



# Osmium (VIII) Catalysed Oxidation of DL-methionine by Alkaline Sodium Periodate - A Kinetic Study

## KEYWORDS

Oxidation; methionine; Periodate; Osmium(VIII).

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**ABSTRACT** Osmium (VIII) catalysed oxidation of DL-methionine (Met) by sodium periodate (Per) was studied spectrophotometrically at 280 nm in aqueous alkaline medium and at 30°C. A micro amount of osmium(VIII) was sufficient to catalyse the reaction between DL-methionine and sodium periodate. The reaction is first order in both [periodate] and [osmium(VIII)]. The reaction rate decreased with increase in [methionine] and independent of ionic strength and [OH<sup>-</sup>]. Methionine sulfone was found to be the main product of oxidation and it was identified by IR and Mass spectra. Iodate, the other product was found to have negligible effect on reaction rate. A plausible mechanism was proposed and the rate law derived.

## 1. INTRODUCTION

Methionine is a naturally occurring sulfur containing amino acid, has three coordination sites at the N, O and S centers. Sulfur has been established as the most susceptible to attack by various metal ions, where the formation of an intermediate provides a low energy path for electron transfer. Methionine acts as methyl group donor in biological transmethylation and this process in the body is activated by adenosine triphosphate (ATP) and a liver enzyme such as phosphatase or dehydrogenase (Saxen and Soni (1982)). It is also an intermediate in the biosynthesis of cysteine, carnitine, taurine, lecithin, phosphatidylcholine and other phospholipids. Very few kinetic studies were reported [Gench and Higuchi (1967); Laloo and Mahendra (1985); Upadyaya (1983); Mittal, Sharma and Banerji (1986); Ananda, Rangappa and Mahadevappa (1986)] on the mechanism of oxidation of methionine in alkaline medium. Periodate(Per) is a two electron oxidant with a redox potential of 0.70V in alkaline medium and is a more suitable reagent for the study of oxidation reactions of both organic and inorganic substrates [Srinivas, Vani and Dikshitulu (1995); Singh, Chaurasia and Rahmani (2004) and Koli and Nandibewoor (2009)]. In continuation of our kinetic investigations on the oxidation of methionine in alkaline medium [Rajeswari and Vani (2003); Dharma Rao, Partha Sarathi, Annapurna, and Vani (2011); Dharma Rao, Baby Nirmala and Vani (2013)], we now report the spectrophotometric study on the osmium(VIII) catalysed oxidation of DL-methionine by periodate in 0.4 mol dm<sup>-3</sup> alkali.

## 2. EXPERIMENTAL

0.2 mol dm<sup>-3</sup> solution of DL-methionine was prepared afresh by dissolving the sample in a requisite volume of sodium hydroxide and its strength was checked iodometrically (Gench et.al (1967)). Sodium periodate (E.Merck) was prepared by dissolving the requisite amount of the solid in double distilled water. Osmium(VIII) solution was prepared in 0.25 mol dm<sup>-3</sup> sodium hydroxide from osmium tetroxide (Johnson Matthey, London) and its strength was determined by taking an aliquot volume of the solution into 0.5 mol dm<sup>-3</sup> hydrochloric acid, adding 10 ml of KI and titrating the liberated iodine with sodium thiosulfate using starch as indicator. Solutions of desired concentration are prepared from this stock by suitable dilution. Sodium hydroxide (E.Merck) solution was prepared and standardised by potassium hydrogen phthalate. All Chemicals used were of AR grade.

Reaction was initiated by mixing thermally equilibrated solu-

tion of DL-methionine to a mixture solution of periodate, osmium (VIII) and sodium hydroxide. Kinetic runs were carried out at a constant temperature of 30 ± 0.1°C by measuring the absorbance of periodate at 280 nm (Fig.1) using Milton Roy Spectronic-1201 UV-visible spectrophotometer. The order with respect to [Per] does not correspond to an integral order when the reaction is initiated with periodate but good pseudo first order plots were obtained when it is initiated with methionine. The plots of log(absorbance) versus time were found to be linear up to 85% completion of the reaction and the pseudo-first order rate constants, *k'* were determined from the slopes of these plots. The rate constants were found to be reproducible within ± 2%. Further, the reaction was also studied titrimetrically by determining the concentration of unreacted periodate using iodometric method. The rate constants thus obtained were found to be in good agreement with those obtained by spectrophotometric method. In view of this, spectrophotometric method was adopted for the kinetic study.

