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Oxidation of L-Serine by alkaline periodate – Kinetics and Mechanism

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ABSTRACT

The reaction between L-serine and periodate was investigated kinetically in alkaline medium at 30 °C. The progress of the reaction was followed by measuring the decrease in the absorbance of periodate spectrophotometrically at a most suitable wavelength of 280 nm. The reaction was found to obey first order dependence on both [serine] and [periodate]. The oxidation rate was retarded by increase in alkali concentration. The initially added product, iodate, did not show any significant effect on the reaction rate. The rate was decreased with increase in ionic strength and the main product of the reaction was identified as 2-hydroxyethanal. Energy of activation, E_a and entropy of activation, $\Delta S^{\neq}$ were evaluated using linear least squares method and were found to be 83.06 ± 2.23 $kJmol^{-1}$ and 1.11 ± 7.36 $JKmol^{-1}$ respectively. A suitable mechanism consistent with the observed kinetics was suggested.

Keywords: Kinetics, L-serine, Periodate, Oxidation, Mechanism.

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INTRODUCTION

L-serine is an important non-essential amino acid with an –OH substituted side chain. It is required for the metabolism of fat, tissue growth and the immune system as it assists in the production of immunoglobulins and antibodies. It is a constituent of brain proteins, nerve coverings and is important in the formation of cell membranes.

Periodate is a stable two – electron oxidant in acidic as well as alkaline media. Although several investigations were performed using periodate as an oxidant but literature survey reveals that less attention was shown on the kinetic studies of oxidation of amino acids by periodate [1-4].

Pascual and Herraez studied the oxidation of serine by periodate in acid medium at pH = 4.0 and at 10 ^{o}C [2]. Since the reaction between serine and periodate proceeds at considerable rate at 30 ^{o}C in alkaline medium, the authors thought of investigating the reaction to compare the mechanism and products of oxidation with the earlier study [2] and thereby to put forward a rate equation consistent with the experimental data.

MATERIALS AND METHODS

A 0.1 mol dm^{-3} solution of L-serine (Himedia) was prepared by dissolving it in water. A 0.01 mol dm^{-3} solution of periodate was prepared by dissolving the requisite amount of sodium periodate in water and the solution was standardized by iodometric method [5]. All the chemicals used were of analytical reagent grade.

Kinetic measurements were carried out under the conditions, $[OH^-] > [ser] > [IO_4^-]$. The progress of the reaction was followed by measuring the absorbance of periodate at 280 nm where the other species of the reaction mixture have negligible absorbance (Fig.1). The plots of log(absorbance) versus time were found to be linear up to 80% completion of the reaction indicating that the reaction was first order with respect to [periodate]. The pseudo-first order rate constants, $k^{/}$ were calculated from the plots of log(absorbance) versus time and the rate constants were found to be reproducible within ±7%.

Milton Roy spectronic 1201 UV-Visible spectrophotometer was used to measure the absorbencies. The temperature is kept constant using a Siskin Julabo-V constant temperature liquid circulatory bath.

