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Kinetics and Mechanism of Oxidation of L-threonine by Periodate in Alkaline Medium

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Abstract

Kinetics of oxidation of L-threonine(Thr) by periodate(Per) was studied in 0.5 mol dm^{-3} *sodium hydroxide medium spectrophotometrically at 280nm and at 303 K. The order with respect to periodate was unity and while the order in [L-threonine] was fractional. The rate of the reaction increases with increase in ionic strength and [OH*$^{-}$*]. Iodate, one of the products has negligible effect on the rate of the reaction. The product of the reaction was identified to be 2-hydroxy propanaldehyde by IR spectroscopy. A plausible mechanism involves the formation of 1:1 complex between substrate and oxidant leading to the rate law.*

$$rate = -\frac{d[Per]}{dt} = \frac{kK_2[Per]_t K_1[OH^-][Thr]_t}{1 + K_1[OH^-] + K_1K_2[Thr]_t[OH^-]}$$

The activation parameters of the rate determining step were computed using linear least squares method and the values of E_a *and* $\Delta S^{\#}$ *were found to be 91.34 ± 2.05 kJ mol*$^{-1}$ *and 2.23 ± 8.12 JK*$^{-1}$ *mol*$^{-1}$*.*

Keywords: L-threonine, periodate, oxidation, kinetics, 2-hydroxy propanaldehyde

Introduction

The kinetic investigations on the oxidation of amino acid become important because of their biological significance and selectivity towards the oxidants. A precise understanding of the mechanism of such biological redox reactions is important as it helps in the synthesis of specific reaction products. Very few reports are available on the oxidation of L-threonine using peroxydisulphate[1], manganese(VII)[3], N–bromo p-toulenesulphonamide[3], peroxodiphosphate[4], manganese(III)[5,6], bis-(hydrogen periodato)argentite[7], N–bromonicotinamide(NBN)[8], N–chloro p-toulenesulfonamide[9], Chloramine-T[10,11], N–bromophthalimide[12] the product of oxidation is aldehyde and in the oxidation of threonine by hexacyanoferrate(III)[13] the oxidation product is α – ketohydroxybutyric acid. Periodate is a stable two electron oxidant with redox potential of 0.70V [14] in alkaline medium and is a more suitable reagent for the study of oxidation reactions of both organic and inorganic substrates[15-19]. In continuation of our studies on the oxidation of L-threonine by different oxidants[20,21], with an attempt to evaluate its degradation mechanism and products, we have undertaken the kinetics of oxidation of L-threonine by periodate in alkaline medium.

Experimental Setup

Materials and Methods

A 0.1 mol dm^{-3} solution of L-threonine(Himedia) was prepared afresh by dissolving in required volume of double distilled water. A 0.1 mol dm^{-3} solution of periodate was prepared from sodium metaperiodate(AR, BDH) and its strength verified iodometrically. The solution was stored in an amber coloured bottle to prevent its photodecomposition.

Kinetic measurements were carried out at 303 K in 0.5 mol dm^{-3} sodium hydroxide medium under the conditions [OH$^-$] >> [threonine] > [periodate]. The progress of the reaction was followed by measuring the absorbance of periodate at 280 nm (Fig.1) using Milton roy 1201 UV-Visible Spectrophotometer with 1 cm quartz cells. The temperature was kept constant using a JULABO constant temperature liquid circulatory bath. The rate constants were found to be reproducible within ± 5%.

