

KINETICS AND MECHANISM OF OXIDATION OF L-TYROSINE BY THALLIUM(III) IN PERCHLORIC ACID MEDIUM

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ABSTRACT

The kinetics of oxidation of L-tyrosine by thallium(III) was studied at 50 °C in perchloric acid medium titrimetrically using iodometric method. The reaction was found to be first order dependent on [thallium(III)] and fractional order on [tyrosine]. Rate of the reaction increased considerably with increase in ionic strength whereas change in $[H^+]$ and [thallium(I)] did not show any significant effect. The main product of oxidation was confirmed as 4-hydroxyphenyl acetaldehyde. A plausible mechanism was proposed invoking complexation between the substrate and oxidant. The energy of activation, E_a and entropy of activation, ΔS^\ddagger for the rate determining step were calculated using linear least squares method and were found to be $109.92 \pm 15.24 \text{ kJmol}^{-1}$ and $16.83 \pm 47.18 \text{ JKmol}^{-1}$ respectively.

KEYWORDS: Kinetics, Mechanism, Oxidation, L-Tyrosine, Thallium(III)

INTRODUCTION

Thallium(III) is a highly stable two-electron oxidant in acidic medium. It oxidizes many inorganic and organic substances. But very few reports are available on the oxidation of amino acids using thallium(III) as oxidant [1]. This prompted us to throw some light to investigate the oxidation of amino acids by thallium(III). In continuation of our studies on the oxidation of tyrosine [2], we have taken up a systematic investigation of the oxidation of tyrosine (tyr) by thallium(III) in perchloric acid medium to explore the mechanistic aspects of the reaction and to deduce the appropriate rate law. Since the reaction between tyrosine and thallium(III) was found to be very slow at room temperature, the title reaction was studied at 50 °C.

EXPERIMENTAL

A 0.25 mol dm^{-3} solution of tyrosine was prepared by dissolving requisite amount of tyrosine (Himedia) in 0.75 mol dm^{-3} perchloric acid.

Thallium(III) perchlorate was prepared by taking thallium(I) solution on oxidation with excess of bromine water in presence of hydrochloric acid. The excess of bromine was boiled off, cooled to room temperature and the thallium was precipitated as thallium(III) hydroxide using dilute ammonium hydroxide solution. Then it was filtered through G_4 sintered glass funnel and washed free from halides (chlorides and bromides). Thallium(III) hydroxide thus prepared was dissolved in appropriate quantity of perchloric acid of known concentration. The strength of the solution was determined by iodometric method [3].

Thallium(I) solution was prepared by dissolving thallos sulphate (AR, BDH) in perchloric acid. Thallium(I) solution thus prepared was standardised bromatometrically [4].

Kinetic measurements were carried out in 1.0 mol dm^{-3} perchloric acid medium under the conditions, $[H^+] > [\text{tyrosine}] > [\text{thallium(III)}]$ at 50 °C. The progress of the reaction was followed by measuring the concentration of

thallium(III) titrimetrically by iodometric method using standard hypo solution. The titre value of hypo solution was taken as a measure of residual concentration of thallium(III) at time 't'. The pseudo-first order rate constants, k' were calculated from the plots of $\log[\text{Tl}^{\text{III}}]$ versus time and these plots were found to be linear upto 80% completion of the reaction. The rate constants of duplicate runs were found to be reproducible within $\pm 4\%$.

The temperature was kept constant using a Siskin Julabo-V constant temperature liquid circulatory bath.

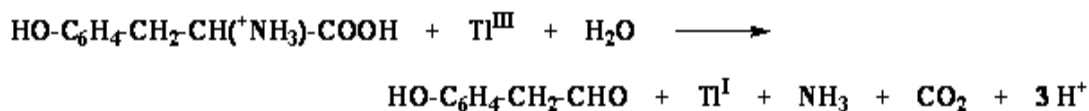
Test for Free Radicals

The test for free radicals was carried out by adding the monomer, acrylonitrile, to the reaction mixture at 50 °C. The negative response indicating the absence of intervention of free radicals during the course of the reaction.

