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# Periodate Influencing Diperiodatocuprate(III) Oxidation of Sulfur Containing Amino Acid in Aqueous Alkaline Medium

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**Abstract** The diperiodatocuprate(III) (DPC) oxidation of DL-methionine, a sulfur containing amino acid, was studied spectrophotometrically in alkaline solution. The reaction rate was first order in the concentration of DPC and fractional order in the concentration of DL-methionine. Increasing the $OH^-$ concentration decreased the rate of reaction, whereas adding $IO_4^-$ enhanced the rate. The reaction was preceded by a small initiation period of about 0.8 minutes. This initiation time decreased when the concentration of $IO_4^-$ or DPC increased. Adding the reaction products did not alter the rate of reaction. A mechanism including the intervention of a DL-methionine free radical is proposed and the corresponding rate law is derived. The reaction rate constants are evaluated as well as the activation parameters.

**Keywords** Kinetics · Oxidation · Mechanism · Diperiodatocuprate(III) · DL-methionine

## 1 Introduction

It is known that copper exists in three different oxidation states, +1, +2 and +3, along with its elemental form. Among these, only the +2 state is stable. However, in the recent past [1], some relatively stable copper(III) complexes have been prepared, viz., the periodate, guinidine and tellurate complexes. The $Cu^{3+}/Cu^{2+}$ reduction potential is $-1.8$ V in alkaline solution [2]. Hence, these compounds have been widely used as oxidants in the analysis of inorganic as well as organic compounds in alkaline media. The other reason for this use is that no other versatile oxidizing agents (in their stable form) are available in alkaline media for quantitative analyses. Moreover, it undergoes reduction by a single equivalent. The kinetics of oxidation by trivalent copper, in particular copper(III) periodate, has received considerable attention in recent years [3]. Its active forms in alkaline media are known to be the diperiodatocuprate(III) (DPC) and monoperiodatocuprate(III) (MPC) complexes [4].

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Nevertheless, their molecular formulae have not been described [3, 5]. Thus, the present study was undertaken to arrive at a plausible molecular formula for its active form.

The sulfur containing amino acid, DL-methionine, is an essential amino acid. It has been widely used in the treatment of liver diseases, allergy and asthma, rheumatoid arthritis, urinary tract infections, in the immune system for wound healing [6], etc. Daily supplement of methionine may prevent the onset of diseases related to smoking [7]. A recent study reports that DL-methionine is an essential molecule in the treatment for Alzheimer's disease because the patient normally suffers from sulfur deficiency. DL-methionine is utilized in the body on par with L-methionine, because D-methionine is deaminated to the corresponding $\alpha$-keto acid, which produces L-methionine by transamination. However, in the normal course of oxidation of $\alpha$-amino acids, deamination and decarboxylation take place. DL-methionine is one molecule in which no such possibilities exist. Instead, it undergoes oxidation at its 'S' site. Hence, the present investigation was undertaken to understand the oxidation of DL-methionine and to provide evidence for the molecular formula of the active form of the copper periodate complex.

## 2 Experimental

### 2.1 Materials and Methods

All chemicals used were of reagent grade and double distilled water was used throughout. Stock solutions of DL-methionine were prepared by dissolving the required quantity of sample "as received" (S.D. fine), i.e. without further purification. Aqueous solutions of KOH and $KNO_3$ were used to maintain the required $[OH^-]$ and ionic strength, respectively. A constant concentration of periodate was also maintained by using a $KIO_4$ solution in the reaction mixture, unless otherwise stated.

### *2.1.1 Preparation of DPC*

The diperiodatocuprate(III), DPC, was prepared [8, 9] by oxidizing Cu(II) in an alkaline medium as follows. Copper sulfate (3.54 g), potassium metaperiodate (6.8 g), potassium persulfate (2.2 g) and KOH (9 g) were added to 250 $cm^3$ of water. The mixture was heated to boiling on a hotplate, with constant stirring. The boiling mixture turned intensely red and the boiling was continued for another 20 minutes to allow the reaction to reach completion. The mixture was then cooled, filtered through a sintered glass crucible (G-4) and diluted to 250 $cm^3$ with distilled water. The resulting solution was found to be fairly stable for several months at room temperature. The DPC was characterized by its UV–Vis spectrum and compared with literature results [8, 9]. The concentration of the solution was ascertained by a reported method [8, 9], and also confirmed spectrophotometrically at 415 nm.

