
Kinetics and Mechanistic Study of Permanganate Oxidation of L-Citrulline in Acidic and Basic Media

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Abstract: Kinetics of oxidation of L-citrulline (Cit) by permanganate ion in both acidic and basic media has been investigated spectrophotometrically at constant ionic strengths and at 25°C. In both media the reactions exhibited first order dependence in [permanganate] and less than unit order dependences in L-citrulline concentration. A fractional-second order dependence with respect to [H⁺] and a fractional-first order dependence with respect to [OH⁻] were revealed in acidic and basic media, respectively. Increasing ionic strength in basic medium increased the oxidation rate of L-citrulline, whereas it had a negligible effect on the oxidation rate in acidic medium. The rate-determining step in both media is suggested to involve a one-electron change, but the stoichiometry (L-citrulline: permanganate) was different, being 5:2 in acidic medium and 1:2 in basic medium. The proposed oxidation mechanisms involve formation of 1:1 intermediate complexes between kinetically active species of both L-citrulline and permanganate ion in pre-equilibrium steps. The final oxidation products of L-citrulline were identified in both acidic and basic media as the corresponding aldehyde (4-(carbamoylamino) butyraldehyde), ammonia and carbon dioxide. The appropriate rate laws are deduced.

Keywords: L-Citrulline, Permanganate, Oxidation, Kinetics, Mechanism

1. Introduction

Various kinetic investigations on the oxidation of amino acids are carried out using various oxidants under various experimental conditions [1-27] because of their biological significance, their selectivities towards the oxidants and to understanding the mechanism of such biological redox reactions. L-citrulline (2-amino-5-(carbamoylamino) pentanoic acid) is a naturally occurring amino acid which is used for Alzheimer's disease, dementia, fatigue, muscle weakness, high blood pressure, and diabetes. It is also used for heart disease, body building, increasing energy, and for improving athletic performance. L-citrulline might help increase the supply of ingredients the body needs to making certain proteins. It is a key intermediate in the urea cycle. In the body, L-citrulline is produced as a byproduct of the enzymatic production of nitric oxide from the amino acid arginine, catalyzed by nitric oxide synthase [28].

Permanganate ion is an efficient oxidant in acidic, neutral and basic media which considered as one of the most important, eco-friendly and powerful oxidants used in the kinetic investigations [29]. The mechanism of oxidation by this multivalent oxidant depends on both the substrate and the medium used for the study. During oxidation by permanganate ion, it is evident that the Mn(VII) species in permanganate is reduced to various oxidation states in different media.

The title reactions represent a full kinetic study on the oxidation of L-citrulline by permanganate ion in both acidic and basic media in order to establish the optimum conditions affecting such oxidation reactions, to understand the different kinetically active species of the reactants in these media, and finally to elucidate plausible oxidation mechanisms on the basis of the obtained kinetic and spectral results.

2. Experimental

2.1. Materials

The chemicals used in this investigation were of analytical grade and their solutions were prepared by dissolving requisite amounts of the samples in double-distilled water. A stock solution of L-citrulline was prepared afresh by dissolving the appropriate amount of the sample (Merck) in the required volume of double-distilled water. Solution of potassium permanganate was freshly prepared and standardized as reported earlier [30]. Perchloric acid and sodium hydroxide solutions were used to provide the required acidity and alkalinity, respectively.

2.2. Kinetic Measurements

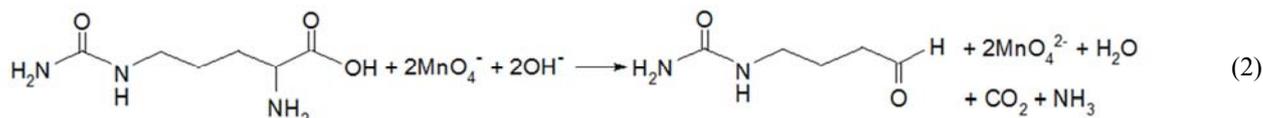
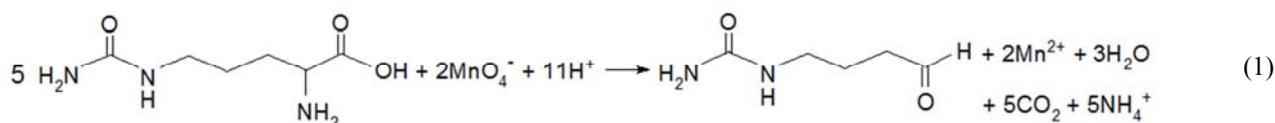
Kinetic runs were performed under pseudo-first order conditions with a large excess of L-citrulline over permanganate. The ionic strength was maintained constant using sodium perchlorate as an inert electrolyte. The reactions temperature (25 °C) was controlled within $\pm 0.1^\circ\text{C}$. The progress of the reactions in both media was followed by monitoring the decrease in the absorbance of permanganate ion, as a function of time, at $\lambda = 526\text{ nm}$, its absorption maximum, on a thermostatted Shimadzu UV-VIS-NIR-3600 double-beam spectrophotometer. First order plots, $\ln(\text{absorbance}) - \text{time}$ plots, were straight lines for about two

half-lives of the reactions completion, and the observed first order rate constants (k_{obs}) were calculated as the slopes of such plots. Average values of at least two kinetic measurements of the rate constants were taken. The rate constants were reproducible to within 3%. The reactions orders with respect to the reactants were determined from the plots of $\log k_{\text{obs}}$ versus $\log(\text{conc.})$ by varying the concentrations of L-citrulline, perchloric acid or sodium hydroxide, in turn, while keeping all others constant. Some kinetic runs were performed under purified nitrogen and compared with those taken under air, and the results were the same. Thus, dissolved oxygen did not affect the oxidation rates.

