

## Kinetics of Oxidative Decarboxylation of L-Lysine by Potassium Permanganate

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Oxidative decarboxylation of L-lysine by permanganate in sulfuric acid medium has been found to be first order in both oxidant and substrate concentrations. Various hypotheses for the mechanism of acid catalysis have been tested. The energy and entropy of activation have been calculated as 11.00 and 9.412 kJ mol<sup>-1</sup> and -38.29 and -32.08 J mol<sup>-1</sup> K<sup>-1</sup> for two stages of the reaction, respectively. A kinetic mechanism is proposed, which is in agreement with the experimental data.

**Key Words:** Kinetics, Oxidative decarboxylation, L-Lysine, Potassium permanganate.

### INTRODUCTION

Potassium permanganate has been found to be a good oxidising agent and the kinetics of oxidation of various organic compounds have been reported by previous workers<sup>1-4</sup>. However, careful survey of the literature reveals that oxidative decarboxylation of amino acids by permanganate has received little attention<sup>5,6</sup>. The present paper deals with the kinetic studies of the oxidative decarboxylation of L-lysine by potassium permanganate in sulfuric acid medium.

L-Lysine has a —SH group, which is rapidly oxidized by potassium permanganate. The object of the present investigation was to study the oxidative decarboxylation, which is a relatively much slower process as compared to the oxidation of —SH group to —SO<sub>3</sub>H group. The amount of potassium permanganate required for the oxidation of the thiol group to sulphonic acid group was determined by adding permanganate solution to a solution of L-lysine to give a pink colour (in excess) and titrating the excess of permanganate against previously standardized hypo solution.

### EXPERIMENTAL

L-Lysine, potassium permanganate and other chemicals used were BDH AR/SM GR grade. Doubly distilled water was used to prepare all solutions. The reaction vessels were coated with black paint to exclude any photochemical effect.

Solutions of sulfuric acid were standardized against previously standardized sodium hydroxide solution.

The requisite amounts of L-lysine and sulfuric acid were taken in the reaction flask and kept in a thermostat at the desired temperature within ±0.1°C. The flask of potassium permanganate was also kept in the thermostat. Requisite volume of permanganate was then rapidly mixed. The kinetics of the reaction was followed by estimating unreacted permanganate iodometrically.

## RESULTS AND DISCUSSION

Stoichiometry of the reaction was studied. It was observed that two equivalents of permanganate were consumed by five equivalents of L-lysine. Formation of ammonium ions and carbon dioxide was confirmed by usual tests. 2-Sulfoacetaldehyde was detected as the reaction product. The induced reduction of mercuric chloride by the reaction mixture indicates the participation of free radicals<sup>7</sup>.

When the concentrations of L-lysine and sulfuric acid were in excess, the fading of permanganate followed a first order rate law. The pseudo-first order rate constants,  $k_1$  and  $k_2$ , are listed in Table-1.

TABLE-1  
VARIATION OF L-LYSINE AND PERMANGANATE CONCENTRATIONS

$c(\text{H}_2\text{SO}_4) = 2.0 \text{ mol dm}^{-2}$		Temperature = 303°K	
$c(\text{KMnO}_4) \times 10^4$ ( $\text{mol dm}^{-2}$ )	$c(\text{L-Lysine})$ $\times 10^4$ ( $\text{mol dm}^{-2}$ )	$k_1$ ( $10^{-4} \text{ s}^{-1}$ )	$k_2$ ( $10^{-4} \text{ s}^{-1}$ )
4.0	2.50	16.400	2.121
5.0	3.75	16.470	4.223
6.0	5.00	16.440	6.566
7.0	6.25	16.480	8.383
8.0	7.50	16.510	10.570

The variation of permanganate concentration has practically no effect on the rate constants, confirming that the order with respect to permanganate is unity.

The plot of  $\log k$  vs.  $\log [\text{L-lysine}]$  was found to be linear and the slope was unity, indicating that the order of the reaction with respect to the substrate L-lysine is one. There is no kinetic evidence for intermediate complex formation between substrate and permanganate. The rate has been found to increase with the increasing concentration of sulfuric acid. The pseudo-first order rate constants are listed in Table-2.

