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Kinetic Studies and Mechanism on the Permanganic Oxidation of L-Lysine in Strong Acid Medium

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Kinetics and mechanism of manganese(VII) oxidation of L-lysine have been studied 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 accordance with Bunnett's hypothesis. The energy and entropy of activation and frequency factor have been calculated using the Eyring and Arrhenius plots. Mechanisms in agreement with the observations are reported. The experimental rate law for the reaction was found to be

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

The reaction appears to involve an acid catalysis and the data showed the role of water molecules in the rate-determining step facilitating proton transfer which satisfies Bunnett's theory.

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[1–8], where no noticeable auto-catalytic effects were found. However, in neutral or weakly alkaline medium, the literature consulted agrees as to the appearance of the cited auto-catalytic effect[9–13]. The purpose of this study is to analyze the manganese(VII) oxidation of L-lysine in sulfuric acid. The applicability of Bunnett's theory was also tested.

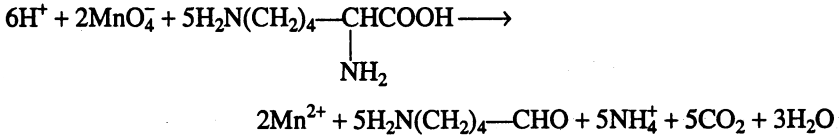
EXPERIMENTAL

Materials: All reagents used were of analytical grade from Merck, Sigma and Fluka. L-lysine was assayed for amino acid content by standard method[14]. 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[15]. Sulfuric acid, potassium sulfate, potassium pyrophosphate, and mercuric chloride were used without further purification.

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 283–303 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[16]. 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[17].

The stoichiometry of the reaction was determined by following the reaction for 1 h and estimating both permanganate and aldehyde before and after $\frac{1}{2}$ h. 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:



$$6H^+ + 2MnO_4^- + 5H_2N(CH_2)_4\text{—}\underset{\displaystyle NH_2}{CH}COOH \longrightarrow$$

$$2Mn^{2+} + 5H_2N(CH_2)_4\text{—}CHO + 5NH_4^+ + 5CO_2 + 3H_2O$$

RESULTS AND DISCUSSION

Under the pseudo-first-order condition of [L-lysine] $\gg$ [$KMnO_4$] in 3.2 M sulfuric acid, plots of log (absorbance) *vs.* time were linear, showing that the reaction is first-order in [$KMnO_4$] (Fig. 1). This was further confirmed by varying [$KMnO_4$], which did not show any change, in the pseudo-first-order of rate constants, k'_0 (Table-1). The reaction also exhibited a first-order dependence in [L-lysine] as could be seen from Fig. 2 and Table-2.

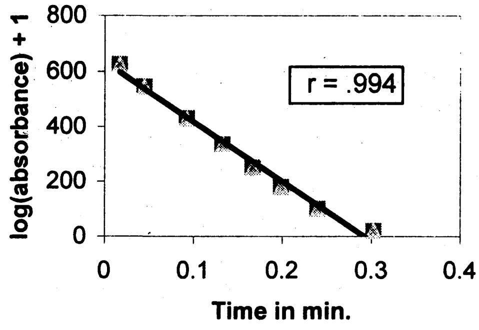


Fig. 1. First-order plot for lysine-permanganate reaction

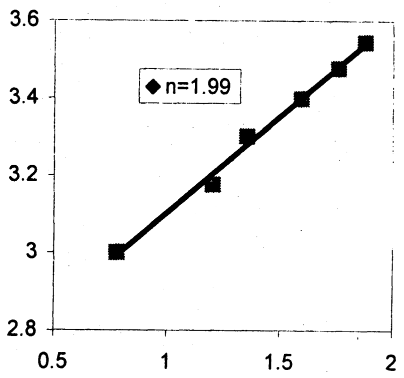


Fig. 2. Order of [Lysine] in reaction, plot of log k_0' + 5 *vs*. log [Lysine] + 5

TABLE-1
EFFECT OF CONCENTRATION OF PERMANGANATE ON THE RATE OF OXIDATION IN STRONG ACID MEDIUM AT 298 K [a]

$[KMnO_4]_0$ (mol dm^{-3})	$k_0' \times 10^4$ (s^{-1})
1.00×10^{-4}	16.34
1.50×10^{-4}	14.69
2.00×10^{-4}	10.79
2.50×10^{-4}	7.08
3.00×10^{-4}	4.90