3. Results

3.1. Stoichiometry and Product Identification

In both acidic and basic media, different sets of reactions mixtures containing varying ratios of permanganate to L-citrulline were mixed at constant pH, ionic strength and temperature, then were kept for about 24 hours. Estimation of the remaining permanganate concentrations was performed spectrophotometrically. The results confirm that the stoichiometry is 5:2 in acidic medium and 1:2 in basic medium which holds by the following equations,



The above stoichiometric equations are consistent with the results of product analysis. The products were identified as the corresponding aldehyde (4-(carbamoylamino) butyraldehyde) by spot test [31], intermediate manganate(VI) by its visible spectrum, ammonia by Nessler's reagent [32] and carbon dioxide by lime water. The product, 4-(carbamoylamino) butyraldehyde was also estimated quantitatively as its 2,4-dinitrophenylhydrazone derivative [32].

3.2. Time-Resolved Spectra

The time-resolved spectra during the oxidation of L-citrulline by permanganate ion in both acidic and basic media are shown in Fig 1 (a) and (b), respectively. The main characteristic feature observed from the figure was the gradual disappearance of permanganate band at $\lambda = 526\text{ nm}$. In basic medium, there was a growth of the absorption band at a wavelength of 415 nm with appearance of an isosbestic point at a wavelengths of 473 nm, Fig. 1b.

3.3. Effect of $[\text{MnO}_4^-]$ on the Oxidation Rates

The effect of permanganate concentration on the rates of reactions in both media was studied by varying its concentration in the range of $2.0 - 10.0 \times 10^{-4}\text{ mol dm}^{-3}$ at fixed concentration of other reactants and constant ionic strength and temperature. The order with respect to $[\text{MnO}_4^-]$ was found to be unity, as plots of $\ln(\text{absorbance})$ versus time were linear about two half-lives of the reactions completion. The first order dependence of the reactions on $[\text{MnO}_4^-]$ was also confirmed by the non-variation of the observed first order rate constant (k_{obs}) at various $[\text{MnO}_4^-]$ while keeping others constant as listed in Table 1.

3.4. Effect of $[\text{Cit}]$ on the Oxidation Rates

The effect of L-citrulline concentration on the oxidation rates was studied by measuring the first order rate constants in both media at different initial concentrations of L-citrulline keeping all other reactants concentrations constant.

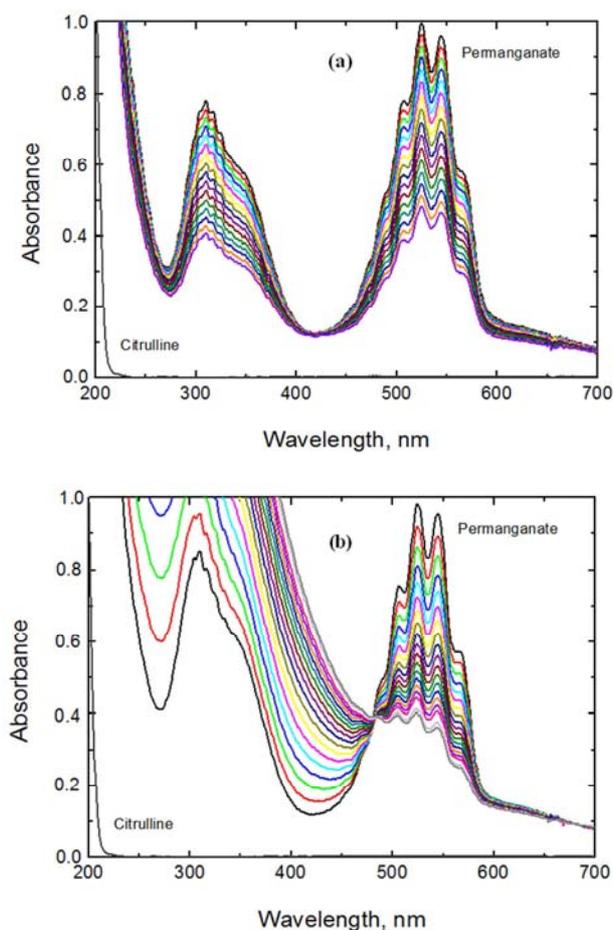


Fig. 1. Time-resolved spectra during the oxidation of L-citrulline by permanganate ion in: (a) perchloric acid medium, $[H^+] = 1.0$ and $I = 2.0$ mol dm^{-3} and (b) sodium hydroxide medium, $[OH^-] = 0.05$, $I = 0.1$ mol dm^{-3} . $[Cit] = 6.0 \times 10^{-3}$, $[MnO_4^-] = 4.0 \times 10^{-4}$ mol dm^{-3} at $25^\circ C$.

Table 1. Effects of variation of $[MnO_4^-]$, $[Cit]$, $[H^+]$ (in acid medium), $[OH^-]$ (in alkaline medium), and ionic strength, I , on the observed-first order rate constants (k_{obs}) in the oxidations of L-citrulline by permanganate ion in acidic and basic media at $25^\circ C$.

