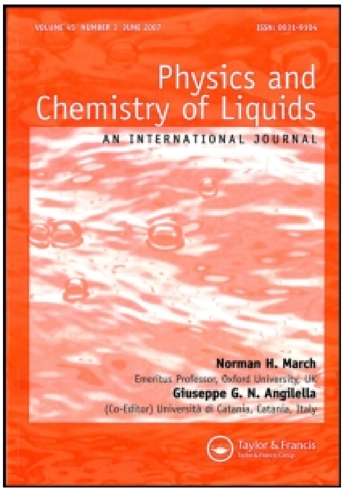

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# Thermodynamic and Kinetic Studies of Oxidation of L-histidine by Manganese(VII) in Concentrated Sulfuric Acid Medium in the Absence and Presence of Silver(I)

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# THERMODYNAMIC AND KINETIC STUDIES OF OXIDATION OF L-HISTIDINE BY MANGANESE(VII) IN CONCENTRATED SULFURIC ACID MEDIUM IN THE ABSENCE AND PRESENCE OF SILVER(I)

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Thermodynamic and kinetic studies and mechanism of manganese(VII) oxidation of L-histidine has been studied both in the absence and presence of silver(I) in aqueous sulfuric acid medium. Various hypotheses for the mechanism of acid catalysis have been tested and it has been found that rate is related to the activity of water in accord with Bunnett's hypothesis. The energy and entropy of activation and frequency factor have been calculated using the Arrhenius and Eyring plots. Mechanisms in agreement with the observations are reported. The experimental rate law for the both uncatalyzed reaction and in the presence of silver was found. The applicability of Burnett's theory has been tested.

*Keywords*: Rate laws; Bunnett's theory

## 1. INTRODUCTION

The manganese(VII) oxidation of amino acids has received considerable attention in previous literature due to the importance of these compounds in biological systems. The oxidation has been widely studied in strong acidic media [1–9], where no noticeable auto-catalytic effects

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*Corresponding author. e-mail: iloukhani@basu.ac.ir were found. However, in neutral or weakly alkaline medium, the literature consulted agrees as to the appearance of the cited autocatalytic effect [10–14]. The purpose of this study is to analyze the manganese(VII) oxidation of L-histidine in sulfuric acid both in the absence and presence of silver(I). This amino acid is important for some organisms because the dissociation of a proton from the imidazole ring is primarily responsible for the buffering action of proteins particularly hemoglobin in blood. The kinetic data show that silver(I) catalyzes the reaction. The applicability of Bunnett's theory was also tested.

## 2. EXPERIMENTAL PROCEDURES AND TECHNIQUES

### 2.1. Materials

All reagents used were of analytical grade from Merck, Sigma and Fluka. L-histidine was assayed for amino acid content by standard method [15]. The solutions were prepared in buffered medium with sulfuric acid and potassium sulfate, with triply distilled water which was deionized. The pH and the ionic strength of the medium were adjusted with the required concentrations of sulfuric acid and potassium sulfate to get the desired values and tested by the Vogel method [16]. Sulfuric acid, potassium sulfate, potassium pyrophosphate, silver nitrate, and mercuric chloride were used without further purification.

### 2.2. Kinetic Measurements

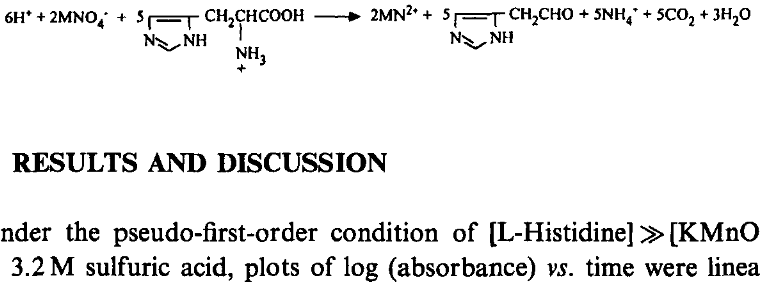
The course of reaction was followed by measuring the absorbance of unreacted permanganate from time to time at 525 nm using a fw-265 spectrophotometer, supplied with a conventional thermostatic bath (± 0.1 K). The reactions were carried out in the temperature range of 298–323 K.

The reaction was usually followed up to 50% completion, and products of the reaction were identified as ammonia, carbon dioxide, and the corresponding aldehyde [17]. Addition of mercuric chloride to the reaction system did not induce the precipitation of mercurous chloride, indicating that no free radicals are produced in the system [18].