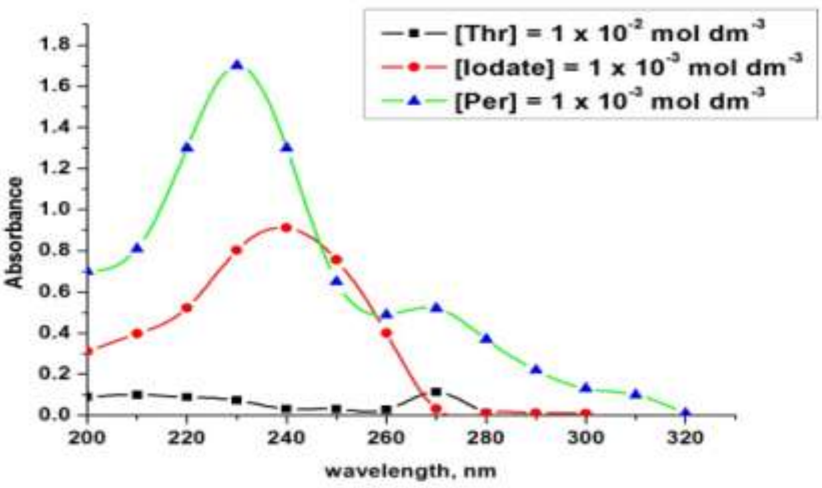


Fig.1: Spectra of Periodate, Iodate and Threonine in 0.5 mol dm^{-3} NaOH

Results and Discussion

Stoichiometry of the reaction

To determine the stoichiometry of the reaction a known amount of threonine was mixed with a known excess of periodate at 303 K in the presence of 0.5 mol dm^{-3} sodium hydroxide and after 24 h the residual [periodate] in each case was determined spectrophotometrically at 280 nm.

The stoichiometry of the reaction was found to correspond to the equation

$$\mathrm{(HO)HC\text{-}CH_3\text{-}\ CH(NH_2)COO^-} + \mathrm{IO_4^-} + \mathrm{H_2O} \longrightarrow$$
$$\mathrm{OHC\text{-}CH_3CH(OH)} + \mathrm{IO_3^-} + \mathrm{NH_3} + \mathrm{CO_2} + \mathrm{OH}$$

Product analysis

The product analysis was carried out by adopting the following procedure.

The reaction mixture containing 1 x 10^{-2} mol dm^{-3} L-threonine, 0.5 mol dm^{-3} sodium hydroxide and 1 x 10^{-3} mol dm^{-3} periodate was allowed to stand at 303 K. After completion of the reaction, the reaction mixture was extracted with ether. The product obtained from the ethereal layer was analysed by FT-IR (Fig. 2) and identified as 2–hydroxy propanaldehyde.

In the IR spectrum, the band at 3421.53 cm^{-1} corresponds to O-H stretching, the band at 3021.17 cm^{-1} corresponds to C-H stretching , the band at 2819. 23 cm^{-1} corresponds to O=C-H stretching and the band at 1648. 27 cm^{-1} corresponds to C=O stretching frequencies.

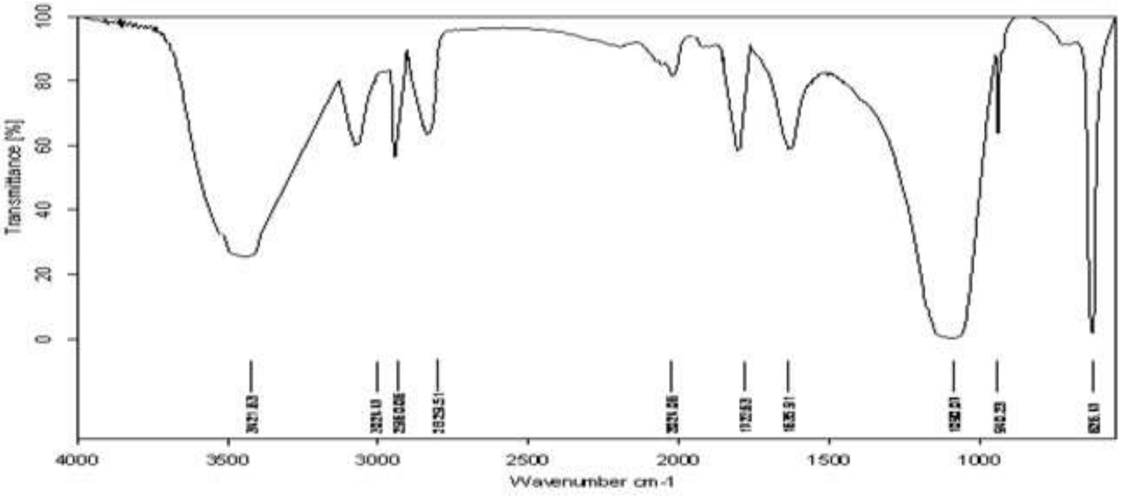


Fig.2: FT – IR spectrum of 2 – hydroxy propanaldehyde

Effect of ionic strength

The effect of ionic strength was studied by varying the ionic strength in the range 0.5- 1.2 mol dm^{-3} using sodium perchlorate. The pseudo-first order rate constants obtained from log(absorbance) versus time plots were found to increase with ionic strength indicating that the ionic strength has significant effect on the rate of the reaction (Table 1).