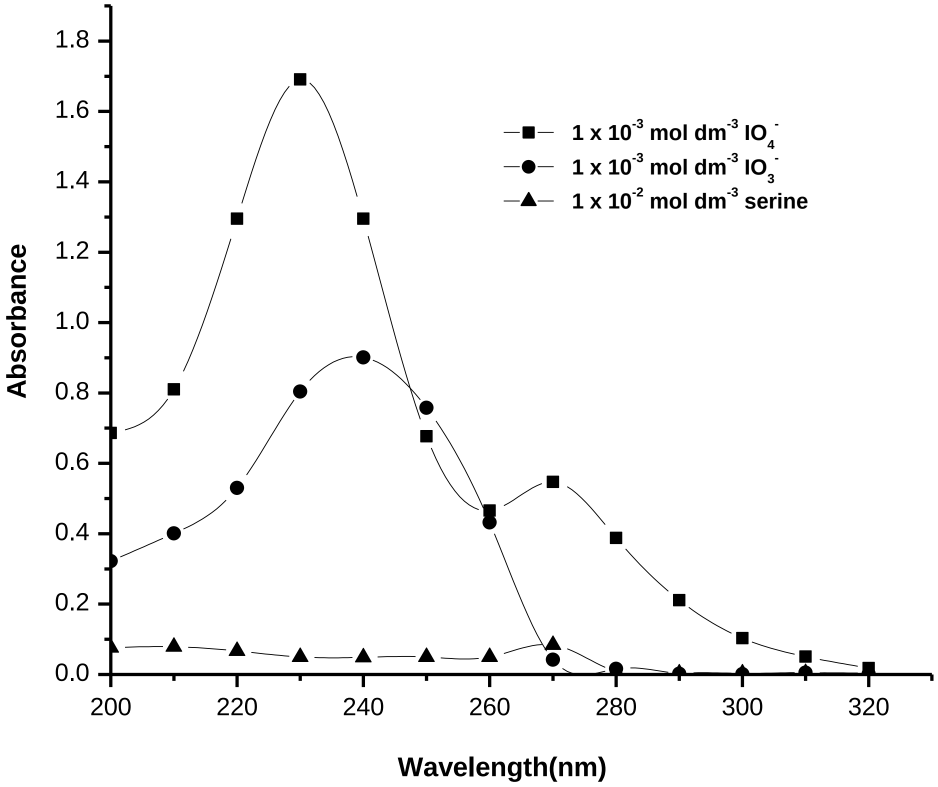


Fig 1: Spectra of periodate, iodate and serine in 0.5 mol dm^{-3} sodium hydroxide

EXPERIMENTAL

Test for free radicals

The test for free radicals was carried out by taking serine and sodium hydroxide in a thumberg tube and acrylonitrile and periodate solution in a bent tube. After evacuating the system, the solutions were mixed by tilting the tube. The reaction mixture was kept aside and even after 24 hours no precipitate was observed indicating the absence of free radical formation.

Product analysis

In order to identify the product formed in this reaction, the product analysis was carried out by adopting the following procedure:

A reaction mixture containing 1 x 10^{-2} mol dm^{-3} serine, 0.5 mol dm^{-3} sodium hydroxide and 1 x 10^{-3} mol dm^{-3} periodate was allowed to stand at 30 ^{o}C. After completion of the reaction, the reaction mixture was extracted with ether. The product obtained from the ethereal layer was identified as 2-hydroxyethanal from FTIR analysis (Fig.2). In the IR spectrum, the peaks at 3436.45 cm^{-1}, 2919.88 cm^{-1}, 2862.61 cm^{-1} and 1640.34 cm^{-1} are corresponding to O-H(str), C-H(str), O=C-H(str) and C=O(str) frequencies respectively.