### 2.2 Kinetic Measurements

The reaction kinetics were studied under a pseudo-first-order condition where [DL-M] > [DPC] by at least 20 fold. The reaction was initiated by mixing DPC with DL-M that also contained the required quantities of KOH, $KNO_3$ and $KIO_4$ needed to maintain a constant alkali concentration, ionic strength and ligand concentration, respectively. The progress of the reaction was monitored spectrophotometrically at 30 °C by measuring the decrease in absorbance of DPC at its absorption maximum $\lambda_{max} = 415$ nm with a molar absorbency

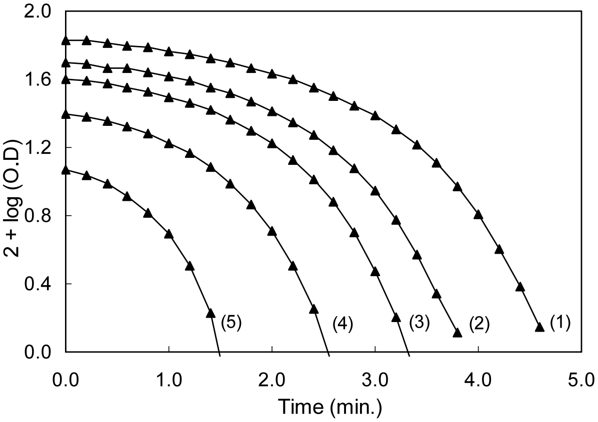


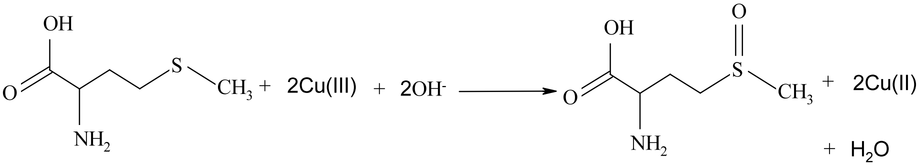
**Fig. 1** Effect of the DPC(III) concentration on the periodate induced oxidation of DL-methionine by diperiodatocuprate(III) in aqueous alkaline medium at 30 °C: [DPC] = $1.0 \times 10^{-4}$ (*1*), $7.7 \times 10^{-5}$ (*2*), $6.1 \times 10^{-5}$ (*3*), $3.8 \times 10^{-5}$ (*4*), $1.8 \times 10^{-5}$ (*5*) $\text{mol·dm}^{-3}$; [DL-methionine] $= 1 \times 10^{-3}\ \text{mol·dm}^{-3}$, $[\text{IO}_4^-] = 2.0 \times 10^{-4}\ \text{mol·dm}^{-3}$, $[\text{OH}^-] = 2.0 \times 10^{-2}\ \text{mol·dm}^{-3}$, and $I = 0.1\ \text{mol·dm}^{-3}$

'$\varepsilon$' $= 6500 \pm 50\ \text{dm}^3\text{·mol}^{-1}\text{·cm}^{-1}$. Earlier, it was confirmed that there were no other species present that absorb significantly at this wavelength, and Beer's law was verified for DPC at 415 nm.

The oxidation of DL-methionine by DPC was initially very slow (up to 0.8 minutes). Hence, pseudo-first-order rate constants were determined only after an appropriate lapse of time (Fig. 1). The '$k_{\text{obs}}$' values were calculated from the slopes of $\log_{10}$(conc.) versus time plots, which were found to be linear up to 80% completion of reaction and to be reproducible to within ±5%. The reaction orders for the various species were determined from the slopes of plots of $\log_{10} k_{\text{obs}}$ versus $\log_{10}$(conc.), except for DPC for which no variation of '$k_{\text{obs}}$' was observed for all its concentrations, as expected, due to the reaction condition.

