versus time were linear to more than 85% of the extent of reaction indicating that the reaction is first order dependent on [MnO$_4^-$] Also, plot of log k_o versus log [H$_2$A] gave a slope of 0.94 suggesting that the reaction is approximately first order in [H$_2$A].

The second order rate constant [k_2] was obtained at constant [H$^+$] from $k_o/$ [H$_2$A] (Table 1). The constancy of the second rate constant shows that the reaction

Table 1: Pseudo- First order rate constant (k_o) and second order rate constant (k_2) for the reaction of MnO$_4^-$ and H$_2$A ([MnO$_4^-$] = 1.0 x 10^{-5} mol dm^{-3} T = 25±1°C and λ_{max} = 540nm)

10^4[H$_2$A] mol dm^{-3}	10^2[H$^+$] mol dm^{-3}	10^1,I, mol dm^{-3}	10^2,k_o s^{-1}	10^2,k_2 dm^{3}mol^{-1} s^{-1}
2.0	1.0	1.0	2.95	1.48
3.0	1.0	1.0	4.47	1.49
4.0	1.0	1.0	5.90	1.48
5.0	1.0	1.0	7.41	1.48
6.0	1.0	1.0	8.80	1.47
7.0	1.0	1.0	10.63	1.52
8.0	1.0	1.0	12.06	1.51
9.0	1.0	1.0	13.23	1.47
10	1.0	1.0	14.98	1.50
7.0	1.0	0.2	10.29	1.43
7.0	1.0	0.4	10.43	1.49
7.0	1.0	0.6	10.50	1.50
7.0	1.0	0.8	10.57	1.51
7.0	1.0	1.0	10.64	1.52
7.0	1.0	1.2	10.85	1.55
7.0	1.0	1.4	11.06	1.58
7.0	1.0	1.6	11.20	1.60
7.0	0.5	1.0	9.80	1.41
7.0	1.0	1.0	10.64	1.52
7.0	1.5	1.0	11.34	1.62
7.0	2.0	1.0	12.60	1.80
7.0	2.5	1.0	13.44	1.92
7.0	3.0	1.0	14.35	2.05
7.0	3.5	1.0	14.70	2.10
7.0	4.0	1.0	15.75	2.25

is also first order with respect to [H$_2$A]. Therefore the overall order for the reaction is second order. The rate equation is

$$-d[\frac{MnO_4^-}{dt}] = k_2 [MnO_4^-][H_2A] \qquad (2)$$

at [H$^+$] = 1 x 10^{-4} mol dm^{-3} and T = 25±1°C. where k_2 = (1.49±0.001) x 10^{-2} dm^3 mol^{-1} s^{-1}.

Similar second order kinetics has been reported for the reduction of MnO$_4^-$ by T^{II} & U^{IV} [10]. This trend has also been reported for the redox reaction of some oxy anions [11].

Effect of [H$^+$]: Within the range of $1 \times 10^{-4} \leq$ [H$^+$] $\leq 4.0 \times 10^{-3}$ mol dm^{-3}, the rate of reaction increases with increase in concentration of hydrogen ions (Table 1). Plots of k_2 versus [H$^+$] was also linear with a positive intercept
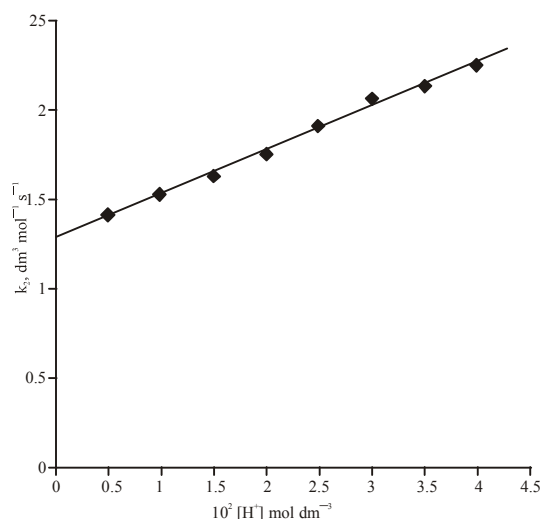
Fig. 1: Plot of k_2 vs [H⁺] for the oxidation of H_2A by MnO_4^-
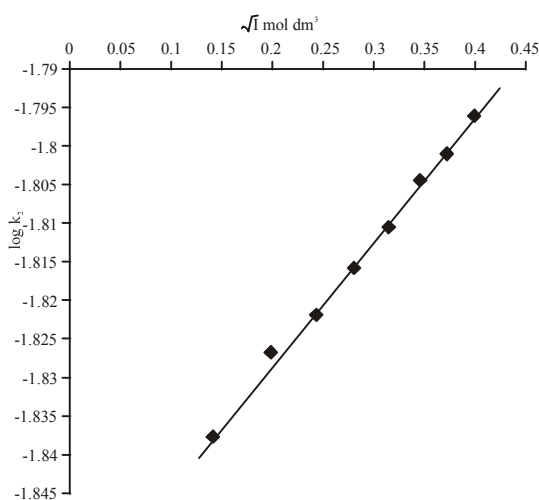
Fig. 2: Plot of log k_2 vs $\sqrt{I}$ for the oxidation of H_2A by MnO_4^-

(Fig. 1) therefore the acid dependent rate constant k_H is given as

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

The rate equation of the reaction as a function of [H⁺] can now be written as:

$$-d[\frac{MnO_4^-}{dt}] = (a + b[H^+])\,[MnO_4^-][H_2A] \qquad (4)$$

where $a = 0.27\ dm^3\ mol^{-1}\ s^{-1}$ $b = 0.38\ dm^6\ mol^{-2}\ s^{-1}$.