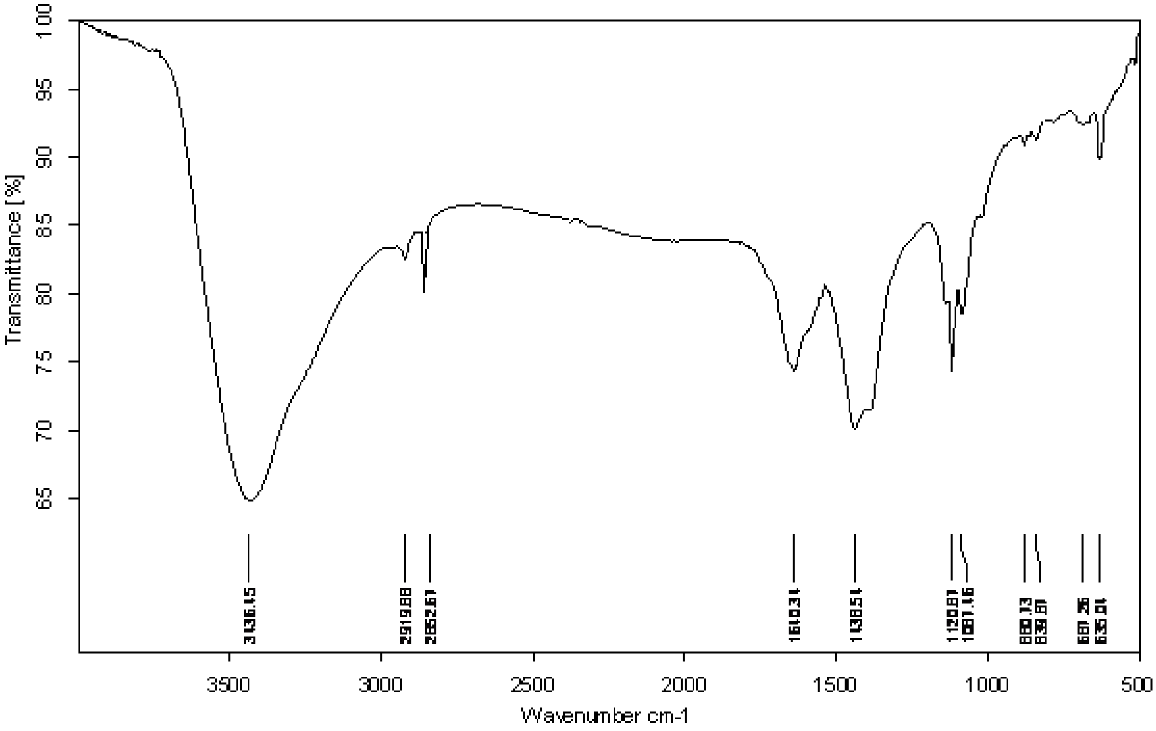


Fig 2: FT-IR spectrum of 2-hydroxyethanal

RESULTS

Stoichiometry of the reaction

The reaction mixture containing an excess of [IO_4^-] over [ser] at 0.5 mol dm^{-3} sodium hydroxide at 30 ^{o}C was allowed to complete the reaction and the residual [IO_4^-] was determined as a measure of its absorbance. It was observed that 1 mole of periodate was enough to oxidise 1 mole of serine as given by the equation:

$$HOCH_2\text{-}CH(NH_2)\text{-}COOH + IO_4^- \xrightarrow{OH^-} HOCH_2\text{-}CHO + IO_3^-$$

Effect of [periodate]

To determine the effect of [periodate] on the rate of the reaction, kinetic runs were carried out at 30 ^{0}C varying the concentration of periodate over the range 0.50 – 1.75 x 10^{-3} mol dm^{-3}. The plots of log(absorbance) versus time were found to be linear up to 80% completion of the reaction indicating that the reaction is first order with respect to [IO_4^-]. The pseudo-first order rate constants calculated from these plots were found to be decreased with increase in the concentration of periodate (Table.1).

Table1: Effect of [IO_4^-] on the pseudo-first order rate constant, $k^/$

[ser] = 1.0×10^{-2} mol dm^{-3} ; [OH^-] = 0.5 mol dm^{-3} ;
μ = 0.6 mol dm^{-3} ; temp. = 30 ± 0.1 °C

[IO_4^-] x 10^3 (mol dm^{-3})	0.50	0.75	1.00	1.25	1.50	1.75
$k^/$ x 10^4 (sec^{-1})	15.54	13.59	10.43	10.13	9.99	9.49

Effect of [serine]

To find out the dependence of rate on [serine], kinetic runs were performed by varying the initial concentration of serine from 0.75 - 2.00 x 10^{-2} mol dm^{-3} keeping the concentrations of all other species of the reaction mixture and the temperature constant. The pseudo-first order rate constants obtained were found to increase with increase in the concentration of serine (Table.2). Further, the plot of k' versus [serine] was found to be a straight line passing through origin indicating unit order dependence on [serine] (Fig.3).