## 3. STOICHIOMETRY

The stoichiometry of the reaction in the absence and presence of silver (I) was determined by following the reaction for four hours and estimating both permanganate and aldehyde before and after two hours. Permanganate was estimated by quenching a known amount of the reaction mixture in a known excess of iron(II) and titrating the unreacted iron(II) against standard cerium(IV). The aldehyde was estimated colorimetrically using chromotropic acid.

It was found that one mole of permanganate oxidized 2.5 moles of aldehyde. The stoichiometry of the reaction is represented by the following equation:



## 4. RESULTS AND DISCUSSION

Under the pseudo-first-order condition of [L-Histidine] $\gg$ [KMnO4] in 3.2 M sulfuric acid, plots of log (absorbance) *vs.* time were linear, showing that the reaction is first-order in [KMnO4] (Fig. 1). This was further confirmed by varying [KMnO4], which did not show any change, in the pseudo-first-order of rate constants, $k'_0$ (Tab. I). The reaction also exhibited a first-order dependence in [L-Histidine] as could be seen from Figure 2(A) and Table II.

However, in the presence of silver(I) the order of [KMnO4] was unity and those of [L-Histidine] and [Ag$^+$] were fractional Figures 2(B) and (C), Tables III–V. At constant [KMnO4]$_0$, [L-Histidine]$_0$, and temperature an increase in [$H_2SO_4$] increased the rate constant $k'_0$ from $1.17 \times 10^{-4}\,s^{-1}$ (2.9 mol dm$^{-3}$ $H_2SO_4$) to $2.45 \times 10^{-4}\,s^{-1}$ (4.3 mol dm$^{-3}$ $H_2SO_4$) (Tab. VI). The addition of sulfate and pyrophosphate ions caused no significant effect on the rate (Tab. VII).

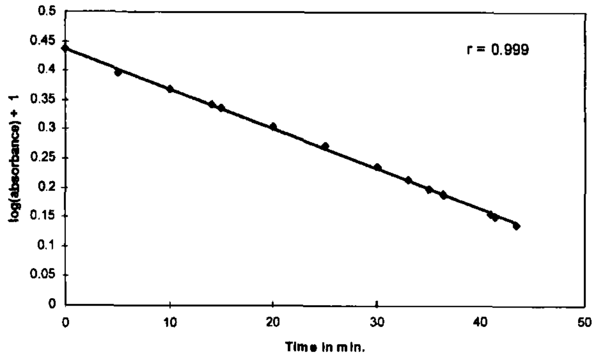


FIGURE 1 First-order plot for histidine – permanganate reaction.

TABLE I Effect of concentration of permanganate on the rate of oxidation in strong acid medium at 313 K[a]

| $[KMnO_4]_0$ (*mol dm*$^{-3}$) | $k'_0 \times 10^2 (s^{-1})$ |
|---|---|
| $1.50 \times 10^{-4}$ | 2.17 |
| $2.00 \times 10^{-4}$ | 2.21 |
| $2.50 \times 10^{-4}$ | 2.14 |
| $3.00 \times 10^{-4}$ | 2.36 |

[a] $[\text{L-Histidine}]_0 = 0.02\,\text{mol dm}^{-3}$ and $[H_2SO_4] = 3.2\,\text{mol dm}^{-3}$.