The positive [H⁺] dependence on the rate of oxidation of MnO_4^- has been explained in terms of protonation of MnO_4^- in a fast step to give $HmnO_3$ which subsequently

Table 2: The summary of the effect of added anions on the second order rate constant for MnO_4^- and H_2A reaction ([MnO_4^-] = 1.0 x 10⁻⁵ mol dm⁻³, [H_2A] = 7.0 x 10⁻⁴ mol dm⁻³ λ_{max} = 540nm, [H⁺] = 1.0 x 10⁻³ mol dm⁻³, I = 1.0 mol dm⁻³(NaClO₄) and T = 25±1°C)

X	$10^4[X]$ mol dm⁻³	$10^2\ k_o$ s⁻¹	$10^2 k_2$ mol dm⁻³ s⁻¹
NO₂⁻	1	11.06	1.58
	5	11.21	1.60
	10	11.48	1.64
	50	12.04	1.72
	100	13.01	1.86
	150	13.87	1.98
NO₃⁻	1	11.20	1.60
	5	11.61	1.66
	10	12.26	1.75
	50	12.67	1.81
	100	13.93	1.99
	150	15.48	2.21
Cl⁻	1	10.29	1.47
	5	10.64	1.52
	10	11.08	1.58
	50	11.27	1.61
	100	12.25	1.75
	150	13.20	1.80

reacts with the substrate in a slow step to give the product. [10].

Effect of ionic strength: The increase in the ionic strength medium from 0.2 x 10⁻¹ to 1.6 x 10⁻¹ mol dm⁻³ using NaClO₄ resulted in an increase in the rate of reaction (Table 1). Plot of log k_2 versus $\sqrt{I}$ gave a linear graph with a slope of 0.78 showing positive salt effect (Fig. 2).

Effect of added anion species: The results obtained from the effect of added anions on the rate of the reaction were presented in Table 2. The added ions led to enhancement on the rate of reaction. This is suggestive of outer –sphere mechanism.

Test for intermediate complex formation: Spectroscopic studies indicate no significant shift from the absorption maxima of 540nm characteristic of [MnO_4^-]. This indicated absence of the formation of an intermediate complex suggesting the absence of inner-sphere mechanism in the reaction.

Plots of $1/k_{obs}$ versus $1/[H_2A]$ were linear with zero intercept (Fig. 3).

Both results suggest absence of the intermediate complex formation prior to electron transfer in the
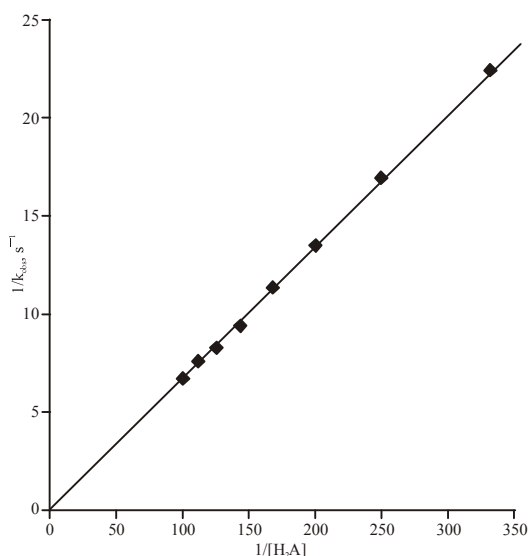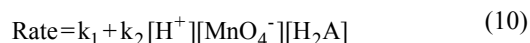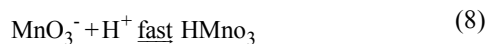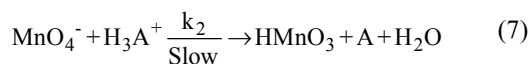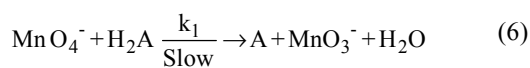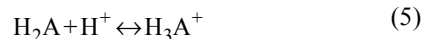
Fig. 3: Michaelis-Menten plot for the oxidation of H_2A by MnO_4^-

reactions. A similar observation was reported for oxidation of H_2A with various reductants [3, 13].

Polymerisation test: Acrylonitrile was added to the partially oxidized reaction mixture of the MnO_4 and H_2A. No gel formation was observed even on addition of a large excess of methanol. This suggests absence of free radical in the reaction mixture.

Reaction mechanism: Based on the result of our investigation under the acid condition used for the stoichiometry and kinetic studies, the reaction scheme consistent with the observed data proposed for the reaction is as below:

$$H_2A + H^+ \leftrightarrow H_3A^+ \qquad (5)$$

$$MnO_4^- + H_2A \xrightarrow[\text{Slow}]{k_1} A + MnO_3^- + H_2O \qquad (6)$$

$$MnO_4^- + H_3A^+ \xrightarrow[\text{Slow}]{k_2} HMnO_3 + A + H_2O \qquad (7)$$

$$MnO_3^- + H^+ \underline{\text{fast}} \ HMno_3 \qquad (8)$$

$$2HMnO_3 + 3H_2A + 4H^+ \underline{\text{fast}} \ 2Mn^{2+} + 3A + 6H_2O \qquad (9)$$

$$\text{Rate} = k_1 + k_2[H^+][MnO_4^-][H_2A] \qquad (10)$$

CONCLUSION

The absence of kinetic and spectrophotometric evidence for intermediate complex formation in this reaction confirms an earlier suggestion that the reaction points towards outersphere pathway. These views are further supported by the fact that Michaelis- Mentens plots was linear with no appreciable intercept.

The enhancement of the rate by added anion species further confirms the presence of outersphere mechanism. Outersphere mechanism has also been proposed for reactions between MnO_4^- and $Fe(CN)_6^{4-}$; $Ru(CN)_6^{-4}$ [9].

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