## 2.3 Stoichiometry and Product Analysis

Different sets of concentrations of DL-methionine and DPC were kept at constant $[\text{IO}_4^-]$, $[\text{OH}^-]$ and ionic strength in an inert atmosphere at 30 °C for more than 6 hours. When [DPC] was in excess of [DL-M], the unreacted DPC was estimated by measuring its absorbance at 415 nm. The results indicated that one mole of DL-methionine was consumed by the two moles of DPC as shown in reaction 1.



(1)

The oxidation product of [DL-methionine] was found to be DL-methionine sulfoxide, which was characterized by the spot test [10] and also confirmed as described below. After completion of the reaction, sodium carbonate was added with vigorous stirring along with drop-wise addition of benzyl chloride solution to give a precipitate of N-benzoyl methionine, whose identity was confirmed by its melting point (183 °C) [11]. The product, DL-methionine sulfoxide, was also confirmed by its IR spectrum that showed a strong absorption at 1045 $\text{cm}^{-1}$, in addition to the normal characteristic bands of the ionized carboxylic group and of an amine salt occurring between 3130 and 2500 $\text{cm}^{-1}$.

## 3 Results and Discussion

### 3.1 Reaction Order

The reaction orders with respect to [DL-methionine], [$IO_4^-$] and [$OH^-$] were determined from $\log_{10} k_{\text{obs}}$ versus $\log_{10}$(conc.) plots. These orders were obtained by varying the concentrations of DL-methionine, $IO_4^-$ and $OH^-$, in turn, while keeping the other concentrations constant.

### 3.2 Effect of [DPC]

The effect of [DPC] on the reaction rate was studied by varying the [DPC] from $2.0 \times 10^{-5}$ to $2.0 \times 10^{-4}$ mol·dm$^{-3}$ at constant concentrations of DL-methionine, alkali, periodate and ionic strength as given in Table 1. It was observed that the slope of the plot of $\log_{10}$(conc.) versus time remained constant for the all of the different [DPC] values. It was also confirmed by the linearity of the first-order plot after a small initial period. Hence, the order in [DPC] was concluded to be unity.

### 3.3 Effect of [DL-Methionine]

The DL-methionine concentration was varied from $6.0 \times 10^{-4}$ to $5.0 \times 10^{-3}$ mol·dm$^{-3}$ while the concentrations all other reactants were held constant. The increase in [DL-methionine] increased the rate of reaction by an order of ~0.6 (Table 1).

### 3.4 Effect of [$OH^-$] and [$IO_4^-$]

The effect of [$OH^-$] on the reaction rate was studied in the concentration range $5.0 \times 10^{-3}$ to $5.0 \times 10^{-2}$ mol·dm$^{-3}$ while the concentrations all other reactants were held constant (Table 1). It was noticed that there was a decrease in '$k_{\text{obs}}$' with an increase in [$OH^-$], with a reaction order of about −0.35.

Similarly, the effect of [$IO_4^-$] was also studied from [$IO_4^-$] $= 2.0 \times 10^{-5}$ to $4.0 \times 10^{-4}$ mol·dm$^{-3}$, while the concentrations all other reactants were held constant. Adding [$IO_4^-$] accelerated the rate by an order of ≈0.3 (Table 1).

### 3.5 Effect of Added Products

The added products, $CuSO_4$ and DL-methionine sulfoxide, did not alter the rate of reaction in the studied concentration range of $1.0 \times 10^{-5}$ to $2.0 \times 10^{-4}$ mol·dm$^{-3}$.

### 3.6 Effect of Ionic Strength and Dielectric Constant of the Medium

The ionic strength of the reaction medium was varied by using different amounts of $KNO_3$ from $I = 0.02$ to 0.4 mol·dm$^{-3}$, while the concentrations all other reactants were held constant. The rate constants decreased with an increase in the ionic strength of the reaction medium. The plot of $\log_{10} k_{\text{obs}}$ versus $\sqrt{I}$ was linear. The slope was found to be −0.9 (Fig. 2).

The effect of polarity of the solvent medium on the rate of reaction was studied by decreasing the solvent polarity using $t$-butyl alcohol + water mixtures as the reaction medium. The dielectric constants of the medium with various ratios $(v/v)$ of $t$-butyl alcohol and water were calculated by a known method [12]. The $k_{\text{obs}}$ values were found to vary little with a decrease in the dielectric constant of the medium ($t$-butyl alcohol + water).