RESULTS

Stoichiometry of the Reaction

The reaction mixture containing an excess of $[\text{Tl}^{\text{III}}]$ over $[\text{tyr}]$ in 1.0 mol dm⁻³ perchloric acid at 50 °C was allowed to react completely. The residual $[\text{Tl}^{\text{III}}]$ was determined by iodometric method and it was observed that one mole of thallium(III) reacts with one mole of tyrosine as shown below:



Product Analysis

The reaction mixture containing 2.0×10^{-2} mol dm⁻³ tyrosine, 1.0×10^{-3} mol dm⁻³ thallium(III) in 1.0 mol dm⁻³ perchloric acid was allowed to react completely at 50 °C and it was extracted with ether, after completion of the reaction. The product obtained from the ethereal layer was identified as 4-hydroxyphenyl acetaldehyde by IR spectral data (Figure 1). In the IR spectrum, the peaks at 3421.63 cm⁻¹, 3024.47 cm⁻¹, 2960.06 cm⁻¹, 2829.51 cm⁻¹, 1723.63 cm⁻¹ and 1635.91 cm⁻¹ are corresponding to O-H(str), C=C-H(str), C-H(str), O=C-H(str), C=O(str) and C=C(str) frequencies respectively.

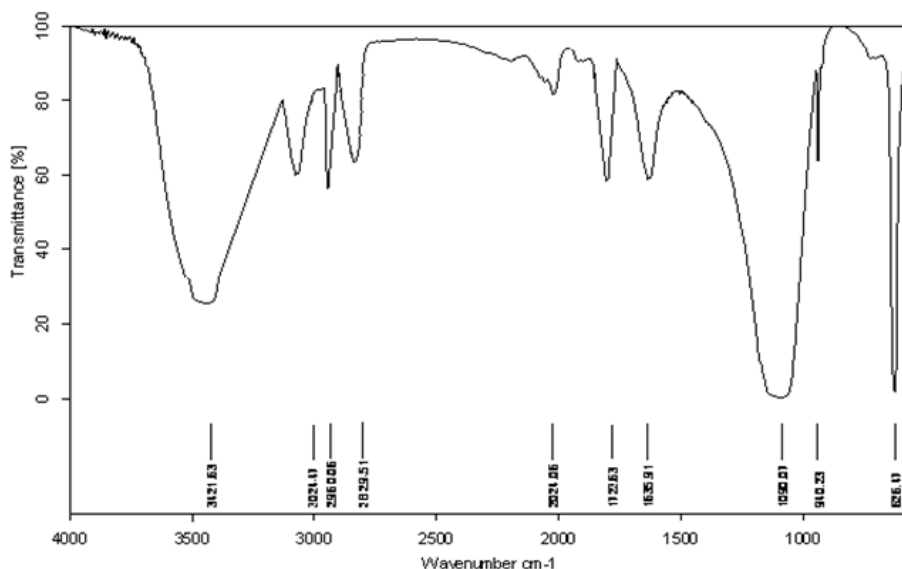


Figure 1: FT-IR Spectrum of 4-Hydroxyphenyl Acetaldehyde

Effect of [Thallium(III)]

In order to view the effect of [thallium(III)] on the rate of oxidation of tyrosine, the reaction was studied at various initial concentrations of thallium(III) by varying its concentration from $0.5 - 3.0 \times 10^{-3}$ mol dm⁻³, keeping $[\text{tyr}]$, $[\text{H}^+]$ and

temperature constant. Plots of $\log[\text{thallium(III)}]$ versus time were found to be linear upto 80% completion of the reaction indicating that the reaction is first order with respect to $[\text{thallium(III)}]$.

Effect of [Tyrosine]

To find out the dependence of $[\text{tyr}]$ on the reduction rate of thallium(III), kinetic runs were carried out at three different temperatures, 318, 323 and 328 K by ranging tyrosine concentration from $0.6 - 4.0 \times 10^{-2} \text{ mol dm}^{-3}$, keeping the concentrations of $[\text{H}^+]$, $[\text{Tl}^{\text{III}}]$ and temperature constant. It was found that the rate was increased with increase in the concentration of tyrosine (Table.1) and the order with respect to tyrosine was found to be 0.35. Further, the plots of $1/k'$ versus $1/[\text{tyr}]$, at three different temperatures, were found to be straight lines with positive intercepts on ordinate, indicating fractional order dependence on $[\text{tyr}]$ (Figure 2).