Table -1: Effect of ionic strength, ‘μ’ on the pseudo-first order rate constant, $k^{/}$
[threonine] = 1.0 x 10^{-2} mol dm^{-3}; [periodate] =1.0 x10^{-3} mol dm^{-3};
[OH^{-}] = 0.5 mol dm^{-3}; T = 303 K

μ, mol dm^{-3}	0.6	0.7	0.8	0.9	1.0	1.1
$k^{/}$ x 10^{4}, s^{-1}	5.15	6.04	7.18	9.24	12.7	16.83

Effect of Product

To study the effect of the product, iodate on the rate of reaction, kinetic runs were carried out keeping the concentrations of all other reactants constant and varying the concentration of iodate in the range of 0.1 – 2.5 mol dm^{-3}. [iodate] does not show any effect on the rate of the reaction (Table-2).

Table-2: Effect of [iodate] on the pseudo-first order rate constant, k/
[threonine] = 1.0 x 10^{-2} mol dm^{-3}; [periodate] =1.0 x10^{-3} mol dm^{-3};
[OH^-] = 0.5 mol dm^{-3}; T = 303 K

[Iodate] x 10^3, mol dm^{-3}	0.1	0.5	1.0	1.5	2.0	2.5
k/ x 10^4, s^{-1}	5.13	5.18	5.09	5.18	5.13	5.09

Effect of periodate

To study the effect of [periodate], kinetic runs were carried out at 303 K varying the concentration of periodate from 0.5 – 3.0 x 10^{-3} mol dm^{-3}, keeping the concentrations of all other ions constant. The plots of log (absorbance) versus time were found to be linear upto 80% completion of the reaction indicating the order with respect to periodate was unity (Table-3).

Table- 3: Effect of [periodate] on pseudo-first order rate constant, k/
[threonine] = 1.0 x 10^{-2} mol dm^{-3}; [OH^-] = 0.5 mol dm^{-3}; T = 303 K

[periodate] x10^3, mol dm^{-3}	0.5	1.0	1.5	2.0	2.5	3.0
k/ x 10^4, s^{-1}	5.13	5.33	5.13	5.13	4.93	4.96

Effect of [threonine]

To determine the dependence of rate on [threonine], kinetic runs were performed at three different temperatures 298, 303 and 308 K varying the initial concentration of threonine in the range 0.5 - 5.0 x 10^{-2} mol dm^{-3} keeping the concentrations of [OH^-] and[periodate] constant. It was found that the rate increased with the concentration of [threonine](Table 4) and the order with respect to threonine was found to be fractional. Further, the plots of 1/k/ versus 1/[Thr], at four different temperatures were found to be linear with positive intercepts on ordinate, indicating fractional order dependence on [Thr](Fig.3).

Table-4: Effect of [threonine] on pseudo-first order rate constant, k/ at 298, 303 and 308 K
[periodate] =1.0 x10^{-3} mol dm^{-3}; [OH^-] = 0.5 mol dm^{-3}; μ = 0.6 mol dm^{-3}

[Thr] x 10^2, mol dm^{-3}	**k/ x 10^4, s^{-1}**		
	298 K	**303 K**	**308 K**
0.5	2.05	3.90	4.92
1.0	2.25	5.33	6.77
1.5	3.28	6.77	9.85
2.0	3.90	8.00	11.45