Table.2: Effect of [ser] on the pseudo-first order rate constant, $k^/$

[OH^-] = 0.5 mol dm^{-3} ; [IO_4^-] = 1.0×10^{-3} mol dm^{-3} ; μ = 0.6 mol dm^{-3}

[ser] x 10^2 (mol dm^{-3})	$k^/$ x 10^4 (sec^{-1}) 298 K	303 K	308 K
0.75	4.22	7.68	11.61
1.00	5.52	9.40	16.63
1.25	7.20	12.20	19.38
1.50	8.83	14.39	23.03
1.75	9.50	17.91	26.87
2.00	10.36	20.03	30.70

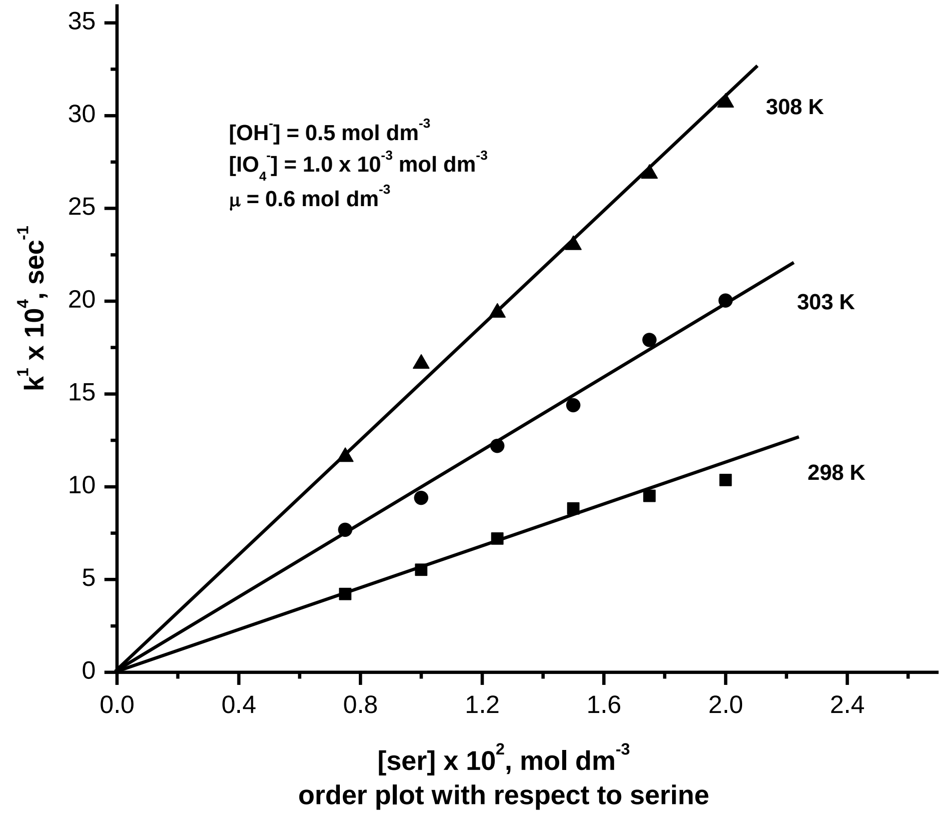


Fig 3: Plot of $k^/$ versus [ser] at three different temperatures

Effect of [alkali]

To study the effect of $[OH^-]$ on the rate of the reaction, kinetic runs were carried out at 30 ^{0}C keeping the concentrations of all other reactants constant and varying the $[OH^-]$ from 0.20 - 0.70 mol dm^{-3} using sodium hydroxide solution. The obtained pseudo-first order rate constants were found to decrease with increase in $[OH^-]$ (Table.3). The effect of $[OH^-]$ was also studied at 25 ^{0}C and 35 ^{0}C and the data was given (Table.3).