Table 1: Effect of $[\text{tyr}]$ on the Pseudo-First Order Rate Constant, k' at Three Different Temperatures

$[\text{Tl}^{\text{III}}] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}; [\text{H}^+] = 1.0 \text{ mol dm}^{-3}; \mu = 1.5 \text{ mol dm}^{-3}$			
$[\text{tyr}] \times 10^2$ (mol dm^{-3})	$k' \times 10^4$ (sec^{-1})		
	318 K	323 K	328 K
0.6	0.51	1.02	2.41
1.0	0.67	1.36	3.16
1.5	0.76	1.56	3.33
2.0	0.83	1.62	3.65
3.0	0.88	1.71	4.16
4.0	0.94	2.01	4.73

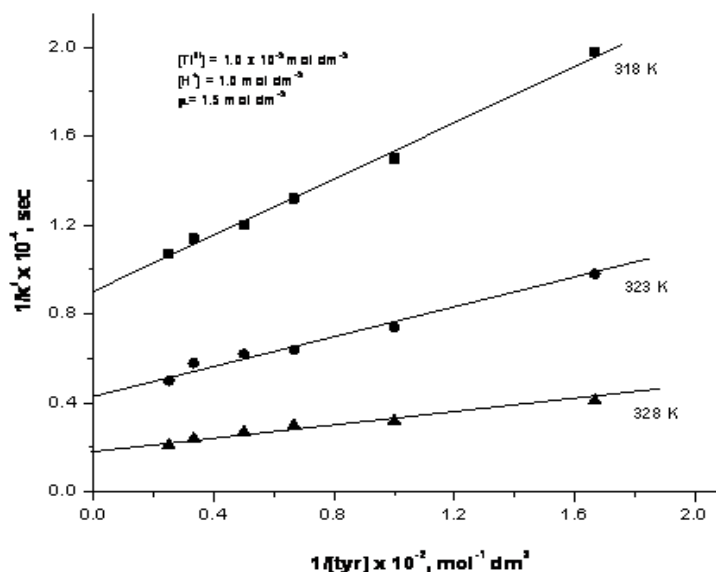


Figure 2: Plot of $1/k'$ versus $1/[\text{tyr}]$ at Three Different Temperatures

Effect of $[\text{H}^+]$

The effect of $[\text{H}^+]$ on the rate of reaction was studied by changing the perchloric acid concentration in the range $1.0 - 2.8 \text{ mol dm}^{-3}$, keeping the concentrations of reductant, oxidant and temperature constant. From the pseudo-first order rate constants, it was found that the rate was unchanged with increase in the concentration of H^+ (Table.2).

Table 2: Effect of $[\text{H}^+]$ on the Pseudo-First Order Rate Constant, k'

$[\text{tyr}] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}; [\text{Tl}^{\text{III}}] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}; \mu = 3.0 \text{ mol dm}^{-3}$						
$[\text{H}^+]$ (mol dm^{-3})	1.0	1.5	1.8	2.0	2.5	2.8
$k' \times 10^4$ (sec^{-1})	6.74	6.69	6.65	6.69	6.60	6.67

Effect of [Cl⁻], [NO₃⁻] and [SO₄²⁻]

The effect of [Cl⁻] on the reaction rate was studied in the range 0.2 – 10.0 x 10⁻⁴ mol dm⁻³, keeping [tyr], [Tl^{III}] and [H⁺] constant at 50 °C. It was observed that the reaction rate was decreased with increase in the [Cl⁻] (Table.3). This effect may be attributed to the lesser reactivity of chlorothallium complexes. But the change in the concentration of NO₃⁻ and SO₄²⁻ did not show any effect on the rate of the reaction.

Table 3: Effect of [Cl⁻] on the Pseudo-First Order Rate Constant, k'

[tyr] = 2.0 x 10 ⁻² mol dm ⁻³ ; [H ⁺] = 1.0 mol dm ⁻³ ; [Tl ^{III}] = 1.0 x 10 ⁻³ mol dm ⁻³ ; μ = 1.5 mol dm ⁻³ ; temp. = 50 ± 0.1 °C						
[Cl ⁻] x 10 ⁴ (mol dm ⁻³)	0.2	0.5	1.0	2.0	5.0	10.0
k' x 10 ⁴ (sec ⁻¹)	1.71	1.60	1.41	1.27	0.64	0.07

Effect of Ionic Strength

The effect of ionic strength was studied by changing the ionic strength from 1.5-3.0 mol dm⁻³ using sodium perchlorate and it was observed that the rate of the reaction was increased with increase in ionic strength (Table.4).