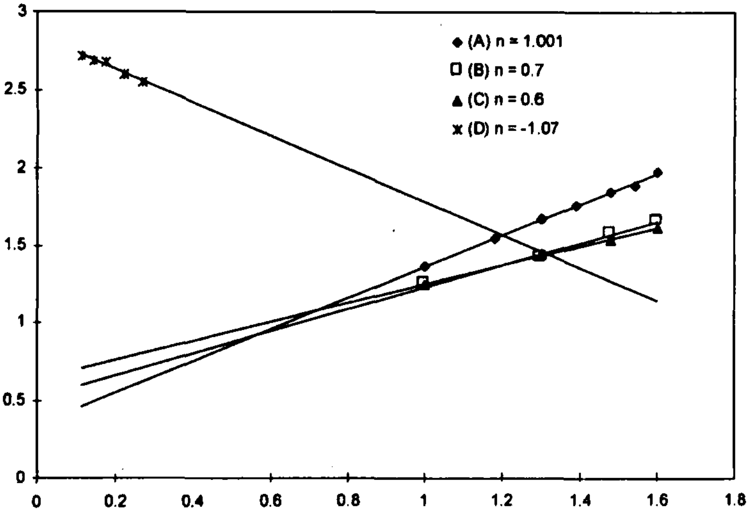


FIGURE 2 (A) Order of [Histidine] in uncatalyzed reaction, plot of log $k'_0 + 3$ *vs.* log[Histidine] + 3. (B) Order of [Histidine] in catalyzed reaction, plot of log $k'_C + 3$ *vs.* log[Histidine] + 3. (C) Order of $[Ag^+]$ in catalyzed reaction, plot of log $k'_C + 3$ *vs.* $\log[Ag^+] + 3$. (D) Bunnett's plot of log $k'_0 - \log[H_2SO_4]$ *vs.* log $a_{H_2O}$.

TABLE II Effect of concentration of L-histidine on the rate of oxidation in strong acid medium at four different temperatures[a]

| *[L-Histidine]$_0$ (mol dm$^{-3}$)* | $k'_0 \times 10^4$ ($s^{-1}$) 298 *K* | 303 *K* | 313 *K* | 323 *K* |
|---|---|---|---|---|
| 0.01 | 0.63 | 0.83 | 2.05 | 3.81 |
| 0.015 | 0.83 | 1.15 | 3.11 | 5.66 |
| 0.02 | 1.32 | 1.73 | 3.78 | 7.53 |
| 0.025 | 1.52 | 1.76 | 4.48 | 9.45 |
| 0.03 | 1.82 | 1.91 | 5.45 | 11.45 |
| 0.035 | 1.97 | 2.11 | 6.45 | 12.60 |
| 0.04 | 2.55 | 2.76 | 7.33 | 15.56 |

[a] $[KMnO_4]_0 = 0.0001$ mol dm$^{-3}$ and $[H_2SO_4] = 3.2$ mol dm$^{-3}$.

TABLE III Effect of concentration of permanganate on the rate of oxidation in strong acid medium in the presence of silver(I) at 303 K[a]

| *[KMnO$_4$]$_0$ (mol dm$^{-3}$)* | $k_{(obs)} \times 10^3$ ($s^{-1}$) | $k'_C \times 10^3$ ($s^{-1}$) |
|---|---|---|
| $1.50 \times 10^{-4}$ | 40.47 | 18.77 |
| $2.00 \times 10^{-4}$ | 35.76 | 13.66 |
| $2.50 \times 10^{-4}$ | 32.40 | 11.00 |
| $3.00 \times 10^{-4}$ | 31.82 | 8.22 |

[a] $[AgNO_3] = 0.001$ mol dm$^{-3}$, [L-Histidine] $= 0.02$ mol dm$^{-3}$ and $[H_2SO_4] = 3.2$ mol dm$^{-3}$.

Activation parameters are calculated using the Eyring equation $k = (RT/Nh)\exp((-\Delta H^{\neq} + T\Delta S^{\neq})/RT)$ plots of ln $(k/T)$ *vs.* $(1/T)$ should be linear. From the intercept and slope values of entropy $\Delta S^{\neq}$ and enthalpy $\Delta H^{\neq}$ of activation were evaluated, respectively, and results are given in Tables VIII and IX, respectively. Frequency factor and experimental energy for uncatalyzed pathway were estimated by using Arrhenius plots of $k''_0$ *vs.* $1/T$ Table VIII.

In agreement with the experimental behavior, two mechanisms are proposed to interpret the reaction pathways, uncatalyzed and catalyzed, separately.

### 4.1. Reaction Mechanism and Activation Parameters for the Uncatalyzed Process

The expected species on permanganate oxidation in acid solution are manganese(III), manganese(IV), and manganese(VII) [19]. If manganese(III) or manganese(IV) were to be the reactive species, the addition