Table.3: Effect of $[OH^-]$ on the pseudo-first order rate constant, $k^/$

[ser] = 0.5 mol dm^{-3} ; $[IO_4^-]$ = 1.0 x 10^{-3} mol dm^{-3} ; μ = 0.8 mol dm^{-3} ;

$[OH^-]$ (mol dm^{-3})	$k^/$ x 10^4 (sec^{-1}) 298 K	303 K	308 K
0.2	12.47	17.03	31.18
0.3	7.68	12.79	24.63
0.4	5.70	9.60	17.27
0.5	4.36	7.42	14.97
0.6	3.84	6.33	11.51
0.7	3.39	5.56	10.17

Effect of ionic strength

Ionic strength effect was studied by varying the ionic strength in the range 0.60 - 1.10 mol dm^{-3} using sodium perchlorate solution and it was observed that the ionic strength has marginal effect on the reaction rate (Table.4).

Table.4: Effect of ionic strength on the pseudo-first order rate constant, $k^{/}$

[ser] = 1.0×10^{-2} mol dm^{-3} ; $[OH^-]$ = 0.5 mol dm^{-3} ;
$[IO_4^-]$ = 1.0×10^{-3} mol dm^{-3} ; temp. = 30 ± 0.1 ^oC

μ (mol dm^{-3})	0.60	0.70	0.80	0.90	1.00	1.10
$k^{/} \times 10^4$ (sec^{-1})	9.27	7.93	7.10	6.33	5.67	5.38

Effect of [iodate]

To know the effect of concentration of one of the products, iodate, on the rate of reaction**,** kinetic runs were carried out by varying the concentration of iodate in the range, 0.10 – 2.50 x 10^{-3} mol dm^{-3}. It was observed that [iodate] did not show any effect on the reaction rate (Table.5).

Table.5: Effect of $[IO_3^-]$ on the pseudo-first order rate constant, $k^{/}$

[ser] = 1.0×10^{-2} mol dm^{-3} ; $[OH^-]$ = 0.5 mol dm^{-3} ; $[IO_4^-]$ = 1.0×10^{-3} mol dm^{-3} ;
μ = 0.6 mol dm^{-3} ; temp. = 30 ± 0.1 ^oC

$[IO_3^-] \times 10^3$ (mol dm^{-3})	0.10	0.50	1.00	1.50	2.00	2.50
$k^{/} \times 10^4$ (sec^{-1})	9.39	9.95	9.98	9.45	9.52	9.80

Effect of temperature

The effect of temperature on the rate of the reaction was studied by carrying out the reaction at four different temperatures, 25, 30, 35 and 40 ^oC (Table.6). The plot of $\log k^{/}$ against 1/T was linear indicating that the reaction obeys Arrhenius temperature dependence. The energy of activation, E_a and the entropy of activation, $\Delta S^{\#}$ were calculated using linear least squares method and are found to be 83.06 ± 2.23 $kJmol^{-1}$ and 1.11 ± 7.36 $JK^{-1}mol^{-1}$ respectively.

Table.6: Effect of temperature on the pseudo-first order rate constant, $k^{/}$

[ser] = 1.0×10^{-2} mol dm^{-3} ; $[OH^-]$ = 0.5 mol dm^{-3} ;
$[IO_4^-]$ = 1.0×10^{-3} mol dm^{-3} ; μ = 0.6 mol dm^{-3}

Temp. (K)	298	303	313	318
$k^{/} \times 10^4$ (sec^{-1})	5.48	9.46	16.70	27.63

DISCUSSION

In alkaline medium, the redox potential of periodate was found to be 0.70V [6] and periodate exists in different forms at different pH values [7]. 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 in the present experimental conditions ($[OH^-] = 0.5$ mol dm^{-3}), periodate exists as $H_2IO_6^{3-}$ and is presumed to the active species of periodate.

Serine mainly exists as its anionic species, ser$^-$ ($HOH_2C - CH(NH_2) - COO^-$) under the reaction conditions.