TABLE-2  
VARIATION OF SULFURIC ACID CONCENTRATION

$c(\text{L-Lysine})$ $= 10^{-4} \text{ mol dm}^{-4}$	$c(\text{KMnO}_4)$ $= 10^{-2} \text{ mol dm}^{-2}$	Temperature = 303 K
$c(\text{H}_2\text{SO}_4) \text{ mol dm}^{-2}$	$k_1$ ( $10^{-4} \text{ s}^{-1}$ )	$k_2$ ( $10^{-4} \text{ s}^{-1}$ )
0.75	2.371	5.213
1.00	4.223	16.470
1.25	5.676	27.750
1.50	7.9860	49.560
1.75	10.510	83.250
2.00	13.810	136.900

Further in an attempt to correlate the rate of oxidation with acid concentration, various hypotheses for the mechanism of acid catalysis were tested. In this case, either of two Zucker-Hammett plots<sup>8</sup>, are linear, indicating that the reaction is acid catalyzed; however, none of these plots produces the ideal slope of unity. In view of these departures of ideal slope values, applicability of Bunnett's hypothesis<sup>9</sup> and the Bunnett-Olsen l.f.e.r.<sup>10</sup> were tested. The values of  $-\text{H}_0$  and  $\log a_{\text{H}_2\text{O}}$  corresponding to acid concentration have been taken from Paul and Long<sup>11</sup> and Bunnett<sup>12</sup> respectively.

The values of Bunnett parameters  $\omega$ ,  $\omega^*$  and  $\Phi$  were found to be  $-10.75$ ,  $3.0$  and  $1.43$ , respectively.

Primary salt effect was not observed, but a linear plot of  $\log k$  against ionic strength was obtained at higher concentrations of added neutral salts. This indicated that the reaction involves at least a neutral molecule in the rate determining step.

### Activation parameters

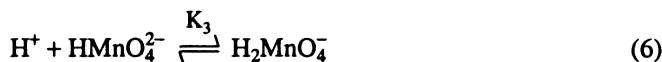
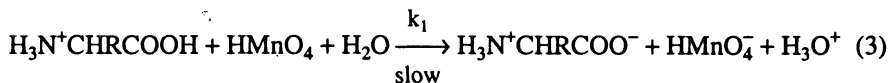
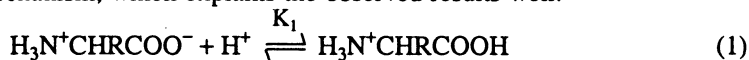
The reaction was studied at different temperatures to evaluate the activation parameters. The results are summarized in Table-3.

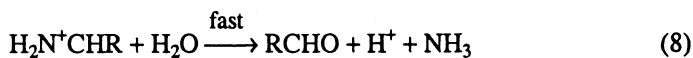
TABLE-3  
ACTIVATION PARAMETERS

$c(\text{L-Lysine}) = 10^{-2} \text{ mol dm}^{-2}$ ,  $c(\text{KMnO}_4) = 10^{-4} \text{ mol dm}^{-2}$ ,  $c(\text{H}_2\text{SO}_4) = 2.0 \text{ mol dm}^{-2}$

Stage	$\Delta H^\ddagger$ (kcal mol <sup>-1</sup> )	$\Delta E^\ddagger$ (kJ mol <sup>-1</sup> )	$\Delta S^\ddagger$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$pZ$ (dm <sup>2</sup> mol <sup>-2</sup> s <sup>-1</sup> )
First	8.809	9.412	-38.29	$2.797 \times 10^4$
Second	10.397	11.00	-32.08	$6.322 \times 10^5$

The information gained from the experimental data leads to the following probable mechanism, which explains the observed results well.





where R stands for L-lysine.

The concentration of HMnO<sub>4</sub> was determined from the equation (9) as

$$K_2 = \frac{[\text{HMnO}_4]}{[\text{H}^+][\text{MnO}_4^-]_{\text{free}}}$$

Free [MnO<sub>4</sub><sup>-</sup>] can be calculated as

$$\text{Free } [\text{MnO}_4^-] = \text{initial } [\text{MnO}_4^-] - [\text{HMnO}_4] \text{ formed} \quad (10)$$

It will lead to the inclusion of a K<sub>2</sub> term in the numerator of the rate law. The rate expression for this mechanism has been derived as

$$\frac{d[\text{MnO}_4^-]}{dt} = \frac{k_1 K_1 K_2 [\text{H}_3\text{N}^+\text{CHR}\text{COO}^-][\text{H}^+]^2 [\text{MnO}_4^-][\text{H}_2\text{O}]}{1 + K_2 [\text{H}^+]} \quad (11)$$

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