$10^4 [MnO_4^-]$ (mol dm^{-3})	Acidic medium				Basic medium			
	$10^3 [Cit]$ (mol dm^{-3})	$[H^+]$ (mol dm^{-3})	I (mol dm^{-3})	$10^5 k_{obs}$ (s^{-1})	$[Cit]$ (mol dm^{-3})	$[OH^-]$ (mol dm^{-3})	I (mol dm^{-3})	$10^5 k_{obs}$ (s^{-1})
2.0	6.0	1.0	2.0	71.6	6.0	0.05	0.1	107.0
4.0	6.0	1.0	2.0	70.9	6.0	0.05	0.1	106.8
6.0	6.0	1.0	2.0	72.1	6.0	0.05	0.1	105.4
8.0	6.0	1.0	2.0	69.8	6.0	0.05	0.1	110.2
10.0	6.0	1.0	2.0	69.4	6.0	0.05	0.1	107.8
4.0	2.0	1.0	2.0	35.3	2.0	0.05	0.1	55.0
4.0	4.0	1.0	2.0	53.0	4.0	0.05	0.1	78.4
4.0	6.0	1.0	2.0	70.9	6.0	0.05	0.1	106.8
4.0	8.0	1.0	2.0	85.7	8.0	0.05	0.1	131.0
4.0	10.0	1.0	2.0	102.1	10.0	0.05	0.1	155.5
4.0	6.0	0.3	2.0	13.2	6.0	0.01	0.1	32.1
4.0	6.0	0.6	2.0	33.0	6.0	0.03	0.1	77.0
4.0	6.0	1.0	2.0	70.9	6.0	0.05	0.1	106.8
4.0	6.0	1.4	2.0	108.2	6.0	0.07	0.1	146.1
4.0	6.0	1.8	2.0	138.7	6.0	0.09	0.1	187.9
4.0	6.0	1.0	2.0	70.9	6.0	0.05	0.10	106.8
4.0	6.0	1.0	2.5	71.0	6.0	0.05	0.15	112.0
4.0	6.0	1.0	3.0	73.4	6.0	0.05	0.20	117.8
4.0	6.0	1.0	3.5	70.2	6.0	0.05	0.25	123.3
4.0	6.0	1.0	4.0	71.7	6.0	0.05	0.30	128.4

Experimental error $\pm 3\%$

It was found that the rates of the reactions increased with increasing the concentration of L-citrulline as listed in Table 1. Plots of k_{obs} versus $[Cit]$ were found to be linear with positive intercepts on k_{obs} axes as shown in Fig. 2 suggesting that the orders with respect to $[Cit]$ in both media were less than unity.

3.5. Effect of pH on the Oxidation Rates

To study the effect of pH of the medium on the rates, kinetic runs were performed by changing the hydrogen ion concentration (0.3 – 1.8) mol dm^{-3} using perchloric acid (in acidic medium) and by varying the hydroxyl ion concentration (0.01–0.09) mol dm^{-3} using sodium hydroxide (in basic medium) while keeping the concentrations of all other reactants constant. It was observed that the rates of the reactions in both acidic and basic media were found to increase with increasing $[H^+]$ and $[OH^-]$, respectively, as listed in Table 1. In acidic medium, the order with respect to $[H^+]$ was fractional-second as a plot of $\log k_{obs}$ versus $\log [H^+]$ was linear with a slope of 1.71 (Fig. 3). In basic medium, a plot of $\log k_{obs}$ versus $\log [OH^-]$ was also linear with a slope of 0.78 (Fig. 4) showing a less than unit order dependence for the reaction with respect to $[OH^-]$.

3.6. Effect of Ionic Strength on the Oxidation Rates

At constant concentrations of the reactants and with other conditions constant, the ionic strength was varied between 2.0 and 4.0 mol dm^{-3} in acidic medium and between 0.1 and 0.3 mol dm^{-3} in basic medium using sodium perchlorate. The results listed in Table 1 indicated that increasing ionic strength in basic medium increased the oxidation rate as shown in Fig. 5, whereas it had a negligible effect on the oxidation rate in acidic medium.

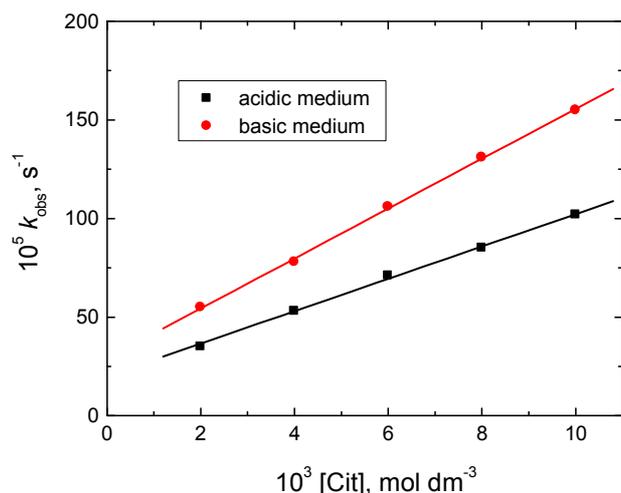


Fig. 2. Plots of k_{obs} versus $[\text{Cit}]$ in the oxidations of L-citrulline by permanganate ion in acidic ($[\text{H}^+] = 1.0$ and $I = 2.0 \text{ mol dm}^{-3}$) and basic ($[\text{OH}^-] = 0.05$ and $I = 0.1 \text{ mol dm}^{-3}$), media. $[\text{MnO}_4^-] = 4.0 \times 10^{-4}$ at 25°C .

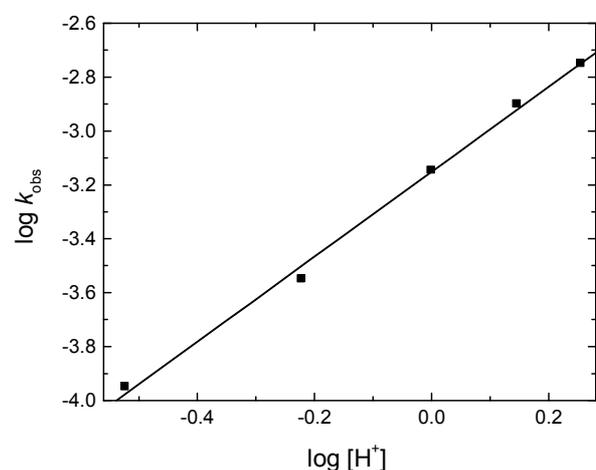


Fig. 3. Plot of $\log k_{\text{obs}}$ versus $\log [\text{H}^+]$ in the oxidation of L-citrulline by permanganate ion in acidic medium. $[\text{Cit}] = 6.0 \times 10^{-3}$, $[\text{MnO}_4^-] = 4.0 \times 10^{-4}$ and $I = 2.0 \text{ mol dm}^{-3}$ at 25°C .