Table 4: Effect of Ionic Strength on the Pseudo-First Order Rate Constant, k'

[tyr] = 2.0 x 10 ⁻² mol dm ⁻³ ; [H ⁺] = 1.0 mol dm ⁻³ ; [Tl ^{III}] = 1.0 x 10 ⁻³ mol dm ⁻³ ; temp. = 50 ± 0.1 °C						
μ (mol dm ⁻³)	1.5	1.7	2.0	2.2	2.5	3.0
k' x 10 ⁴ (sec ⁻¹)	1.64	2.48	2.69	3.98	4.68	6.75

Effect of [Thallium(I)]

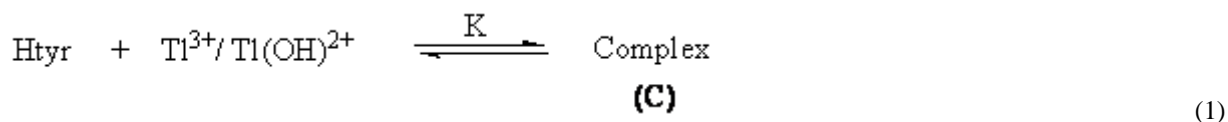
The effect of one of the products, thallium(I), was studied on the reaction rate using thallos sulphate solution by varying its concentration from 0.5 – 10.0 x 10⁻³ mol dm⁻³. It was observed that the reaction rate did not alter with [thallium(I)].

DISCUSSIONS

Tyrosine possesses three pK_a values corresponding to -COOH, ⁺NH₃ and phenolic -OH groups (2.20, 9.01 and 10.10) [5]. Under the present experimental conditions (1.0 mol dm⁻³ perchloric acid), tyrosine mainly exists as its protonated form, Htyr (HO-C₆H₄-CH₂-CH(⁺NH₃)-COOH).

In 1.0 mol dm⁻³ perchloric acid medium, the redox potential of the thallium(III) - thallium(I) couple is 1.25V [6] and the existing species of thallium(III) are Tl³⁺ and TlOH²⁺.

In view of the insignificant effect of hydrogen ion concentration, both Tl³⁺ and Tl(OH)²⁺ were presumed to be the reactive species of the oxidant and the following mechanism was proposed:



Where Htyr = HO-C₆H₄-CH₂-CH(⁺NH₃)-COOH

From the above equations, the rate law can be written as

$$\begin{aligned} \text{rate} &= - \frac{d[\text{Tl}^{\text{III}}]}{dt} = k[\text{C}] \\ &= kK[\text{Htyr}]_e[\text{Tl}^{\text{III}}]_e \end{aligned} \quad (3)$$

$$\begin{aligned} \text{Since } [\text{Tl}^{\text{III}}]_t &= [\text{Tl}^{\text{III}}]_e + [\text{C}] \\ \text{and } [\text{Htyr}]_e &= [\text{tyr}]_t \end{aligned} \quad (4)$$

$$\text{Hence } [\text{Tl}^{\text{III}}]_e = \frac{[\text{Tl}^{\text{III}}]_t}{1 + K[\text{tyr}]_t} \quad (5)$$

Substituting for $[\text{Tl}^{\text{III}}]_e$ from equation(5) in equation(3) leads to

$$\text{rate} = \frac{kK[\text{tyr}]_t[\text{Tl}^{\text{III}}]_t}{1 + K[\text{tyr}]_t} \quad (6)$$

This rate equation better explains the experimental kinetics like unit order on $[\text{Tl}^{\text{III}}]$ and fractional order on $[\text{tyr}]$.

$$\frac{\text{rate}}{[\text{Tl}^{\text{III}}]_t} = k' = \frac{kK[\text{tyr}]_t}{1 + K[\text{tyr}]_t} \quad (7)$$