**Table 1** Effect of the variation of [DPC], [DL-methionine], [$OH^-$] and [$IO_4^-$] concentrations on the oxidation of DL-methionine by [DPC] at 30 °C and $I = 0.1$ mol·dm$^{-3}$

| [DPC] $\times 10^{-4}$ (mol·dm$^{-3}$) | [DL-M] $\times 10^{-3}$ (mol·dm$^{-3}$) | [$OH^-$] $\times 10^{-2}$ (mol·dm$^{-3}$) | [$IO_4^-$] $\times 10^{-4}$ (mol·dm$^{-3}$) | $k_{obs} \times 10^{-2}$ ($s^{-1}$) | |
|---|---|---|---|---|---|
| | | | | Exptl.[a] | Calc.[b] |
| 2.0 | 1.0 | 2.0 | 2.0 | 1.34 | 1.40 |
| 4.0 | 1.0 | 2.0 | 2.0 | 1.37 | 1.40 |
| 6.0 | 1.0 | 2.0 | 2.0 | 1.34 | 1 40 |
| 8.0 | 1.0 | 2.0 | 2.0 | 1.36 | 1.40 |
| 10 | 1.0 | 2.0 | 2.0 | 1.36 | 1.40 |
| 20 | 1.0 | 2.0 | 2.0 | 1.36 | 1.40 |
| 1.0 | 0.6 | 2.0 | 2.0 | 0.96 | 0.96 |
| 1.0 | 0.8 | 2.0 | 2.0 | 1.20 | 1.20 |
| 1.0 | 1.0 | 2.0 | 2.0 | 1.36 | 1.40 |
| 1.0 | 2.0 | 2.0 | 2.0 | 2.10 | 2.16 |
| 1.0 | 4.0 | 2.0 | 2.0 | 2.82 | 2.90 |
| 1.0 | 5.0 | 2.0 | 2.0 | 3.20 | 3.18 |
| 1.0 | 1.0 | 0.5 | 2.0 | 2.00 | 1.84 |
| 1.0 | 1.0 | 0.8 | 2.0 | 1.73 | 1.72 |
| 1.0 | 1.0 | 1.0 | 2.0 | 1.63 | 1.66 |
| 1.0 | 1.0 | 2.0 | 2.0 | 1.36 | 1.40 |
| 1.0 | 1.0 | 4.0 | 2.0 | 1.05 | 1.08 |
| 1.0 | 1.0 | 5.0 | 2.0 | 0.95 | 0.97 |
| 1.0 | 1.0 | 2.0 | 0.2 | 0.60 | 0.54 |
| 1.0 | 1.0 | 2.0 | 0.4 | 0.82 | 0.82 |
| 1.0 | 1.0 | 2.0 | 0.6 | 1.02 | 0.99 |
| 1.0 | 1.0 | 2.0 | 1.0 | 1.12 | 1.19 |
| 1.0 | 1.0 | 2.0 | 2.0 | 1.36 | 1.40 |
| 1.0 | 1.0 | 2.0 | 4.0 | 1.60 | 1.55 |

[a] Experimental

[b] Calculated

### 3.7 Polymerization Study

The intervention of free radicals generated during the oxidation of DL-methionine with a single equivalent of oxidant, DPC, was expected as it is a non-complimentary reaction. This possibility was tested by adding a free-radical scavenger, acrylonitrile, while the reaction was in progress. On diluting the reaction mixture with methyl alcohol after the reaction was complete, a copious precipitate resulted, indicating that the oxidation occurred via the intervention of a free radical. Earlier, it was ascertained that no precipitate formed with either the oxidant or reductant alone.

