

Kinetics of oxidative decarboxylation of L-citrulline by permanganate

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Abstract

Potassium permanganate is a good oxidizing agent L-citrulline has an – SH group which is rapidly oxidized by potassium permanganate. In the present study it was observed that two equivalent of permanganate were consumed by five equivalent of L-citrulline. Beside this an attempt to correlate the rate of oxidation with acid concentration, with various Hypothesis for the mechanism of acid catalysis were also observed.

Key Words: *Permanganate, L-citrulline, oxidized decarboxylation*

Introduction

Oxidative decarboxylation of L-citrulline 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 12.76 and 7.13 kJ mol⁻¹ and -41.69 and -25.55 J mol⁻¹ K⁻¹ for two stages of the reaction, respectively. A mechanism is proposed, which is in agreement with the experimental data.

Potassium permanganate has been found to be a good oxidising agent and the kinetics of oxidation of various organic compounds have been studied by previous workers Ghosh and Ghosh (1955), Marcus (1994), Ghosh (1999), Swaminathan and Harris (1996), Mohanty *et al.* (1985) However, careful survey of the literature reveals that oxidative decarboxylation of amino acids by permanganate has received little attention Iyun and Onu (1998), Goto and Krishimoto (1989), Mallamma *et al.* (2001) The present paper deals with the kinetic studies of the oxidative decarboxylation of L-citrulline by potassium permanganate in sulfuric acid medium.

L-citrulline has an – SH group, which is rapidly oxidized by potassium permanganate. The objective of the present investigation was to study the oxidative decarboxylation, which is a relatively much slower process when compared to the oxidation of –SH group to –SO₃H group. The amount of potassium permanganate required for the oxidation of the thio 1 group to sulfonic acid group was determined by adding permanganate solution to solution of L-citrulline to give a pink colour (in excess) and titrating the excess of permanganate against previously standardized hypo solution.

Experiment

L-citrulline, potassium permanganate and other chemicals used were BDHAR’/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. Potassium permanganate solution was prepared by the method of Vogel (1964)

The requisite amounts of L-citrulline and sulfuric acid were taken in the reaction flask and kept in a thermostat at the desired temperature within +0.1⁰C. 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-citrulline. 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 Drummond *et al.* (1953)

When the concentrations of L-citrulline and sulfuric acid were in excess, the fading of permanganate followed a first order rate law. The pseudo-first order rate constants, k₁ and k₂, are listed in Table I.

Table I Variation of L-citrulline and permanganate concentrations

c(H ₂ SO ₄)=2.0 mol dm ⁻²		Temperature=303 ⁰ K	
c(KMnO ₄) x 10 ⁴ (mol dm ⁻²)	c(L-citrulline) x 10 ⁴ (mol dm ⁻²)	k ₁ (10 ⁻⁴ s ⁻¹)	k ₂ (10 ⁻⁴ s ⁻¹)
4.0	2.50	18.07	18.11
5.0	3.75	18.11	23.89
6.0	5.00	18.06	29.68
7.0	6.25	18.12	35.10
8.0	7.50	18.14	40.30

Table II Variation of sulfuric acid concentration

c(L-citrulline) = 10 ⁻⁴ mol dm ⁻⁴	C(KMnO ₄) = 10 ⁻² ol dm ⁻²	Temperature = 303
c(H ₂ SO ₄) mol dm ⁻²	K ₁ (10 ⁻⁴ s ⁻¹)	k ₂ (10 ⁻⁴ s ⁻¹)
0.75	14.91	29.61
1.0	18.11	37.09
1.25	20.93	48.37
1.50	25.13	60.37
1.75	29.43	76.78
2.00	33.27	80.81

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 [L-citrulline] was found to be linear and the slope was unity indicating that the order on the reaction with respect to the substrate L-citrulline 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 II.

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 (1939), 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 (1961) and the Bunnett-Olsen l.f.e.r (1966)], were tested. The values of –H₀ and log a H O corresponding to acid concentrations have been taken from Paul and Long (1957)] and Bunnett (1961) respectively.

The values of Bunnett parameters ω , ω^* and Φ were found to be -11.6, 3.2 and 0.94, 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.

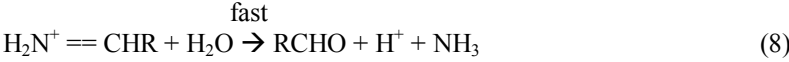
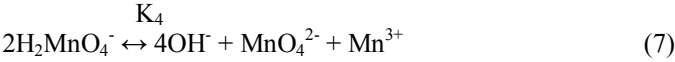
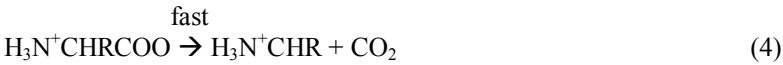
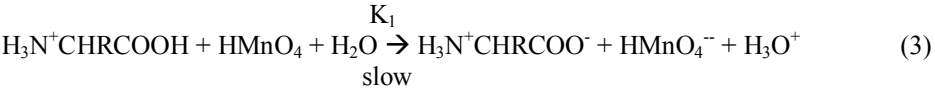
Activation parameters

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

Table III Activation parameters

c(L-citrulline) = 10 ⁻² mol dm ⁻² mol dm ⁻² ;		c(KMnO ₄) = 10 ⁻⁴ c(H ₂ SO ₄) = 2.0 mol dm ⁻²		
Stage	Δ H (k cal mol ⁻¹)	Δ E (kJ mol ⁻¹)	Δ S (J mol ⁻¹ K ⁻¹)	pZ (dm ² mol ⁻² s ⁻¹)
First	6.528	7.131	-41.69	2.79 x 10 ²
Second	12.157	12.76	-24.55	5.072 x 10 ³

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



where R == for L-citrulline.
The concentration of HMnO₄ was determined from the equation (9) as

$$\text{K}_2 = \frac{[\text{HMnO}_4]}{[\text{H}^+][\text{MnO}_4^-]_{\text{free}}}$$

Free $[\text{MnO}_2^-]$ 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_2 term in the numerator of the rate law.

The rate expression for this mechanism has been derived as

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

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