[a] $[L\text{-Lysine}]_0 = 0.035$ mol dm^{-3} and $[H_2SO_4] = 3.2$ mol dm^{-3}

At constant $[KMnO_4]$, $[L\text{-lysine}]_0$, and temperature an increase in $[H_2SO_4]$ increased the rate constant k_0' from 7.28×10^{-4} s^{-1} (3.2 mol dm^{-3} H_2SO_4) to 24.02×10^{-4} s^{-1} (5.5 mol dm^{-3} H_2SO_4) (Table-3). The addition of sulfate and pyrophosphate ions caused no significant effect on the rate (Table-4).

TABLE-2
EFFECT OF CONCENTRATION OF L-LYSINE ON THE RATE OF OXIDATION IN STRONG ACID MEDIUM AT FIVE DIFFERENT TEMPERATURES [a]

$[L\text{-Lysine}]_0$ (mol dm^{-3})	$k_0' \times 10^5$ (s^{-1})				
	283 K	288 K	293 K	298 K	303 K
0.01	6.04	8.55	11.24	9.83	29.97
0.015	16.05	22.56	30.53	42.89	66.33
0.02	32.72	40.40	57.14	72.80	125.60
0.025	39.54	68.36	79.90	94.70	151.60
0.03	57.42	87.72	101.90	108.60	275.40
0.035	75.41	115.00	139.90	163.40	280.30

[a] $[KMnO_4]_0 = 0.01$ $[L\text{-lysine}]_0$ and $[H_2SO_4] = 3.2$ mol dm^{-3}

TABLE-3
EFFECT OF CONCENTRATION OF SULFURIC ACID ON THE RATE OF OXIDATION AT 298 K [a]

$[H_2SO_4]$ (mol dm^{-3})	$k'_0 \times 10^4$ (s^{-1})
3.2	7.28
3.5	9.08
4.0	15.59
4.5	17.64
5.0	18.02
5.5	24.02

[a] $[\text{L-Lysine}]_0 = 0.02$ mol dm^{-3} and $[KMnO_4]_0 \equiv 0.01[\text{L-Lysine}]_0$

TABLE-4
EFFECT OF CONCENTRATION OF SULFATE AND PYROPHOSPHATE IONS ON THE RATE OF OXIDATION AT 293 K [a]

Concentration (mol dm^{-3})	$k'_0 \times 10^3$ (s^{-1})
$[SO_4^{2-}] = 0.02$	1.48
$[P_2O_7^{4-}] = 0.02$	1.31

[a] $[\text{L-Lysine}]_0 = 0.02$ mol dm^{-3}, $[H_2SO_4] = 3.2$ mol dm^{-3} and $[KMnO_4]_0 \equiv 0.01[\text{L-Lysine}]_0$

Activation parameters are calculated using the Eyring equation

$$k_0 = \frac{RT}{Nh} \exp\left(\frac{-\Delta H^{\neq} + \Delta S^{\neq}}{RT}\right)$$

Plots of ln k_0/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 Table-5. Frequency factor A and experimental energy E_{exp} were also estimated by using Arrhenius plots of k_0 *vs.* 1/T (Table-5).

TABLE-5
ACTIVATION PARAMETERS ON THE OXIDATION OF L-LYSINE BY PERMANGANATE IN STRONG ACID MEDIUM AT FIVE DIFFERENT TEMPERATURES [a]

Temp. (K)	$k_0 \times 10^8$ ($mol^{-1} dm^3 s^{-1}$)	$\Delta S^{\neq}$ ($J mol^{-1} K^{-1}$)	$\Delta H^{\neq}$ ($kJ mol^{-1}$)	E_{expt} ($kJ mol^{-1}$)	log A
283	3.61	–221.83	46.82	49.22	1.63
288	5.07	–221.83	46.82	49.22	1.63
293	6.87	–221.83	46.82	49.22	1.63
298	9.65	–221.83	46.82	49.22	1.63
303	14.92	–221.83	46.82	49.22	1.63

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

In agreement with the experimental behaviour, mechanisms are proposed to interpret the reaction pathways.