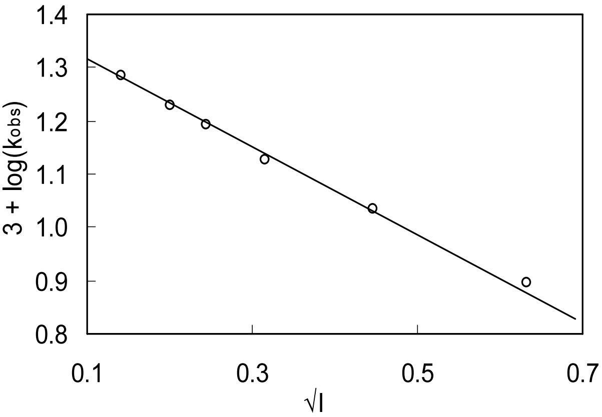


**Fig. 2** Effect of ionic strength on the oxidation of DL-methionine by DPC at 30 °C: [DPC] = $1.0 \times 10^{-4}$ mol·dm$^{-3}$, [DL-methionine] = $1.0 \times 10^{-3}$ mol·dm$^{-3}$, [$IO_4^-$] = $2.0 \times 10^{-4}$ mol·dm$^{-3}$, and [$OH^-$] = $2.0 \times 10^{-2}$ mol·dm$^{-3}$

**Table 2** Effect of temperature on the oxidation of DL-methionine by alkaline DPC: [DPC] = $1.0 \times 10^{-4}$ mol·dm$^{-3}$, [DL-methionine] = $1.0 \times 10^{-3}$ mol·dm$^{-3}$, [$IO_4^-$] = $2.0 \times 10^{-4}$ mol·dm$^{-3}$, [$OH^-$] = $2.0 \times 10^{-2}$ mol·dm$^{-3}$, and $I = 0.1$ mol·dm$^{-3}$

| (A) Effect of temperature | |
|---|---|
| Temp. (K) | $k_{obs} \times 10^{-2}$ (s$^{-1}$) |
| 303 | 1.34 |
| 308 | 2.48 |
| 313 | 3.92 |
| 318 | 6.59 |
| (B) Activation parameters | |
| $E_a$ (kJ·mol$^{-1}$) | $85 \pm 2$ |
| $\Delta H^{\#}$ (kJ·mol$^{-1}$) | $82 \pm 2$ |
| $\Delta S^{\#}$ (J·K$^{-1}$·mol$^{-1}$) | $-9.0 \pm 0.2$ |
| $\Delta G^{\#}$ (kJ·mol$^{-1}$) | $85 \pm 2$ |
| $\log_{10} A$ | $12.7 \pm 0.2$ |

### 3.8 Effect of Temperature

The effect of temperature on the reaction rate was studied at various temperatures (Table 2) at constant concentrations of oxidant and reductant, with the other reaction conditions being kept constant. The $k_{obs}$ values increased with increasing temperature. The activation parameters were calculated and are tabulated in Table 2.

A powerful oxidant, the copper(III) periodate complex in alkaline medium is relatively stable compared to other copper(III) complexes. Malaprade et al. [1] and Rozovski et al. [13, 14], and Jensovsky and Rabe [15] have prepared a copper(III) periodate complex in pure form. It was found to be crystalline, diamagnetic and have a dsp$^2$ configuration with a square-planar structure.

Water soluble DPC in alkaline medium shows an UV-Vis spectrum [15] with two strong bands at 413 and 265 nm, one fairly strong band at 334 nm, and a weak one at 560 nm. When solid $K_3H_3[Cu(IO_6)_2] \cdot 4H_2O$ is dissolved in water it undergoes ionization to give a complex ion [16]. In alkaline solution it may exist as $[Cu(HL)_2]^x$, $[CuL(HL)]^y$ and $[Cu(HL)]^z$, where, HL contains an indefinite number of protons and L denotes the unprotonated periodate molecule in the complex.