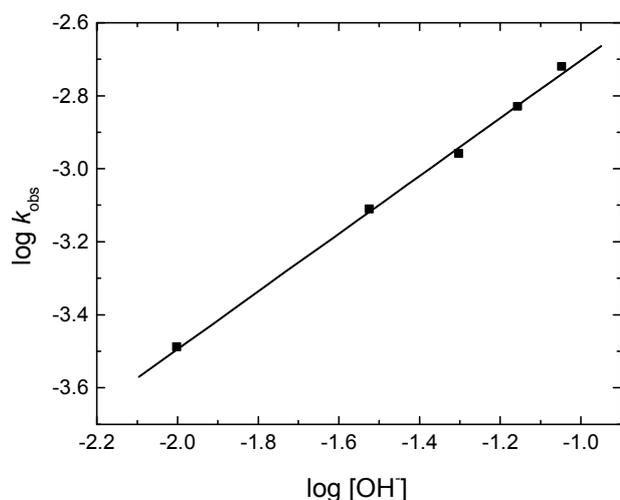


Fig. 4. Plot of $\log k_{\text{obs}}$ versus $\log [\text{OH}^-]$ in the oxidation of L-citrulline by permanganate ion in basic medium. $[\text{Cit}] = 6.0 \times 10^{-3}$, $[\text{MnO}_4^-] = 4.0 \times 10^{-4}$ and $I = 0.1 \text{ mol dm}^{-3}$ at 25°C .

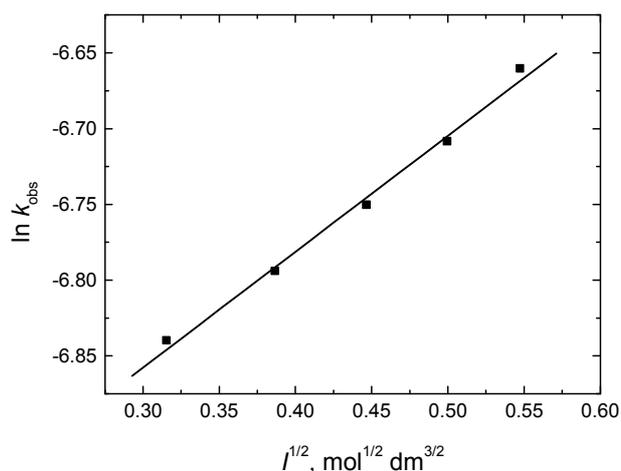


Fig. 5. Debye-Huckel plot in the oxidation of L-citrulline by permanganate ion in basic medium. $[\text{Cit}] = 6.0 \times 10^{-3}$, $[\text{MnO}_4^-] = 4.0 \times 10^{-4}$ and $[\text{OH}^-] = 0.05 \text{ mol dm}^{-3}$ at 25°C .

3.7. Polymerization Test for Free Radical Intermediates

Known quantities of acrylonitrile were added to the reactions mixtures in both media and were kept in an inert atmosphere for about 6 hours at room temperature. When the reactions mixtures were diluted with methanol, progressive white precipitates were formed suggesting that there were participation of free radicals in the present oxidation reactions. When the experiments were repeated in the absence of the L-citrulline under similar conditions, the tests were negative. This indicates that the reactions were routed through free radical paths.

4. Discussion

Permanganate ion in various media provides excellent results when used in oxidation processes. In the permanganate ion, manganese has an oxidation state of 7. It is stable in neutral or slightly basic media, but, in a strongly basic medium, [29] it disproportionates or reacts with hydroxide ion to form manganese(V) (hypomanganate) or manganese(VI) (manganate). Consequently, at high pH values, it is sometimes difficult to ascertain whether an oxidation is proceeding via a one- or a two-electron process. Manganese(VII) is reduced to Mn(II) during oxidation processes via many manganese species having different oxidation states such as Mn(VI), Mn(V), Mn(IV) and Mn(III). The appearance of these intermediate oxidation states depends upon various reaction conditions and the type of substrate. In neutral or slightly basic solutions, permanganate used as a powerful oxidizing agent which is reduced to Mn(IV) ($E_0 = +1.23 \text{ V}$). In very strong basic medium, manganate ion, Mn(VI), is produced ($E_0 = +0.56 \text{ V}$). In acidic medium, permanganate is reduced to Mn(II) ($E_0 = +1.51 \text{ V}$). Since MnO_4^- oxidizes Mn(II) ($E_0 = +0.46 \text{ V}$), the product in the presence of an excess of permanganate is MnO_2 .