TABLE IV Effect of concentration of L-histidine on the rate of oxidation in strong acid medium in the presence of silver(I) at four different temperatures[a]

| | 298 *K* | | 303 *K* | | 313 *K* | | 323 *K* | |
|---|---|---|---|---|---|---|---|---|
| [*L-Histidine*]$_0$ (*mol dm*$^{-3}$) | $K_{(obs)} \times 10^4$ ($s^{-1}$) | $k'_C \times 10^4$ ($s^{-1}$) | $K_{(obs)} \times 10^4$ ($s^{-1}$) | $k'_C \times 10^4$ ($s^{-1}$) | $k_{(obs)} \times 10^4$ ($s^{-1}$) | $k'_C \times 10^4$ ($s^{-1}$) | $k_{(obs)} \times 10^4$ ($s^{-1}$) | $k'_C \times 10^4$ ($s^{-1}$) |
| 0.01 | 1.07 | 0.44 | 1.41 | 0.58 | 4.91 | 2.86 | 6.45 | 2.64 |
| 0.02 | 1.84 | 0.52 | 2.75 | 1.02 | 8.15 | 4.37 | 11.66 | 4.13 |
| 0.03 | 2.41 | 0.59 | 3.13 | 1.22 | 11.58 | 6.13 | 17.66 | 6.21 |
| 0.04 | 3.69 | 1.14 | 4.26 | 1.50 | 14.80 | 7.53 | 27.30 | 11.74 |

[a] $[AgNO_3] = 0.001$ mol dm$^{-3}$, $[KMnO_4]_0 = 0.0001$ mol dm$^{-3}$ and $[H_2SO_4] = 3.2$ mol dm$^{-3}$.

TABLE V Effect of concentration of silver (I) on the rate oxidation in strong acid medium at 313 K[a]

| $[Ag^+]$ ($mol\ dm^{-3}$) | $k_{(obs)} \times 10^2$ ($s^{-1}$) | $k'_C \times 10^2$ ($s^{-1}$) |
|---|---|---|
| $1.00 \times 10^{-3}$ | 2.95 | 1.72 |
| $2.00 \times 10^{-3}$ | 3.95 | 2.72 |
| $3.00 \times 10^{-3}$ | 4.56 | 3.33 |
| $4.00 \times 10^{-3}$ | 5.24 | 4.01 |

[a] [L-Histidine]$_0$ = 0.01 mol dm$^{-3}$, [$KMnO_4$]$_0$ = 0.0001 mol dm$^{-3}$ and [$H_2SO_4$] = 3.2 mol dm$^{-3}$.

TABLE VI Effect of concentration of sulfuric acid on the rate of oxidation at 313 K[a]

| $[H_2SO_4]$ ($mol\ dm^{-3}$) | $k'_C \times 10^2 (s^{-1})$ |
|---|---|
| 2.9 | 1.17 |
| 3.5 | 1.45 |
| 3.9 | 1.63 |
| 4.3 | 2.45 |

[a] [L-Histidine]$_0$ = 0.02 mol dm$^{-3}$ and [$KMnO_4$]$_0$ ≅ 0.0001 mol dm$^{-3}$.

TABLE VII Effect of concentration of sulfate and pyrophosphate ions on the rate of oxidation at 313 K[a]

| *Concentration* ($mol\ dm^{-3}$) | $log\ k_{(obs)}$ ($s^{-1}$) |
|---|---|
| $[SO_4^{2-}] = 0.02$ | 1.3 |
| $[P_2O_7^{4-}] = 0.02$ | 1.29 |

[a] [L-Histidine]$_0$ = 0.02 mol dm$^{-3}$, [$H_2SO_4$] = 3.2 mol dm$^{-3}$ and [$KMnO_4$]$_0$ = 0.0001 mol dm$^{-3}$.

TABLE VIII Activation parameters on the oxidation of L-histidine by permanganate in strong acid medium at four different temperature[a]

| *Temp.* (*K*) | $k''_0 \times 10^3$ ($mol^{-1}\ dm^3\ s^{-1}$) | $\Delta S^{\neq}$ ($J\ mol^{-1}\ K^{-1}$) | $\Delta H^{\neq}$ ($kJ\ mol^{-1}$) | $E_{expt}$ ($kJ\ mol^{-1}$) | *LnA* |
|---|---|---|---|---|---|
| 298 | 5.92 | −79.08 | 62.28 | 64.92 | 20.92 |
| 303 | 8.30 | −79.08 | 62.28 | 64.92 | 20.92 |
| 313 | 20.5 | −79.08 | 62.28 | 64.92 | 20.92 |
| 323 | 38.2 | −79.08 | 62.28 | 64.92 | 20.92 |

[a] [$KMnO_4$]$_0$ = 0.0001 mol dm$^{-3}$ and [$H_2SO_4$] = 3.2 mol dm$^{-3}$.

of complexing agents like sulfate and pyrophosphate ions should have decreased the rate. In fact there is no effect of these ions on the rate [20], showing that only manganese(VII) is the most probable reactive species.