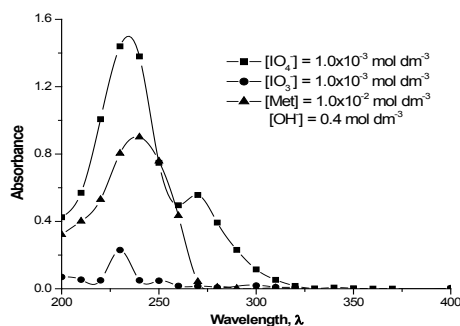


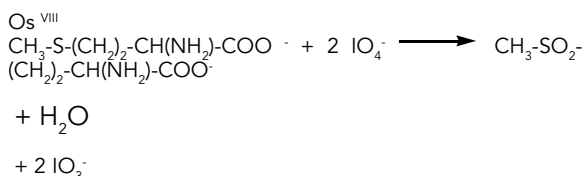
Fig.1.0: Spectra of periodate, iodate and methionine.

## 3. RESULTS AND DISCUSSION

### 3.1. Stoichiometry and Product Analysis

The reaction mixtures containing excess [periodate] over [methionine] in presence of osmium(VIII) in 0.4 mol dm<sup>-3</sup> alkali were allowed to react at 30 ± 0.1°C. After 24 hours, the residual [periodate] in each case was determined spectrophotometrically at 280 nm. The results obtained indicated that two moles of periodate was consumed by one mole of methionine and the product was identified as methionine sulfone. The stoichiometry of the reaction was found to cor-

respond to the equation



The reaction product was isolated by solvent extraction method using an organic solvent, diethyl ether and it was identified by its IR spectrum (Fig.2), which showed the bands( $\nu$ ) at 1195 and 1384.37  $\text{cm}^{-1}$  corresponding to O=S=O stretching while the band( $\nu$ ) at 1640  $\text{cm}^{-1}$  due to -COOH stretching and a broad band( $\nu$ ) at 3431  $\text{cm}^{-1}$  corresponds -NH stretching respectively. The positions of the absorption bands for sulfone were found to be in good agreement with the literature values of symmetric and asymmetric  $\text{SO}_2$  stretching frequencies.

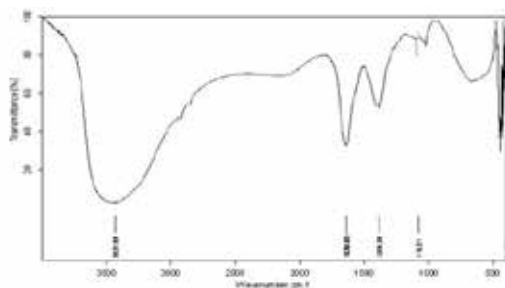


Fig. 2. IR Spectrum of methionine sulfone

Further, the reaction product was also confirmed by mass spectral analysis (Fig. 3). The mass spectrum showed a peak at  $m/z$  183 which was very close to the reported value of the oxidation product, methionine sulfone. Based on these observations the product of oxidation of methionine by alkaline periodate in presence of osmium(VIII) was confirmed to be methionine sulfone.

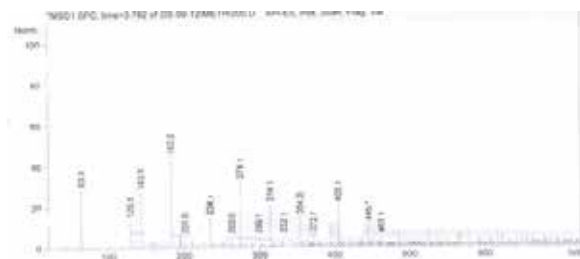


Fig. 3.0. Mass Spectrum of methionine sulfone

### 3.2. Effect of ionic strength

To study the effect of ionic strength on the rate of the reaction, kinetic runs were carried out keeping the concentrations of all other reactants constant and varying the ionic strength in the range 0.5-1.0  $\text{mol dm}^{-3}$  using sodium perchlorate. The ionic strength was found to have negligible effect on the reaction rate (Table 1).

**Table. 1 Effect of ionic strength on the pseudo-first order rate constants(  $k'$  ) at  $30 \pm 0.1^\circ\text{C}$ .**

Ionic strength ( $\text{mol dm}^{-3}$ )	0.5	0.6	0.7	0.8	0.9	1.0
$k' \times 10^3$ ( $\text{sec}^{-1}$ )	8.06	8.07	8.20	8.06	8.07	8.05

### 3.3. Effect of [iodate]

The [periodate], [methionine], [osmium(VIII)] and [OH<sup>-</sup>] were kept constant in order to examine the effect of [IO<sub>3</sub><sup>-</sup>], one of

the products, on the rate of reaction. It was observed that the constancy of rate constants obtained from the slopes of pseudo-first order plots showed that [IO<sub>3</sub><sup>-</sup>] did not have any effect on the reaction rate (Table 2).