However, it is well known that periodate exists [17] as $H_5IO_6$, $H_4IO_6^-$, $H_3IO_6^{2-}$, $H_2IO_6^{3-}$ and dimeric forms, depending on the pH of the medium and total concentration of periodate. In the present study, the [$OH^-$] was varied from 0.005 to 0.05 mol·dm$^{-3}$. Thus, the periodate species should be in the form of $H_3IO_6^{2-}$ and $H_2IO_6^{3-}$. The other species are expected to occur in acidic medium. The existence of dimeric forms can be ruled out as they occur only at higher [$IO_4^-$]. Consequently, the active forms of $IO_4^-$ can be considered as being $H_3IO_6^{3-}$ and $H_2IO_6^{2-}$. Thus, as an alternative to the notation HL and L, respectively, and on incorporating the same into the [$Cu(HL)_2^x$], [$CuL(HL)^y$] and [$Cu(HL)^z$] formulae, leads the structures [$Cu(H_3IO_6)_2^-$], [$Cu(H_2IO_6)(H_3IO_6)^{2-}$] and [$Cu(H_3IO_6)(H_2O)^+$]. These structures retain the dsp$^2$ configuration with square-planar structures. The bidentate ligands $H_3IO_6^{2-}$ and $H_2IO_6^{3-}$ satisfy the coordination number of $Cu^{3+}$. Similar structures of periodate complexes have been deduced for the Ni(IV) and Ag(III) periodate complexes [18, 19].

In the present study, the observations that the reaction is first order in [DPC], fractional order in [DL-methionine], retarded by increasing [$OH^-$], and enhanced by increasing [periodate] can be accommodated in the following mechanism:

$$\mathrm{Cu(H_3IO_6)(H_2O)_2^+ + H_2IO_6^{3-} \underset{\leftarrow}{\overset{K_1}{\rightarrow}} Cu(H_3IO_6)(H_2IO_6)^{2-} + 2H_2O}$$

$$\mathrm{Cu(H_3IO_6)(H_2IO_6)^{2-} + H_2O \underset{\leftarrow}{\overset{K_2}{\rightarrow}} Cu(H_3IO_6)_2^- + OH^-}$$

$$\mathrm{Cu(H_3IO_6)_2^- + DL-M \underset{\leftarrow}{\overset{K_3}{\rightarrow}} complex(C)}$$

$$\mathrm{complex(C)} \underset{\text{slow}}{\overset{k}{\rightarrow}} \mathrm{DL-\overset{\bullet}{M} + Cu^{2+} + 2H_3IO_6^{2-}}$$

$$\mathrm{DL-\overset{\bullet}{M} + Cu(H_3IO_6)_2^-} \underset{\text{fast}}{\rightarrow} \mathrm{Cu^{2+} + DL-MSO + 2H_3IO_6^{2-}}$$

Scheme 1

In most of the studies of kinetics of periodate related metal complexes, the added periodate either had a retarding effect or no effect on the rate of reaction. In the present study, the accelerating effect of periodate on the reaction rate might result from the formation of DPC from MPC(monoperiodatocuprate(III)). This could occur during the small initial time lapse after the start of the reaction. Evidence for this is the relatively small initial reaction rate. This indicates that an optimum concentration of [$Cu(H_3IO_6)_2$] is necessary to transform DL-methionine to DL-methionine sulfoxide, which is formed by the combination of monoperiodatocuprate(III) and periodate (Steps 1 and 2).

Scheme 1 also incorporates the intervention of a free radical during the transformation of DL-methionine to DL-methionine sulfoxide. The retarding effect of [$OH^-$] on the rate of reaction was due to the formation of cuprate(III) periodate by the hydrolysis of the less protonated diperiodatocuprate(III) (Step 2). Scheme 1 leads to the following rate law:

$$-\frac{\mathrm{d[DPC]}}{\mathrm{d}t} = \text{rate} = \frac{kK_1K_2K_3[\mathrm{Cu(III)}]_\mathrm{T}[\mathrm{H_3IO_6^{2-}}][\mathrm{DL\text{-}M}]_\mathrm{T}}{[\mathrm{OH^-}] + K_1[\mathrm{OH^-}][\mathrm{H_3IO_6^{2-}}] + K_1K_2[\mathrm{H_3IO_6^{2-}}] + K_1K_2K_3[\mathrm{H_3IO_6^{2-}}][\mathrm{DL\text{-}M}]} \tag{2}$$