TABLE IX Activation parameters on the oxidation of L-histidine by permanganate in strong acid medium for catalyzed path at four different temperatures

| | *Temperature (K)* | | | |
|---|---|---|---|---|
| *Parameter* | 298 | 303 | 313 | 323 |
| $k''_C$/mol$^{-1}$ dm$^3$ s$^{-1}$ | 13.5 | 13.7 | 14.1 | 14.5 |
| $\Delta H^{\neq}$/kJ mol$^{-1}$ | −2.91 | −2.91 | −2.91 | −2.91 |
| $\Delta S^{\neq}$/J mol$^{-1}$ K$^{-1}$ | −224.2 | −224.2 | −224.2 | −224.2 |
| $K$/mol$^{-1}$ dm$^3$ | 29.78 | 27.80 | 25.71 | 22.4 |

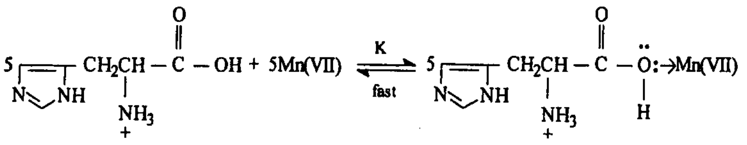
With increasing $[H^+]$, the rate enhances due to protonation of the oxidant resulting in the formation of a more powerful oxidant, namely, acid permanganate by the following equilibrium:

$$H^+MnO_4^- \Leftrightarrow HMnO_4$$

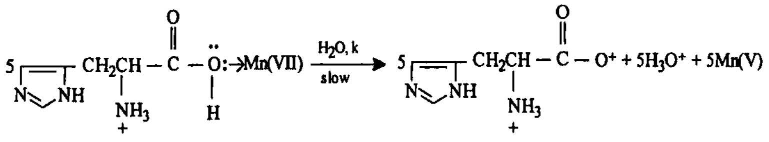
The same explanation has also been given in the oxidation of alcohols [19] and esters [21] by acid permanganate.

Plots of log $k'_0$ *vs.* log $[H_2SO_4]$ and log $k'_0$ *vs.* $H'_0$ were found to be linear, indicating that the reaction is acid catalyzed, but none of the above plots gave an ideal slope of unity. In view of the departure from the ideal behavior, the applicability of Bunnett's theory [22] was tested. A plot of log $k'_0$ − log$[H_2SO_4]$ *vs.* log$a_{H_2O}$ was linear Figure 2(D), and the slope was found to be −1.07. According to Bunnett's theory if the slope of such a plot is greater than −2, it will indicate the involvement of a water molecule in the rate-determining step as a proton-abstracting base from the substrate. The values of Hammett's acidity function $H'_0$ and log$a_{H_2O}$ have been taken from the literature [23, 24].

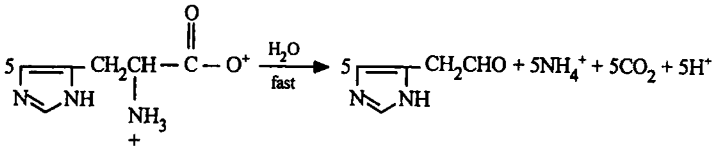
The mechanisms consistent with the observed kinetic data is as follows:



(1)



(2)



(3)

$$4Mn(V) \xrightarrow[\text{fast}]{} 2Mn(VII) + 2Mn(III) \tag{4}$$

$$2Mn(III) \xrightarrow[\text{fast}]{} Mn(IV) + Mn(II) \tag{5}$$

$$Mn(V) + Mn(IV) \xrightarrow[\text{fast}]{} Mn(VII) + Mn(II) \tag{6}$$

The rate law for the above scheme comes out to be

$$\frac{-d[\mathrm{Mn(VII)}]}{dt} = k_0[\mathrm{L-Histidine}][\mathrm{Mn(VII)}]$$

where

$$k_0 = Kk$$

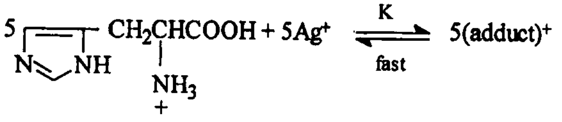
From the bimolecular rate constants at different temperatures 298–323 K, activation parameters for uncatalyzed reaction were evaluated (Tab. VIII).