The above equation can be transformed into

$$\frac{1}{k'} = \frac{1}{kK[\text{tyr}]_t} + \frac{1}{k} \quad (8)$$

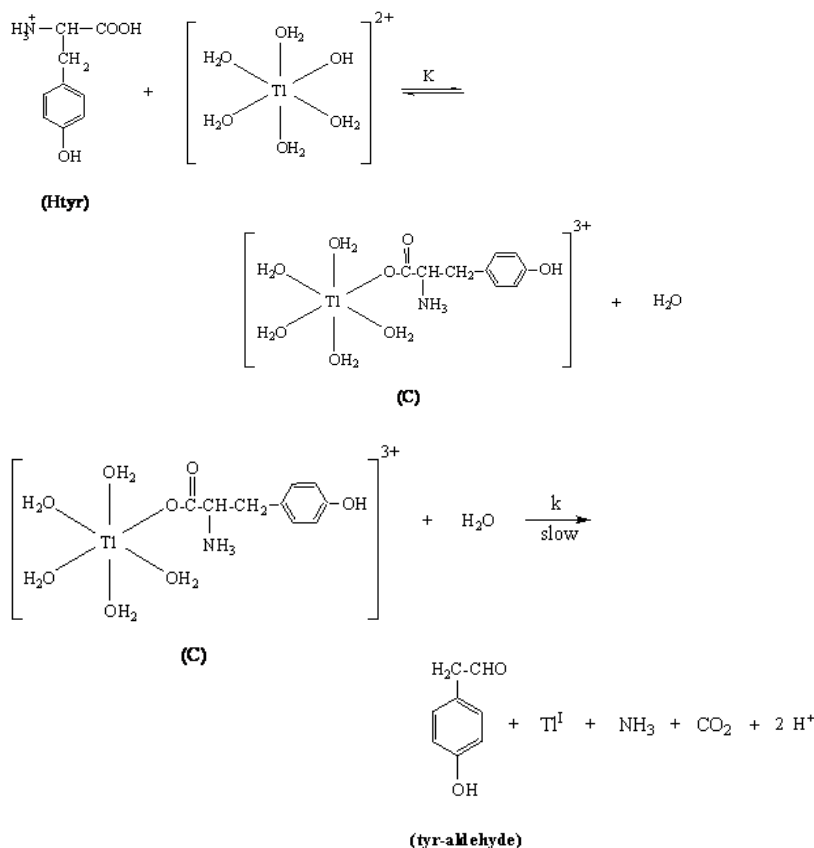
Equation(8) predicts the plot of $1/k'$ versus $1/[\text{tyr}]$ should be a straight line with a positive intercept on y-axis and the same was obtained experimentally thus substantiating the proposed mechanism.

Further, from the slopes and intercepts of the plots of $1/k'$ versus $1/[\text{tyr}]$ at three different temperatures, the equilibrium constant of complex formation, K and the decomposition constant of the thallium(III)-tyrosine complex, k were calculated (Table.5). The energy of activation, E_a and entropy of activation, ΔS^\ddagger for the rate determining step were computed using linear least squares method and are found to be $109.92 \pm 15.24 \text{ kJmol}^{-1}$ and $16.83 \pm 47.18 \text{ JK}^{-1} \text{ mol}^{-1}$ respectively.

Table 5: k and K Values at Three Different Temperatures

$[\text{Tl}^{\text{III}}] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}; [\text{H}^+] = 1.0 \text{ mol dm}^{-3}; \mu = 1.5 \text{ mol dm}^{-3}$		
Temp. (K)	$k \times 10^4$ (sec^{-1})	K ($\text{mol}^{-1} \text{ dm}^3$)
318	1.11	72.97
323	2.33	66.89
328	5.56	61.58

Intimate Mechanism



The following arguments are in support of the proposed intimate mechanism:

- The protonated species of tyrosine coordinates with $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ or $[\text{Ti}(\text{H}_2\text{O})_5\text{OH}]^{2+}$ through carboxylate oxygen by the replacement of a water molecule and forms a complex.
- This complex undergoes redox decomposition in the slow step to form the products, 4-hydroxyphenyl acetaldehyde and thallium(I), carbon dioxide and ammonia.

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