

Oxidation of DL - Methionine by Imidazolium Chlorochromate and Benzimidazolium Chlorochromate in Aqueous Perchlorate Medium

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Received 29 June 2012 / Accepted 22 July 2012

Abstract: The oxidation of methionine by oxidants such as imidazolium chlorochromate (ICC) and benzimidazolium chlorochromate (BCC) in aqueous perchlorate medium has been studied spectrophotometrically over the range $3.00 \leq 10^3 [\text{methionine}] \leq 6.00$, $0.01 \leq [\text{H}^+] \leq 0.03 \text{ mol dm}^{-3}$ and $20 \text{ }^\circ\text{C} \leq T \leq 40 \text{ }^\circ\text{C}$. The rate of reaction was found to increase with the increase of total concentration of methionine and total concentration of H^+ . The reaction was found to exhibit first order dependence in $[\text{methionine}]$, $[\text{H}^+]$ and the oxidants $[\text{ICC}]$ and $[\text{BCC}]$. The ΔH^\ddagger (kJ/mol) and ΔS^\ddagger ($\text{JK}^{-1}\text{mol}^{-1}$) for the electron transfer reaction were found to be 12.5 and -154.1 in case of ICC and 17.53 and -136.9 in case of BCC respectively. The product of the reaction was found to be methionine sulphoxide. The negative values of ΔS^\ddagger support ordered transition state for both the electron transfer reactions due to ICC and BCC.

Keywords: Imidazolium chlorochromate, Benzimidazolium chlorochromate, Methionine, Electron transfer

Introduction

A survey of literature shows that kinetics and mechanism of oxidation of methionine (Figure 1) by various oxidants are well understood¹⁻⁵. ICC (Figure 2) and BCC (Figure 3) are mild oxidizing agents. The redox reactions of methionine with other oxidant like pyridinium⁶, substituted pyridinium⁷, nicotinium⁸, prolinium⁹ chlorochromate have been studied. However methionine is reported to behave differently in comparison to other amino acids towards many oxidants¹⁰⁻¹². Due to presence of electron rich sulphur centre which is easily oxidisable, strong oxidant such as Cr(VI) ^{13,14} oxidises methionine to methioninesulphoxide and subsequently to sulfone. The sulphur containing amino acid and peptide oxidation reactions are studied mostly for their biological importance^{15,16}. DL - methionine has O, N & S as three coordinating centers. Of these sulphur has been established as the most susceptible to attack by the oxidants. The compound has been used extensively for the study of redox reactions of many biomolecules, but the electron transfer reaction of oxidant such as ICC and BCC with methionine has not been studied. In order to understand the electron transfer reaction, the work has been undertaken.

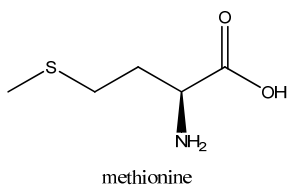


Figure 1

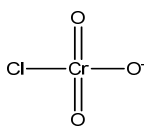


Figure 2

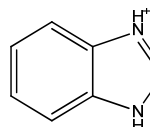
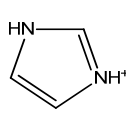


Figure 3

Experimental

The oxidants ICC and BCC were prepared and characterized according to reported method^{17,18}. All other chemicals used were of AnalaR grade. Doubly distilled water was used to prepare all the solutions. The acid strength of the medium was maintained by addition of HClO₄. Kinetic measurements were recorded on a SYTRONIC 119 PC scanning UV-Vis spectrophotometer. Reaction progress was monitored at 350 nm. (Figure 4(A) for ICC and 4(B) for BCC) Pseudo first order condition were maintained throughout the runs by using a large excess (>5 fold) of methionine. The constant (k_{obs}) were obtained from the slope of $-\ln(A_t - A_\infty)$ versus 't' plots. $-\ln(A_t - A_\infty) = k_{obs} t - C$.