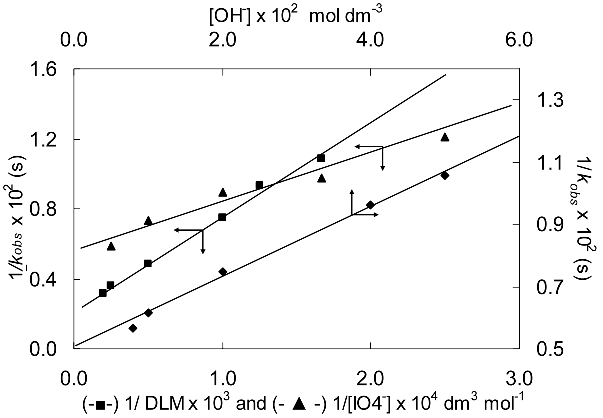


**Fig. 3** Verification of the rate law for oxidation of DL-methionine by alkaline DPC at 30 °C (conditions as in Table 1)

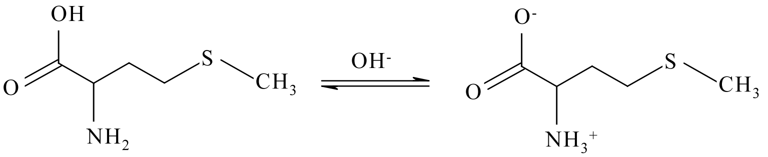
$$k_{\mathrm{obs}}=\frac{kK_1K_2K_3[\mathrm{H_3IO_6^{2-}}][\text{DL-M}]_{\mathrm{T}}}{[\mathrm{OH^-}]+K_1[\mathrm{OH^-}][\mathrm{H_3IO_6^{2-}}]+K_1K_2[\mathrm{H_3IO_6^{2-}}]+K_1K_2K_3[\mathrm{H_3IO_6^{2-}}][\text{DL-M}]} \tag{3}$$

Rate law (3) in the form of (4) is verified by plotting $1/k_{\mathrm{obs}}$ versus $[\mathrm{OH^-}]$, $1/[\text{DL-M}]$ and $1/[\mathrm{H_3IO_6^{2-}}]$, all of which should be linear and is found to be so as shown in Fig. 3.

$$\frac{1}{k_{\mathrm{obs}}}=\frac{[\mathrm{OH^-}]}{kK_1K_2K_3[\mathrm{H_3IO_6^{-2}}][\mathrm{DLM}]}+\frac{[\mathrm{OH^-}]}{kK_2K_3[\mathrm{DLM}]}+\frac{1}{kK_3[\text{DL-M}]}+\frac{1}{k}. \tag{4}$$

The slopes and intercepts of such plots lead to the constants $k=4.63\times10^{-2}\ \mathrm{s^{-1}}$, $K_1=3.28\times10^{3}\ \mathrm{dm^3{\cdot}mol^{-1}}$, $K_2=6.71\times10^{-2}\ \mathrm{mol{\cdot}dm^{-3}}$, and $K_3=7.70\times10^{2}\ \mathrm{dm^3{\cdot}mol^{-1}}$. These values were used in (3) to regenerate the $k_{\mathrm{obs}}$ values and the results were compared with experimental results. They are found to be reasonably consistent with each other (Table 1). This strengthens the evidence for the proposed mechanism.

The mechanism written in Scheme 1 does not account for the decrease in rate with increasing ionic strength, as it is generally expected that an amino acid in alkaline solution exists in its anionic form. The anion of DL-methionine and other anionic forms of DPC are involved in a pre-equilibrium step for which a positive effect of ionic strength is anticipated. However, such a contradicting observation may be explained by assuming that some of the amino acids in alkaline pH exists in a zwitterionic form [20–22] that can be described as



(5)

The positive part of this dipolar molecule may be oriented toward the negatively charged DPC, which would retard the rate of reaction when the ionic strength of the reaction media is increased.

The effect of polarity on the reaction medium is in the expected direction if the oppositely charged species that are involved in the mechanism form a single activated complex sphere, by losing a degree of freedom in the low dielectric constant medium. This is strongly supported [23] by a negative value of $\Delta S^{\#}$ and large value of $\log_{10} A$ (Table 2). A relatively large value of $k_{\mathrm{obs}}$ also strengthens the argument that the reaction occurs through the interaction of oppositely charged ions to form a single sphere at the slow step of the reaction.

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