**Table. 2 Effect of [iodate] on the pseudo-first order rate constants(  $k'$  ) at  $30 \pm 0.1^\circ\text{C}$ .**

[Iodate] ( $\text{mol dm}^{-3}$ )	0.5	0.6	0.7	0.8	0.9	1.0
$k' \times 10^3$ ( $\text{sec}^{-1}$ )	8.14	8.10	8.06	8.07	8.22	8.06

### 3.4. Effect of [periodate]

To determine the order with respect to [periodate], kinetic runs were carried out in 0.4  $\text{mol dm}^{-3}$  sodium hydroxide at  $30^\circ\text{C}$  varying the concentration of periodate from 0.5 to 3.0  $\times 10^{-3}$   $\text{mol dm}^{-3}$ , keeping the concentrations of all other species constant. Plots of log(absorbance) versus time were good straight lines, indicating that the order with respect to periodate is unity. Further, the pseudo-first order rate constants,  $k'$  obtained at different initial concentrations of periodate were found to remain constant (Table 3).

### 3.5. Effect of [methionine]

Effect of [methionine] on the reaction rate was investigated by varying the concentration of methionine in the range of 1.0-6.0  $\times 10^{-2}$   $\text{mol dm}^{-3}$  at  $30^\circ\text{C}$  keeping the concentrations of all other reactants constant. The pseudo-first order rate constants,  $k'$  were found to be decreased with increase in [methionine] (Table 3).

### 3.6. Effect of [alkali]:

To study the effect of the [OH<sup>-</sup>] on the rate of the reaction, kinetic runs were carried out at  $30^\circ\text{C}$  by varying the [alkali], keeping the concentrations of all other reactants constant. The  $k'$  values were found to be unaltered with increase in [OH<sup>-</sup>] (Table 3) indicating that [OH<sup>-</sup>] has negligible effect on reaction rate.

### 3.7. Effect of [osmium(VIII)]

To know the order with respect to [osmium(VIII)] on the reaction rate, kinetic runs were carried out at  $30^\circ\text{C}$  varying [osmium(VIII)] in the range of 2.0-7.0  $\times 10^{-6}$   $\text{mol dm}^{-3}$  by keeping the concentrations of all other reactants constant. The plot of  $k'$  versus [osmium(VIII)] (Fig.4) was found to be a straight line passing through the origin indicating unit order dependence on [catalyst] (Table 3).

**Table. 3 Effect of [IO<sub>4</sub><sup>-</sup>], [Met], [Os<sup>VIII</sup>] and [OH<sup>-</sup>] on the pseudo-first order rate constants(  $k'$  ) at  $30 \pm 0.1^\circ\text{C}$ .**

[IO <sub>4</sub> <sup>-</sup> ] $\times 10^3$ ( $\text{mol dm}^{-3}$ )	[Met] $\times 10^2$ ( $\text{mol dm}^{-3}$ )	[Os <sup>VIII</sup> ] $\times 10^6$ ( $\text{mol dm}^{-3}$ )	[OH <sup>-</sup> ] ( $\text{mol dm}^{-3}$ )	$k' \times 10^3$ ( $\text{sec}^{-1}$ )
0.50	1.00	4.0	0.40	8.06
1.00	1.00	4.0	0.40	8.44
1.50	1.00	4.0	0.40	8.06
2.00	1.00	4.0	0.40	8.12
2.50	1.00	4.0	0.40	8.24
3.00	1.00	4.0	0.40	8.06
1.00	1.00	4.0	0.40	8.06
1.00	2.00	4.0	0.40	6.91
1.00	3.00	4.0	0.40	6.04
1.00	4.00	4.0	0.40	5.37
1.00	5.00	4.0	0.40	4.60
1.00	6.00	4.0	0.40	3.83
1.00	1.00	2.0	0.40	4.60
1.00	1.00	3.0	0.40	6.40
1.00	1.00	4.0	0.40	8.04
1.00	1.00	5.0	0.40	10.52
1.00	1.00	6.0	0.40	12.28
1.00	1.00	7.0	0.40	14.50

1.00	1.00	4.0	0.10	8.07
1.00	1.00	4.0	0.20	8.06
1.00	1.00	4.0	0.30	8.12
1.00	1.00	4.0	0.40	8.06
1.00	1.00	4.0	0.50	8.07
1.00	1.00	4.0	0.60	8.06