2.5	4.72	9.44	13.32
3.0	5.74	10.88	14.43

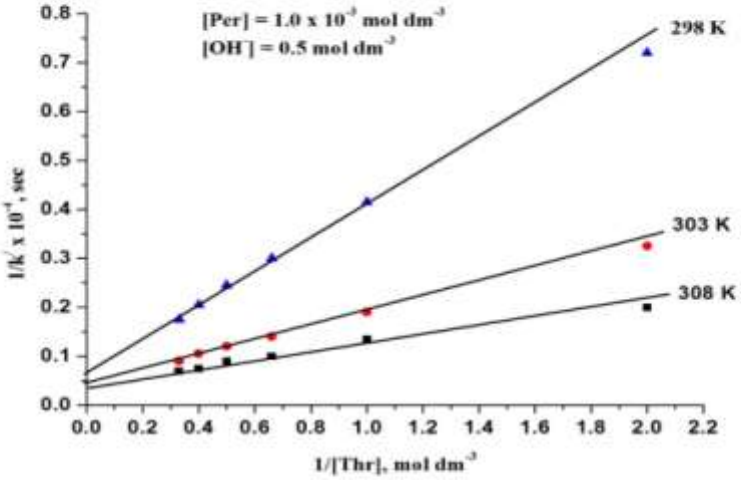


Fig. 3: Plots of $1/k^{/}$ versus 1/[Thr] at three different temperatures

Effect of alkali concentration

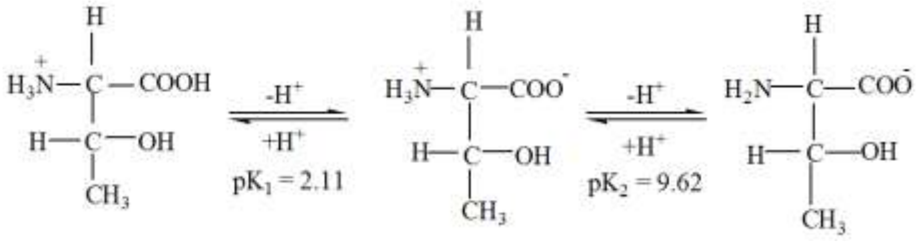
To study the effect of $[OH^-]$ on the rate of the reaction, kinetic runs are carried out by varying the $[OH^-]$ from 0.2- 0.7 mol dm^{-3} with sodium hydroxide and keeping the concentrations of oxidant and reductant constant. From the pseudo-first order constants, it was found that the rate increased with $[OH^-]$ (Table-5).

Table-5: Effect of $[OH^-]$ on pseudo-first order rate constant, $k^{/}$
[threonine] = 1.0×10^{-2} mol dm^{-3} ; [periodate] =1.0×10^{-3} mol dm^{-3} ;
$\mu = 0.8$ mol dm^{-3} ; T = 303 K

$[OH^-]$, mol dm^{-3}	0.2	0.3	0.4	0.5	0.6	0.7
$k^{/} \times 10^4$, s^{-1}	3.08	4.10	5.33	7.18	9.65	12.73

Discussion

Threonine is an essential amino acid that possesses two pK_a values[22], one corresponding to the carboxylic ($pK_1 = 2.11$) and the other for amino ($pK_{2} = 9.62$) group.



HThr **Thr_z** **Thr^-**

In the present reaction, in $[OH^-]$ 0.5 mol dm^{-3}, threonine exists in anionic form(Thr^-) (H_3C - CH(OH) -$CH(NH_2)$- COO^-) to the extent of 98.5%, while the remaining is present in the zwitterionic form(Thr_z) (H_3C-CH(OH)-CH($^+NH_3$)-COO^-).

Periodate is a stable two electron oxidant, capable of oxidising many organic substrates in acid, neutral and alkaline medium. The species of the periodate varies with pH[23]. At pH 1, 75% as H_5IO_6; at pH 6.5, 97% as IO_4^- and 3% as $H_4IO_6^-$; at pH 10.2, almost completely as $H_3IO_6^{2-}$ and at pH 13.6, almost entirely as $H_2IO_6^{3-}$. Hence under the present experimental conditions ($[OH^-]$= 0.5 mol dm^{-3}), periodate exists as $H_2IO_6^{3-}$ and it is presumed to be the active species of periodate.
On the basis of observed kinetics the following mechanism was proposed:

$$Thr_z + OH^- \overset{K}{\rightleftharpoons} Thr^- \qquad (1)$$

$$[H_3IO_6^{2-}] + OH^- \overset{K_1}{\rightleftharpoons} H_2IO_6^{3-} + H_2O \qquad (2)$$

$$H_2IO_6^{3-} + Thr^- \overset{K_2}{\rightleftharpoons} \text{complex(C)} \qquad (3)$$

$$C \xrightarrow[\text{slow}]{k} \text{products} \qquad (4)$$

where $Thr_z = H_3C\text{-}CH(OH)\text{-}CH(\overset{+}{N}H_3)CO\overset{-}{O}$ and