On the basis of the observed kinetics the following mechanism was proposed:

$$ser^- + H_2IO_6^{3-} \overset{K}{\rightleftharpoons} X + OH^- \quad \text{---------(1)}$$

$$X \xrightarrow[\text{slow}]{k} \text{ser-aldehyde} + I^V + NH_3 + CO_2 \quad \text{---------(2)}$$

This mechanism leads to the rate equation,

$$\text{rate} = -\frac{d\,[per]}{dt} = k\,[X]$$

$$= \frac{k\,K\,[ser^-]\,[H_2IO_6^{3-}]_e}{[OH^-]} \quad \text{---------(3)}$$

$$\text{Since} \quad [ser^-] = [ser]_t$$

$$\text{and} \quad [H_2IO_6^{3-}]_e = [per]_t \quad \text{---------(4)}$$

Substituting for $[ser^-]_e$ and $[H_2IO_6^{3-}]_e$ from equation(4) in equation(3)

$$\text{rate} = \frac{k\,K\,[ser]_t\,[per]_t}{[OH^-]} \quad \text{---------(5)}$$

The above rate equation explains the first order dependence on $[IO_4^-]$, [serine] and inverse unit order dependence on $[OH^-]$.

Equation(5) may be transformed into

$$\frac{\text{rate}}{[\text{per}]_t} = k^{/} = \frac{k\,K\,[\text{ser}]_t}{[\text{OH}^-]} \qquad \text{---------(6)}$$

$$\frac{1}{k^{/}} = \frac{[\text{OH}^-]}{k\,K\,[\text{ser}]_t} \qquad \text{---------(7)}$$

Equation(7) predicts the plot of $1/k^{/}$ versus $[OH^-]$ should be a straight line passing through origin. Exactly similar plots were obtained experimentally when $[OH^-]$ variation studies were carried out at three different temperatures, 298, 303 and 308K (Fig.4) which supports the proposed mechanism.

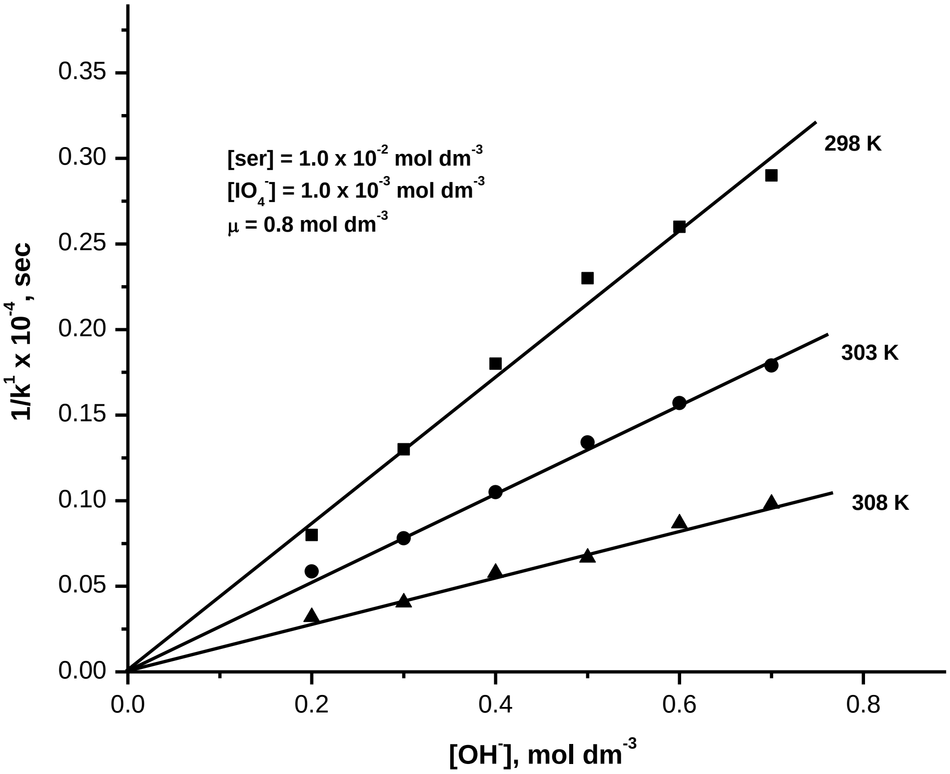
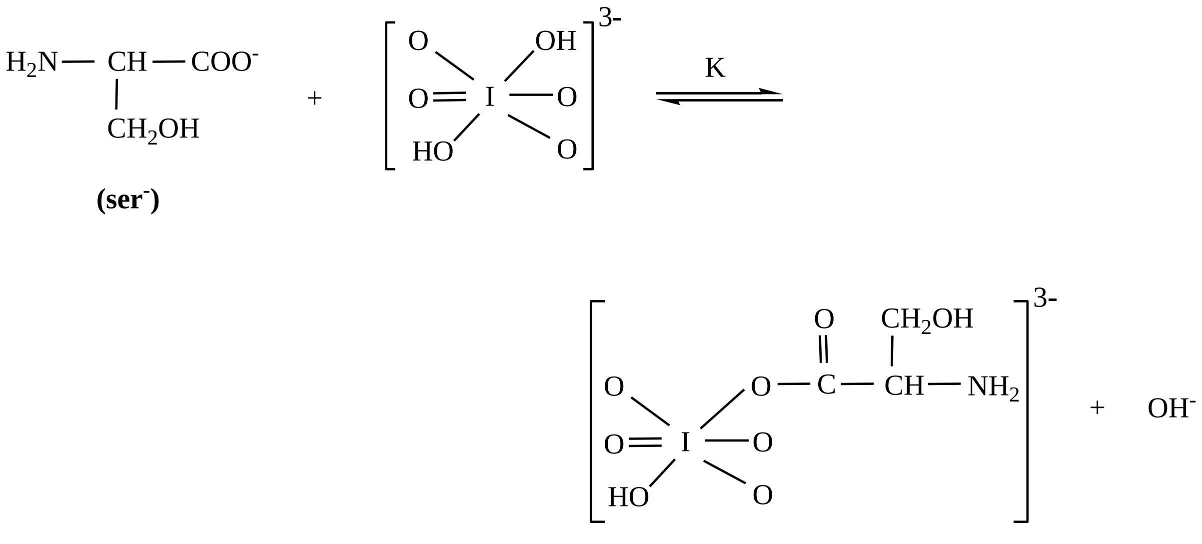