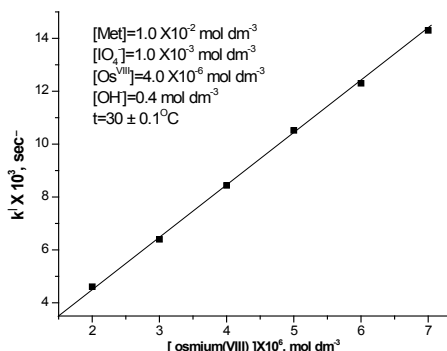


Fig.4.0: Plot of k versus [osmium(VIII)]  
(Order with respect to [osmium(VIII)])

### 3.8. Test for free radicals

Test for free radicals was carried out by taking methionine, sodium hydroxide and osmium(VIII) in a thumbert tube and acrylonitrile and periodate in the 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 radicals.

### 3.9. Effect of temperature

To study the effect of temperature on the reaction rate, kinetic runs were carried out at four different temperatures (25, 30, 35 and 40 °C). The plot of log k versus 1/T was found to be linear, indicating that the reaction obeys Arrhenius temperature dependence (Fig.5). The energy of activation, E<sub>a</sub> and entropy of activation, ΔS<sup>‡</sup> were computed using linear least squares method and were found to be 74.48 ± 2.13 kJ/mol and -293.42 ± 7.24 JK<sup>-1</sup>mol<sup>-1</sup> respectively.

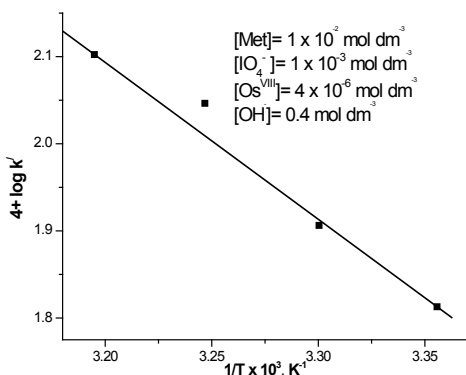
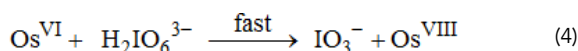
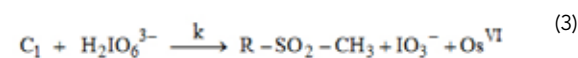
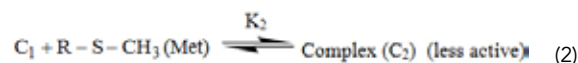


Fig.5.0: Plot of log k versus 1/T  
(Arrhenius temperature dependence)

### 3.10. Discussion

Methionine is a non polar amino acid and acts as a reductant. Under the present experimental conditions ([OH<sup>-</sup>] = 0.4 mol dm<sup>-3</sup>) methionine exists in the form of anionic species, H<sub>3</sub>CSCH<sub>2</sub>CH<sub>2</sub>CH(NH<sub>2</sub>)COO<sup>-</sup>(Met) which is presumed to be the active form of the substrate. The species of periodate varies with pH. In this present kinetic study, pH=13.40 periodate exists as H<sub>2</sub>IO<sub>6</sub><sup>3-</sup>. Osmium(VIII) is known to form different complexes with hydroxide ion and species such as OsO<sub>4</sub>, [OsO<sub>4</sub>(OH)(H<sub>2</sub>O)], [OsO<sub>4</sub>(OH)<sub>2</sub>]<sup>2-</sup> and [OsO<sub>5</sub>(OH)]<sup>3-</sup> coexist in fast equilibrium with each other in basic medium. Since the rate of the reaction is independent of [OH<sup>-</sup>], all of them are considered to be reactive.

Basing on these observations the following mechanism was proposed.



where R = -CH<sub>2</sub>CH<sub>2</sub>CH(NH<sub>2</sub>)COO<sup>-</sup>

This mechanism leads to the rate equation,

$$\text{rate} = \frac{-d[\text{periodate}]}{dt} = k[C_1][\text{H}_2\text{IO}_6^{3-}]$$

$$= kK_1[\text{Met}]_e[\text{Os}^{\text{VIII}}]_e[\text{H}_2\text{IO}_6^{3-}]$$

Where [Met]<sub>e</sub> = [Met]<sub>t</sub> and since

$$[\text{Os}^{\text{VIII}}]_t = [\text{Os}^{\text{VIII}}]_e + [C_1]_e + [C_2]_e$$