$Thr^- = H_3C\ \text{-}CH(OH)\text{-}CH(NH_2)\text{-}COO^-$

This mechanism leads to the rate equation,

$$\text{rate} = -\frac{d\,[\text{per}]}{dt} = k\,[C] \qquad (5)$$

But $[C] = K_2[H_2IO_6^{3-}]\,[Thr^-]$ and

$[Thr^-] = [Thr]_t$

$$\therefore \text{rate} = -\frac{d\,[\text{per}]}{dt} = kK_2\,[H_2IO_6^{3-}]\,[Thr]_t \qquad (6)$$

$$[Per]_t = [H_3IO_6^{2-}] + [H_2IO_6^{3-}] + [C] \qquad (7)$$

since $K_1 = \dfrac{[H_2IO_6^{3-}]}{[H_3IO_6^{2-}]\,[OH^-]}$ and

$$K_2 = \frac{[C]}{[H_2IO_6^{3-}]\,[Thr]}$$

$$[Per]_t = \frac{[H_2IO_6^{3-}] + K_1[OH^-]\,[H_2IO_6^{3-}] + K_1K_2\,[Thr]_t\,[H_2IO_6^{3-}]\,[OH^-]}{K_1[OH^-]} \qquad (8)$$

and $$[H_2IO_6^{3-}] = \frac{[Per]_t\,K_1[OH^-]}{1 + K_1[OH^-] + K_1K_2[Thr]_t\,[OH^-]} \qquad (9)$$

Substituting $[H_2IO_6^{3-}]$ from Equation (9) in Equation (6) gives

$$rate = \frac{-d[per]}{dt} = \frac{kK_2.[Per]_t.K_1[OH^-].\,[Thr]_t}{1 + K_1[OH^-] + K_1K_2\,[Thr]_t[OH^-]} \qquad (10)$$

But $$\frac{rate}{[Per]_t} = k^{/} = \frac{kK_1K_2[Thr]_t[OH^-]}{1 + K_1[OH^-] + K_1K_2[Thr]_t\,[OH^-]}$$

Taking reciprocals on both sides leads to

$$\frac{1}{k^{/}} = \frac{1}{kK_1K_2[Thr]_t[OH^-]} + \frac{K_1}{kK_1K_2[Thr]_t} + \frac{1}{k} \qquad (11)$$

The above equation predicts the plots of $1/k^{/}$ versus 1/[Thr] to be straight lines with positive intercepts on Y-axis and the similar plots were obtained experimentally (Fig. 3) when [threonine] variation studies were carried out at three different temperatures, 298, 303, 308K thus supporting the proposed mechanism. This suggests a Michaelis – Menten type of behaviour with the formation of 1:1 complex between threonine and periodate.

Further, spectrophotometric studies were also carried out and it was noticed that there was no spectral evidence for complex formation between threonine and periodate even in UV region.

For the plot of $1/k^{/}$ versus 1/[Thr] (Fig. 3),

$$slope = \frac{1}{kK_1K_2\,[OH^-]} + \frac{1}{kK_2}$$

and $$intercept = \frac{1}{k}$$

The values of k at three different temperatures were calculated from the intercepts of the plots of $1/k^{/}$ versus 1/[Thr](Table 6).

Table-6: Calculated values of k at three different temperatures
[threonine] = 1.0 x 10^{-2} mol dm^{-3} ; [periodate] =1.0 x10^{-3} mol dm^{-3} ;
[OH^-] = 0.5 mol dm^{-3} ; μ= 0.6 mol dm^{-3}

Temperature, K	k x 10^4, sec^{-1}
298	11.62
303	20.40
308	28.87

The energy of activation, Ea and the entropy of activation, $\Delta S^{\#}$ were calculated using linear least squares method and found to be 91.34 ± 2.05 kJ mol^{-1} and 2.23 ± 8.12 JK^{-1} mol^{-1} , respectively.

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