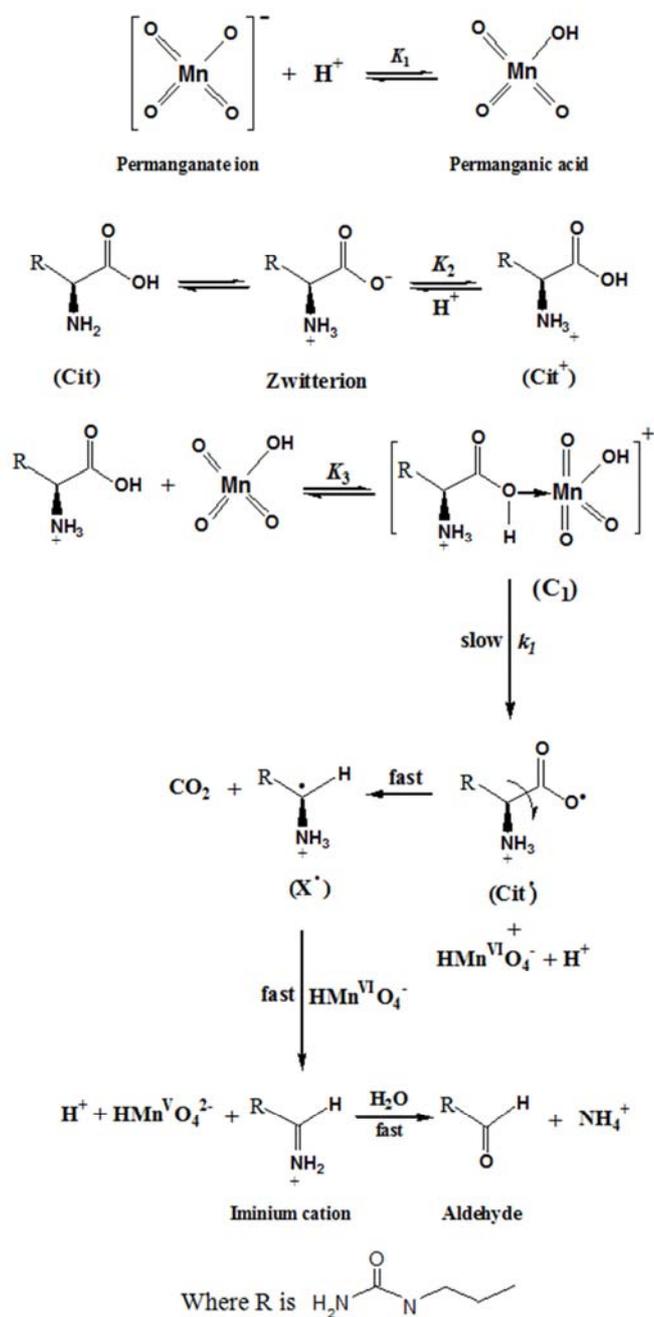
Many investigators [18-23] suggested that most of the oxidation reactions by permanganate ion especially in neutral and basic media proceed through intermediate complex formation between oxidant and substrate. The kinetic evidence that supports formation of an intermediate complex between the oxidant and substrate may be represented by the linearity of the plots of $1/k_{\text{obs}}$ versus $1/[\text{Cit}]$ (Fig. 6), similar to the well-known Michaelis–Menten [33] mechanism for enzyme–substrate reactions. The formation of manganate(VI) and/or hypomanganate(V) short-lived intermediates was also confirmed by the change in the color of the solution mixtures as the reactions proceeded from purple-pink, Mn(VII), to blue, Mn(V), to green, Mn(VI). As the reactions proceed, a yellow turbidity slowly develops and on prolonged standing, the solutions turn to colorless with a brown colloidal precipitate, $\text{Mn}^{\text{IV}}\text{O}_2$ [34, 35]. The failure to detect Mn(V), absence of an absorption maximum around $\lambda = 700$ nm, may be interpreted by its extreme short lifetime and undergoing a rapid disproportionation [36, 37] concentration of the reactants used and, hence, the expected lower absorbitivity of the formed complex and/or the fast subsequent decomposition of such intermediate in comparison with its formation.

4.1. Mechanism of Oxidation in Acidic Medium

In acidic medium, the observed enhancement of the reaction rate with increasing acid concentration and the chemistry of potassium permanganate [29] suggests formation of a more powerful oxidant, namely permanganic acid, as illustrated by the first step in Scheme 1. The protonation of permanganate ion shifts the Mn(VII)/ Mn(VI) couple to a more positive value (+1.3 V), which makes HMnO_4 a stronger oxidizing agent than MnO_4^- [38]. Also, it is reported [39] that in acid solutions, amino acids (AA) exist in zwitterions and predominantly tend to protonate at higher acid concentrations according to the second step in Scheme 1. The obtained second order dependence of the reaction in $[\text{H}^+]$ supports the above-mentioned discussion where both the amino acid L-citrulline and the oxidant permanganate are subjected to protonation, i.e. the protonated forms of both reactants will be considered as the kinetically reactive species in the rate-determining step. On the other hand, the less than unit order with respect to $[\text{Cit}]$ may be as a result of complex formation between the kinetically active species of both permanganate and L-citrulline prior to the rate-determining step.

In view of the above aspects, the following reaction mechanism may be suggested (illustrated in Scheme 1) which involves attack of the powerful oxidant, acid permanganate, on the protonated L-citrulline leading to the formation a complex (C_1) in a pre-equilibrium step. The cleavage of such complex leads to the formation of a free radical intermediate of L-citrulline and Mn(VI) followed by decarboxylation of L-

citrulline free radical forming a new radical intermediate (X^{\cdot}). The latter is rapidly attacked by Mn(VI) species of the oxidant to yield the final oxidation products. The instability in Mn(V) species in strong acid medium leads to conversion of Mn(V) into Mn(II) and Mn(VII) by means of a rapid disproportionation.



Scheme 1. Mechanism of oxidation of L-citrulline by permanganate ion in acidic medium.

Based on the above-mentioned mechanism, the relationship between the rate of oxidation and the oxidant, substrate and hydrogen ion concentrations can be deduced (See Appendix A) to give the following rate law expression:

$$\text{Rate} = \frac{k_1 K_1 K_2 K_3 [\text{MnO}_4^-] [\text{Cit}] [\text{H}^+]^2}{1 + K_1 [\text{H}^+] + K_1 K_2 K_3 [\text{Cit}] [\text{H}^+]^2} \quad (3)$$

Under pseudo-first order condition, the rate-law can be expressed by Eq. (4)

$$\text{Rate} = \frac{-d[\text{MnO}_4^-]}{dt} = k_{\text{obs}} [\text{MnO}_4^-] \quad (4)$$

Comparing Eqs. (3) and (4) and rearrangement, the following relationship is obtained:

$$\frac{1}{k_{\text{obs}}} = \left(\frac{1 + K_1 [\text{H}^+]}{k_1 K_1 K_2 K_3 [\text{H}^+]^2} \right) \frac{1}{[\text{Cit}]} + \frac{1}{k_1} \quad (5)$$

According to Eq. (5), plots of $1/k_{\text{obs}}$ versus $1/[\text{Cit}]$ at constant $[\text{H}^+]$ and $1/k_{\text{obs}}$ versus $1/[\text{H}^+]^2$ at constant $[\text{Cit}]$ should be straight line with positive intercepts on $1/k_{\text{obs}}$ axis as observed experimentally as shown in Figures 6 and 7.