### 4.2. Reaction Mechanism and Activation Parameters for the Catalyzed Process

Addition of silver(I) ion to the reaction system increased the rates, and in the presence of silver(I), the order in [L-Histidine] changed from unity to fractional Figure 2(B), indicating that it might be involved in complexation either with manganese(VII) or with silver(I). It is well known that silver(I) forms colorless adducuts with oxygen containing compounds with the lone pair of electrons on the oxygen atom [25]. It is, therefore, assumed that an adduct might be formed between silver(I) and L-histidine in a fast step before it is oxidized by manganese(VII) in a slow step to yield the silver(III) substrate adduct.

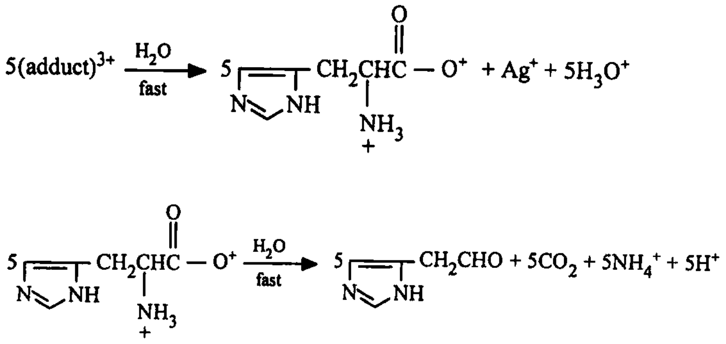
This silver(III) adduct might then disproportionate in subsequent fast steps to give the final product.

The reaction scheme involving L-histidine coordination could be written as in the following steps:



(1)

$$5(\text{adduct})^{+} + 5\text{Mn(VII)} \xrightarrow[\text{slow}]{k_c''} 5(\text{adduct})^{3+} + 5\text{Mn(V)} \qquad (2)$$



(3)

(4)

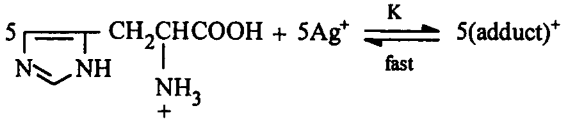
$$4\text{Mn(V)} \xrightarrow[\text{fast}]{} 2\text{Mn(VII)} + 2\text{Mn(III)} \qquad (5)$$

$$2\text{Mn(III)} \xrightarrow[\text{fast}]{} \text{Mn(IV)} + \text{Mn(II)} \qquad (6)$$

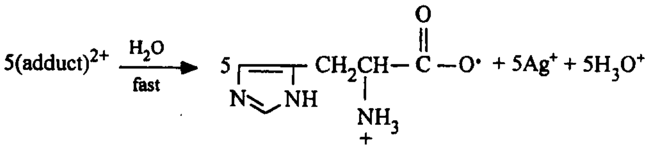
$$\text{Mn(V)} + \text{Mn(IV)} \xrightarrow[\text{fast}]{} \text{Mn(VII)} + \text{Mn(II)} \qquad (7)$$

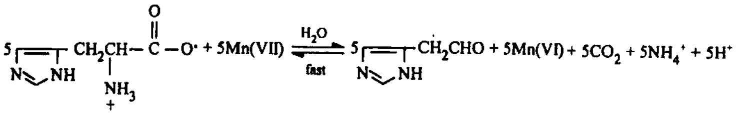
Though catalysis is generally explained by a one-electron transfer mechanism, we prefer a two-electron transfer mechanism since free radical and silver(II) [26] were not detected in the system.

This type of two-electron transfer mechanism was proposed by Harkness [27] in the oxidation of carbon monoxide by permanganate in the presence of silver(I). However, a one-electron transfer mechanism can be considered only if the silver(II) formed is assumed to disproportionate rapidly to elude detection by ordinary tests. In such a case the mechanism of the reaction could be shown as in the following steps:


(1)

$$5(\text{adduct})^+ + 5\text{Mn(VII)} \xrightarrow[\text{slow}]{k_c''} 5(\text{adduct})^{2+} + 5\text{Mn(VI)} \qquad (2)$$


(3)