The expected species on permanganate oxidation in acid solution are manganese(III), manganese(IV), and manganese(VII).[18] If manganese(III) or manganese(IV) were to be the reactive species, the addition 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[19], showing that only manganese(VII) is the most probable reactive species.

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[18] and esters[20] 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 behaviour, the applicability of Bunnett's theory[21] was tested. A plot of log k_0' – log $[H_2SO_4]$ vs. log a_{H_2O} was linear (Fig. 3) and the slope was found to be –1.75. According to

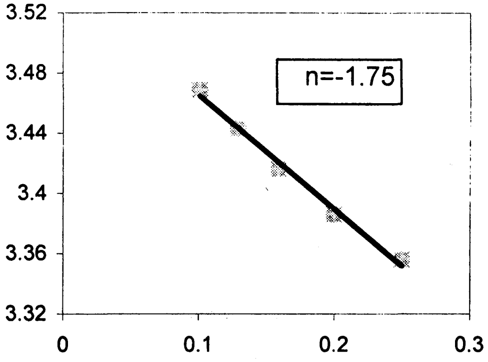
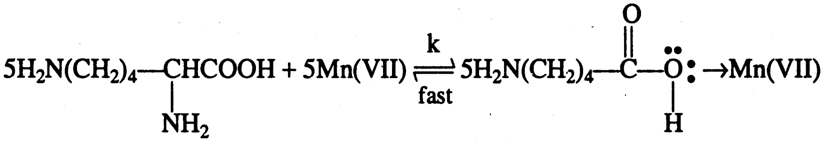


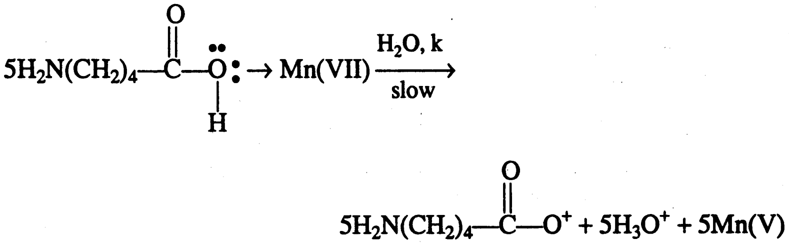
Fig. 3. Bunnett's plot of log k_0' – log $[H_2SO_4]$ vs. log a_{H_2O}

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[22, 23].

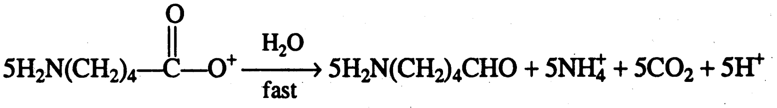
The mechanisms consistent with the oberved kinetic data is as follows:



$$5H_2N(CH_2)_4\text{—}\underset{NH_2}{\underset{|}{C}}HCOOH + 5Mn(VII) \underset{fast}{\overset{k}{\rightleftharpoons}} 5H_2N(CH_2)_4\text{—}\overset{O}{\overset{\|}{C}}\text{—}\underset{H}{\underset{|}{\ddot{O}}}\!: \rightarrow Mn(VII) \qquad (1)$$



$$5H_2N(CH_2)_4\text{—}\overset{O}{\overset{\|}{C}}\text{—}\underset{H}{\underset{|}{\ddot{O}}}\!: \rightarrow Mn(VII) \xrightarrow[slow]{H_2O,\ k} 5H_2N(CH_2)_4\text{—}\overset{O}{\overset{\|}{C}}\text{—}O^+ + 5H_3O^+ + 5Mn(V) \qquad (2)$$



$$5H_2N(CH_2)_4\text{—}\overset{O}{\overset{\|}{C}}\text{—}O^+ \xrightarrow[fast]{H_2O} 5H_2N(CH_2)_4CHO + 5NH_4^+ + 5CO_2 + 5H^+ \qquad (3)$$

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

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

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

The rate law for the above scheme comes out to be

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

where $k_0 = Kk$.

From the bimolecular rate constants at different temperatures 283–303 K, activation parameters for reaction were evaluated (Table-5).

Finally we concluded that the kinetic studies on the manganese(VII) oxidation of L-lysine in moderately acid medium could get an insight into the mechanism. The order in both [L-lysine] and [$KMnO_4$] 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 –1.75, indicating that involvement of the water molecule in the rate determining step is as a proton abstracting base from the substrate.

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