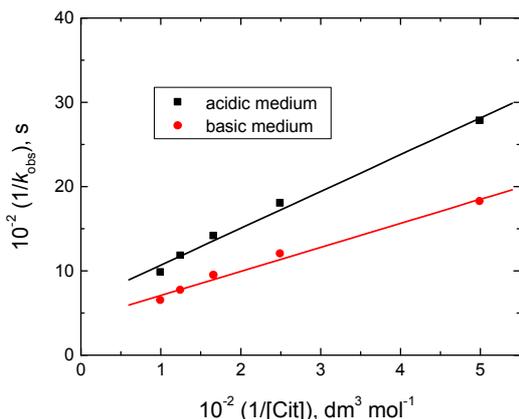


Fig. 6. Plots of $1/k_{\text{obs}}$ versus $1/[\text{Cit}]$ in the oxidations of L-citrulline by permanganate ion in acidic ($[\text{H}^+] = 1.0$ and $I = 2.0 \text{ mol dm}^{-3}$) and basic ($[\text{OH}^-] = 0.05$ and $I = 0.1 \text{ mol dm}^{-3}$) media. $[\text{MnO}_4^-] = 4.0 \times 10^{-4}$ at 25°C .

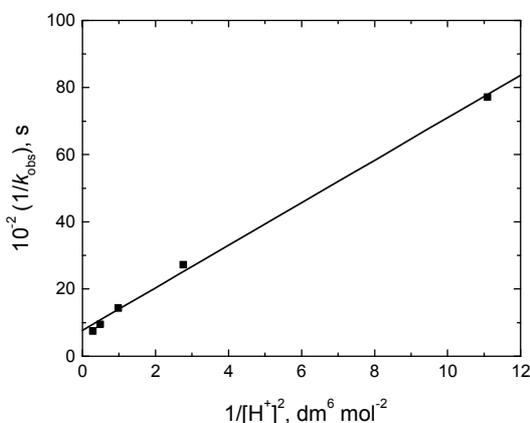
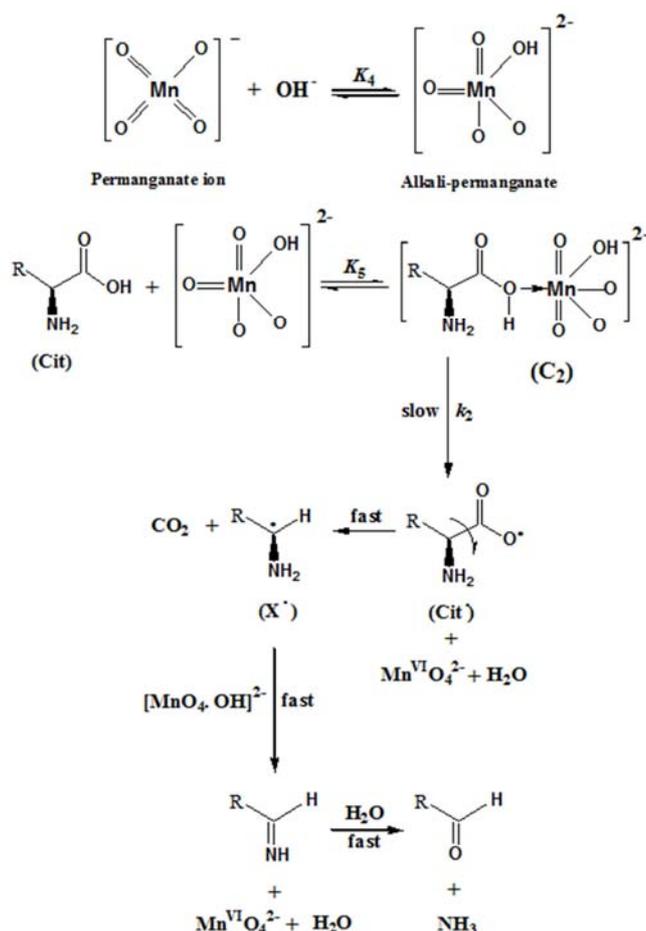


Fig. 7. Plot of $1/k_{\text{obs}}$ versus $1/[\text{H}^+]^2$ in the oxidation of L-citrulline by permanganate ion in acidic medium. $[\text{Cit}] = 6.0 \times 10^{-3}$, $[\text{MnO}_4^-] = 4.0 \times 10^{-4}$ and $I = 2.0 \text{ mol dm}^{-3}$ at 25°C .

4.2. Mechanism of Oxidation in Basic Medium

In basic medium [40, 41] permanganate ion first combines with alkali to form an alkali-permanganate species in a pre-equilibrium step, as described by the first step in Scheme 2. This is consistent with the apparent order of less than unity in OH^- . The formation of $[\text{MnO}_4\text{OH}]^{2-}$ in alkaline medium in the present systems is further supported by the plot of $1/k_{\text{obs}}$ versus $1/[\text{OH}^-]$ shown in Fig. 8, which was linear with a positive intercept. On the other hand, amino acid is known [42] to exist as anion (deprotonate) according to the second step in Scheme 2. In view of the above arguments, the following reaction mechanism can be suggested which involve attack of the active species of permanganate, $[\text{MnO}_4\text{OH}]^{2-}$, on the deprotonated L-citrulline leading to the formation of a complex (C_2) in a prior equilibrium step. This was confirmed, as discussed before, by the kinetic evidence (Fig. 8). The complex decomposes leading to formation of a free radical intermediate derived from L-citrulline and Mn(VI) intermediate followed by decarboxylation of L-citrulline free radical to form a new radical intermediate (X). This intermediate is rapidly attacked by another mole of the oxidant to yield the final oxidation products. The suggested mechanism is illustrated in the following sequence (Scheme 2):



Scheme 2 Mechanism of oxidation of L-citrulline by permanganate ion in basic medium.