(4)

$$10\text{Mn(VI)} \xrightarrow[\text{fast}]{} 5\text{Mn(VII)} + 5\text{Mn(V)} \qquad (5)$$

$$4\text{Mn(V)} \xrightarrow[\text{Fast}]{} 2\text{Mn(VII)} + 2\text{Mn(III)} \qquad (6)$$

$$2\text{Mn(III)} \xrightarrow[\text{fast}]{} \text{Mn(IV)} + \text{Mn(II)} \qquad (7)$$

$$\text{Mn(V)} + \text{Mn(IV)} \xrightarrow[\text{fast}]{} \text{Mn(VII)} + \text{Mn(II)} \qquad (8)$$

In either of the cases, the rate equation for the catalyzed path comes out to be:

$$\frac{-d[\text{Mn(VII)}]}{dt} = \frac{Kk''_C[\text{L}-\text{Histidine}]_0[\text{Ag}^+]}{1 + K[\text{L}-\text{Histidine}]_0 + K[\text{Ag}^+]} \cdot [\text{Mn(VII)}]$$
$$= k'_C[\text{Mn(VII)}]$$

where $k'_0$ is the pseudo-first-order rate constant for the uncatalyzed reaction, $k''_C$ is the bimolecular rate constant for step (2) in the catalyzed path, and $K$ is the formation constant of adduct. As the observed pseudo-first-order rate constant $k_{(\mathrm{obs})}$ in the presence of silver(I), when plotted against $[\mathrm{Ag}^+]$, gives an intercept on the $y$ axis, the uncatalyzed reaction might also be taking place along with the catalyzed one.

Hence, the rate equation for the catalyzed reaction should include a term for the uncatalyzed path ways.

Hence $k_{(\mathrm{obs})} = k'_0 + k'_C$, where $k'_0$ and $k'_C$ are the pseudo-first-order rate constants for the uncatalyzed and catalyzed path ways for the same concentration of *L*-histidine.

Writing $k'_0$ and $k'_C$ in terms of bimolecular rate constants, the rate equation for the catalyzed reaction comes out to be:

$$k_{(\mathrm{obs})} = k''_0[\mathrm{L-Histidine}] + \frac{Kk''_C[\mathrm{L-Histidine}]_0[\mathrm{Ag}^+]}{1 + K[\mathrm{L-Histidine}]_0 + K[\mathrm{Ag}^+]}$$

$$k_{(\mathrm{obs})} - k''_0[\mathrm{L-Histidine}] + \frac{Kk''_C[\mathrm{L-Histidine}]_0[\mathrm{Ag}^+]}{1 + K[\mathrm{L-Histidine}]_0 + K[\mathrm{Ag}^+]} \qquad *$$

Taking the reciprocals of Eq. (∗), we get

$$\frac{1}{k_{(\mathrm{obs})} - k''_0[\mathrm{L-Histidine}]_0} = \frac{1}{[\mathrm{L-Histidine}]_0} \times \left[\frac{1}{Kk''_C[\mathrm{Ag}^+]} + \frac{1}{k''_C}\right] + \frac{1}{k''_C[\mathrm{Ag}^+]}$$

It is clear that the plots of $(1/k_{(\mathrm{obs})-k''_0[\mathrm{L-Histidine}]_0})$ *vs.* $(1/[\mathrm{L-Histidine}]_0)$ at constant $[\mathrm{Ag}^+]$ should be linear.

Such plots were obtained in the present study for L-histidine. From the intercept and slope values the bimolecular rate constant for the slow step $k''_C$ and the formation constant of the adduct $K$ were evaluated at different temperatures 298–323 K to calculate the activation parameters (Tab. IX).

Kinetic studies on the manganese(VII) oxidation of L-histidine in moderately acid medium was carried out in order to get an insight in to the mechanism. The order in both [L-Histidine] and [KMnO4] was found to be unity. The effect of complexing agents like sulfate and pyrophosphate ion was nil, from which manganese(VII) was confirmed to be the reactive species.

The slope of the linear plot $\log k'_0 - \log[H_2SO_4]$ *vs.* $\log a_{H_2O}$ (Bunnett's plot) was found to be $-1.07$, indicating that involvement of the water molecule in the rate-determining step is as a proton abstracting base from the substrate.

A probable mechanism in which two electrons are transfered from the substrate to the oxidant is proposed. As silver(I) was found to catalyze this reaction, the oxidation of L-histidine was carried out in the presence of silver(I). In the presence of silver(I) the order in permanganate was unity and that in [L-Histidine] and [$Ag^+$] was fractional. Two probable mechanisms, one involving a two-electron transfer mechanism and the other a one-electron transfer mechanism, have also been discussed.

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