$$= [\text{Os}^{\text{VIII}}]_e + K_1[\text{Met}][\text{Os}^{\text{VIII}}]_e + K_1K_2[\text{Met}]^2[\text{Os}^{\text{VIII}}]_e$$

$$= [\text{Os}^{\text{VIII}}]_e \{ 1 + K_1[\text{Met}] + K_1K_2[\text{Met}]^2 \}$$

$$\therefore [\text{Os}^{\text{VIII}}]_e = \frac{[\text{Os}^{\text{VIII}}]_t}{1 + K_1[\text{Met}]_t + K_1K_2[\text{Met}]_t^2}$$

$$\therefore \text{Rate} = \frac{kK_1K_2[\text{Met}]_t[\text{Os}^{\text{VIII}}]_t[\text{H}_2\text{IO}_6^{3-}]}{1 + K_1[\text{Met}]_t + K_1K_2[\text{Met}]_t^2}$$

But [H<sub>2</sub>IO<sub>6</sub><sup>3-</sup>] = [Per]<sub>t</sub>

Therefore the final rate equation can be represented as

$$\text{Rate} = \frac{kK_1K_2[\text{Met}]_t[\text{Os}^{\text{VIII}}]_t[\text{Per}]_t}{1 + K_1[\text{Met}]_t + K_1K_2[\text{Met}]_t^2}$$

The above rate equation explains the first order dependence on [periodate] and [osmium(VIII)] and decrease in rate with increase in [methionine].

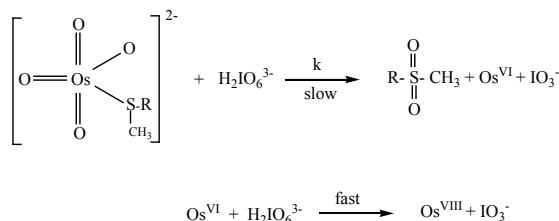
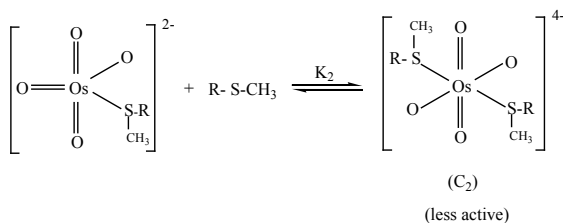
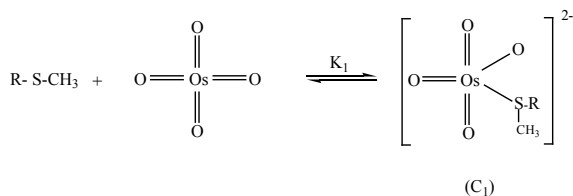
On the basis of the experimental observations made the following arguments may support the proposed intimate mechanism.

1. Sulfur atoms of thioethers have smaller polarisabilities and are weaker electron donors than sulfhydryl groups, but they have fewer lone-pair electrons and should therefore be better π electron acceptors. The only metal ions which are bonded at methionine sulfur are of class 'b' metal ions.
2. In the first step the formation of complex (C<sub>1</sub>) between OsO<sub>4</sub> and methionine, the Os-S bond is facilitated rather than carboxylate oxygen and amine nitrogen since osmium(VIII) acts as a soft acid due to its empty 'd' orbitals and sulfur is a soft base.
3. Further, osmium tetroxide is tetrahedral in nature and favours the formation of five coordinated species (C<sub>1</sub>).

through associative mechanism.

- The complex  $C_1$  reacts with one more molecule of methionine and forms a complex  $C_2$ , which is considered to be less active because of increase in crystal field stabilization energy of octahedral complex. Such possibility decrease the scope for an effective electron transfer from sulfur to osmium, and most likely an equilibrium in electron distribution may exist in the S-Os-S ( $C_2$ ) moiety, thus decreasing the rate of the reaction.
- In the rate determining step the five coordinated complex,  $C_1$  reacts with periodate and undergoes redox decomposition to form methionine sulfone and Os(VI).
- Finally, osmium(VI) reacts with one mole of periodate in a fast step thus regenerating the catalyst, osmium(VIII).

#### Intimate Mechanism



where  $R = -CH_2-CH_2-CH(NH_2)-COO^-$

#### 4. CONCLUSIONS

In conclusion the osmium(VIII) catalysed oxidation of methionine by periodate in alkaline medium showed first order dependence on [periodate], [osmium(VIII)] but decrease in rate with increase in [methionine]. The product of oxidation is methionine sulfone. A negative entropy of activation is suggesting the formation of a rigid transition state.

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