Owing to the above-mentioned mechanism, the rate of oxidation can be expressed by the following rate-law equation:

$$\text{Rate} = \frac{-d[\text{MnO}_4^-]}{dt} = k_2[\text{C}_2] \quad (6)$$

The rate law expressed the change of the oxidation rate with the substrate, hydroxyl ion and oxidant concentrations was deduced (See Appendix B) to give the following equation:

$$\text{Rate} = \frac{k_2 K_4 K_5 [\text{Cit}][\text{OH}^-][\text{MnO}_4^-]}{1 + K_4[\text{OH}^-] + K_4 K_5 [\text{Cit}][\text{OH}^-]} \quad (7)$$

Under pseudo-first order condition, the rate law can be expressed by Eq (8),

$$\text{Rate} = \frac{-d[\text{MnO}_4^-]}{dt} = k_{\text{obs}}[\text{MnO}_4^-] \quad (8)$$

Comparing Eqs (7) and (8) and rearrangement, the following two equations are obtained:

$$\frac{1}{k_{\text{obs}}} = \left(\frac{1 + K_4[\text{OH}^-]}{k_2 K_4 K_5 [\text{OH}^-]} \right) \frac{1}{[\text{Cit}]} + \frac{1}{k_2} \quad (9)$$

$$\frac{1}{k_{\text{obs}}} = \left(\frac{1}{k_2 K_4 K_5 [\text{Cit}]} \right) \frac{1}{[\text{OH}^-]} + \left(\frac{1}{k_2 K_5 [\text{Cit}]} + \frac{1}{k_2} \right) \quad (10)$$

Equation (9) requires that the relationship between $1/k_{\text{obs}}$ and $1/[\text{Cit}]$ at constant $[\text{OH}^-]$ to be linear with a non-zero intercept on the $1/k_{\text{obs}}$ axis as was experimentally satisfied (Fig. 6). Also, regarding to Eq. (10), the plot of $1/k_{\text{obs}}$ versus $1/[\text{OH}^-]$ at constant $[\text{Cit}]$ also should give a straight line with a positive intercept on $1/k_{\text{obs}}$ axis as was experimentally observed, Fig 8.

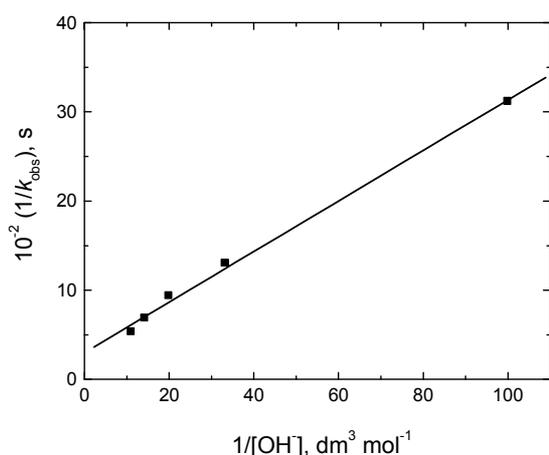


Fig. 8. Plot of $1/k_{\text{obs}}$ versus $1/[\text{OH}^-]$ in the oxidation of L-citrulline by permanganate ion in basic medium. $[\text{Cit}] = 6.0 \times 10^{-3}$, $[\text{MnO}_4^-] = 4.0 \times 10^{-4}$ and $I = 0.1 \text{ mol dm}^{-3}$ at 25°C .

5. Conclusion

A comparative kinetic and mechanistic study of oxidation of L-citrulline by permanganate ion was performed in acidic and basic media. Under our experimental conditions, HMnO_4 and $[\text{MnO}_4\text{OH}]^{2-}$ are regarded as the kinetically active species of permanganate ion in acidic and basic media, respectively. The final oxidation products of L-citrulline in both media were identified as 4-(carbamoylamino) butyraldehyde, ammonia and carbon dioxide. The appropriate rate laws are deduced and the reaction constants involved in the different steps of the mechanisms are evaluated.

Appendix A

Derivation of the rate-law expression in acidic medium:

According to the suggested Scheme 1,

$$\text{Rate} = \frac{-d[\text{MnO}_4^-]}{dt} = k_1[\text{C}_1] \quad (\text{A1})$$

$$K_1 = \frac{[\text{HMnO}_4]}{[\text{MnO}_4^-][\text{H}^+]}, [\text{HMnO}_4] = K_1[\text{MnO}_4^-][\text{H}^+] \quad (\text{A2})$$

$$K_2 = \frac{[\text{Cit}^+]}{[\text{Cit}][\text{H}^+]}, [\text{Cit}^+] = K_2[\text{Cit}][\text{H}^+] \quad (\text{A3})$$

$$K_3 = \frac{[\text{C}_1]}{[\text{Cit}^+][\text{HMnO}_4]}, [\text{C}_1] = K_3[\text{Cit}^+][\text{HMnO}_4] \quad (\text{A4})$$

$$[\text{C}_1] = K_1 K_2 K_3 [\text{Cit}][\text{MnO}_4^-][\text{H}^+]^2 \quad (\text{A5})$$

Substituting Eq. (A5) into Eq. (A1) leads to,

$$\text{Rate} = k_1 K_1 K_2 K_3 [\text{Cit}][\text{MnO}_4^-][\text{H}^+]^2 \quad (\text{A6})$$

The total concentration of MnO_4^- is given by,

$$[\text{MnO}_4^-]_{\text{T}} = [\text{MnO}_4^-]_{\text{F}} + [\text{HMnO}_4] + [\text{C}_1] \quad (\text{A7})$$

where 'T' and 'F' stand for total and free.