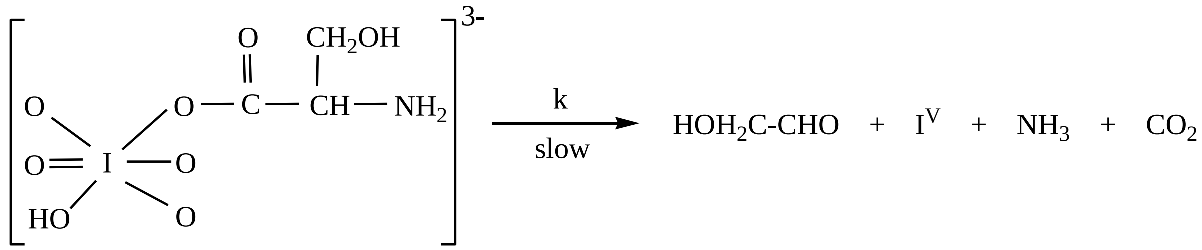
Fig 4: Plot of $1/k^{/}$ versus $[OH^-]$ at three different temperatures

INTIMATE MECHANISM



(ser$^-$)

(X)



The following steps are involved in the proposed intimate mechanism:

1. In the equilibrium step, an adduct is formed from the substrate and the oxidant through the displacement of hydroxide ion of $H_2IO_6^{3-}$.
2. Further, the adduct undergoes deamination followed by decarboxylation to form 2-hydroxyethanal and I^V.

CONCLUSIONS

In the oxidation of L-serine by periodate in alkaline medium, ser$^-$ and $H_2IO_6^{3-}$ are presumed to be the active species of substrate and oxidant respectively and the product was confirmed as 2-hydroxyethanal. According to Pascual and Herraez [2], the products of oxidation of serine by periodate in acid medium at 10 ^oC, were formaldehyde and formic acid. It may be concluded that the product of oxidation vary not only with the nature of the oxidant but also with the species which exists under different conditions of pH.

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