Therefore

$$[\text{MnO}_4^-]_{\text{F}} = \frac{[\text{MnO}_4^-]_{\text{T}}}{1 + K_1[\text{H}^+] + K_1 K_2 K_3 [\text{Cit}][\text{H}^+]^2} \quad (\text{A8})$$

In view of the high concentrations of $[\text{H}^+]$ we can write,

$$[\text{H}^+]_{\text{T}} = [\text{H}^+]_{\text{F}} \quad (\text{A9})$$

Similarly

$$[\text{Cit}]_{\text{T}} = [\text{Cit}]_{\text{F}} \quad (\text{A10})$$

Substituting Eqs. (A8), (A9) and (A10) into Eq. (A6), and omitting 'T' and 'F' subscripts leads to,

$$\text{Rate} = \frac{k_1 K_1 K_2 K_3 [\text{MnO}_4^-][\text{Cit}][\text{H}^+]^2}{1 + K_1[\text{H}^+] + K_1 K_2 K_3 [\text{Cit}][\text{H}^+]^2} \quad (\text{A11})$$

Under pseudo-first order condition, the rate-law can be expressed by equation (A12),

$$\text{Rate} = \frac{-d[\text{MnO}_4^-]}{dt} = k_{\text{obs}}[\text{MnO}_4^-] \quad (\text{A12})$$

Comparing Eqs. (A11) and (A12), the following relationship is obtained,

$$k_{\text{obs}} = \frac{k_1 K_1 K_2 K_3 [\text{Cit}][\text{H}^+]^2}{1 + K_1[\text{H}^+] + K_1 K_2 K_3 [\text{Cit}][\text{H}^+]^2} \quad (\text{A13})$$

and with rearrangement,

$$\frac{1}{k_{\text{obs}}} = \left(\frac{1 + K_1[\text{H}^+]}{k_1 K_1 K_2 K_3 [\text{H}^+]^2} \right) \frac{1}{[\text{Cit}]} + \frac{1}{k_1} \quad (\text{A14})$$

Appendix B

Derivation of the -law expression in alkaline medium:

According to Scheme 2,

$$\text{Rate} = \frac{-d[\text{MnO}_4^-]}{dt} = k_2[\text{C}_2] \quad (\text{B1})$$

$$K_5 = \frac{[\text{MnO}_4 \cdot \text{OH}^{2-}]}{[\text{MnO}_4^-][\text{OH}^-]} \quad (\text{B2})$$

$$[\text{MnO}_4 \cdot \text{OH}^{2-}] = K_5[\text{MnO}_4^-][\text{OH}^-] \quad (\text{B3})$$

$$K_6 = \frac{[\text{C}_2]}{[\text{Cit}][\text{MnO}_4 \cdot \text{OH}^{2-}]} \quad (\text{B4})$$

$$[\text{C}_2] = K_6[\text{Cit}][\text{MnO}_4 \cdot \text{OH}^{2-}] \quad (\text{B5})$$

$$[\text{C}_2] = K_5 K_6 [\text{Cit}][\text{OH}^-][\text{MnO}_4^-] \quad (\text{B6})$$

Substituting Eq. (B6) into Eq. (B1) yields

$$\text{Rate} = k_3 K_5 K_6 [\text{Cit}][\text{OH}^-][\text{MnO}_4^-] \quad (\text{B7})$$

$$[\text{Cit}]_{\text{T}} = [\text{Cit}]_{\text{F}} + [\text{C}_2] \quad (\text{B8})$$

$$[\text{Cit}]_{\text{F}} = \frac{[\text{Cit}]_{\text{T}}}{1 + K_5 K_6 [\text{OH}^-][\text{MnO}_4^-]} \quad (\text{B9})$$

Similarly,

$$[\text{MnO}_4^-]_{\text{T}} = [\text{MnO}_4^-]_{\text{F}} + [\text{MnO}_4 \cdot \text{OH}^{2-}] + [\text{C}_2] \quad (\text{B10})$$

$$[\text{MnO}_4^-]_{\text{F}} = \frac{[\text{MnO}_4^-]_{\text{T}}}{1 + K_5[\text{OH}^-] + K_5 K_6 [\text{Cit}][\text{OH}^-]} \quad (\text{B11})$$

and

$$[\text{OH}^-]_{\text{T}} = [\text{OH}^-]_{\text{F}} + [\text{MnO}_4 \cdot \text{OH}^{2-}] \quad (\text{B12})$$

$$[\text{OH}^-]_{\text{F}} = \frac{[\text{OH}^-]_{\text{T}}}{1 + K_1[\text{MnO}_4^-]} \quad (\text{B13})$$

Substituting Eqs (B11), (B12) and (B13) into Eq. (B7),

$$\text{Rate} = \frac{k_3 K_5 K_6 [\text{Cit}][\text{OH}^-][\text{MnO}_4^-]}{(1 + K_5 K_6 [\text{OH}^-][\text{MnO}_4^-])(1 + K_5[\text{MnO}_4^-])(1 + K_5[\text{OH}^-] + K_5 K_6 [\text{Cit}][\text{OH}^-])} \quad (\text{B14})$$

In view of low concentration of $[\text{MnO}_4^-]$ used, both first and second terms in the denominator of Eq. (B14) approximate to unity. Therefore, Eq (B14) becomes,

$$\text{Rate} = \frac{k_3 K_5 K_6 [\text{Cit}][\text{OH}^-][\text{MnO}_4^-]}{1 + K_5[\text{OH}^-] + K_5 K_6 [\text{Cit}][\text{OH}^-]} \quad (\text{B15})$$

and under pseudo-first order conditions, the following equations are obtained,

$$\frac{1}{k_{\text{obs}}} = \left(\frac{1 + K_5[\text{OH}^-]}{k_3 K_5 K_6 [\text{OH}^-]} \right) \frac{1}{[\text{Cit}]} + \frac{1}{k_3} \quad (\text{B16})$$

$$\frac{1}{k_{\text{obs}}} = \left(\frac{1}{k_3 K_5 K_6 [\text{Cit}]} \right) \frac{1}{[\text{OH}^-]} + \left(\frac{1}{k_3 K_6 [\text{Cit}]} + \frac{1}{k_3} \right) \quad (\text{B17})$$

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