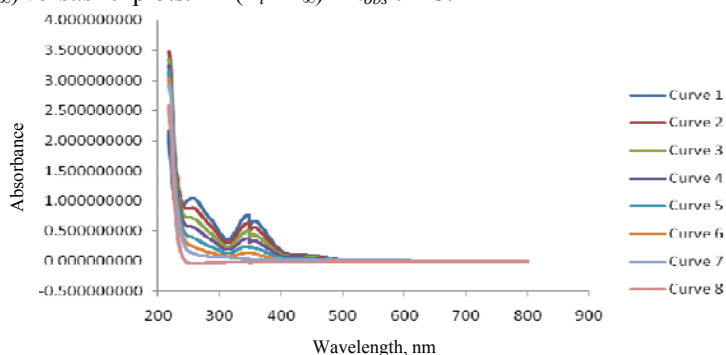


Figure 4(A). Repetitive spectral scan of $[ICC]_T = 4 \times 10^{-4} \text{ mol dm}^{-3}$ Curve 1, with Methionine $= 2 \times 10^{-3} \text{ mol dm}^{-3}$ Curve 8, $[H^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$, Temperature = 30 °C, At different time intervals $\Delta t = 5$ minutes (Curve 2-6), Curve 7 is after 24 h

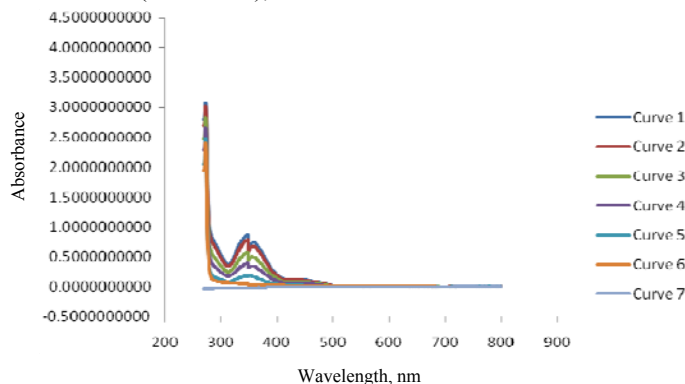


Figure 4(B). Repetitive spectral scan of $[BCC]_T = 4 \times 10^{-4} \text{ mol dm}^{-3}$, Curve 1, with $[Methionine]_T = 2 \times 10^{-3} \text{ mol dm}^{-3}$, Curve 7, $[H^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$, Temperature = 30 °C, At different time intervals $\Delta t = 5$ minutes (Curve 2-5), Curve 6 is after 24 h

Where A_t and A_∞ are the absorbances of the reaction mixture at time 't' and at the completion of the reaction. The reported rate data represented as an average of duplicate runs were reproducible within $\pm 3\%$. The correlation coefficients of the plots used to determine k_{obs} were found to be 0.99 in most of the cases.

Results and Discussion

The kinetic results obtained for the above reaction may be summarized as follows. With varying concentration of 10^3 [methionine] $_T$ in the range 3.00 to 6.00 mol dm $^{-3}$, the $10^4 k_{obs}/s^{-1}$ at (25 $^{\circ}$ C) increased from 5.60 to 8.96 in case of ICC and 6.95 to 11.52 in case of BCC when $[H^+] = 0.01$ mol dm $^{-3}$, $[ICC] = 4 \times 10^{-4}$ mol dm $^{-3}$ (Table 1(A) for ICC and 1(B) for BCC). The [methionine]/[ICC] or [BCC] was varied from 5.00 to 15.00. The k_{obs} versus [methionine] plot (Figure 5(A) in case of ICC and 5(B) for BCC) were linear at all reported $[H^+]$ indicating 1 st order dependence of the reaction on [methionine]. As the order of the reaction is one with respect to [methionine] and over all order of the reaction is two and the order with respect to [ICC] or [BCC] is one. The rate law is therefore given by equation (1).

$$\text{Rate} = k_{obs} \{ [ICC]_T \text{ or } [BCC]_T \} \quad (1)$$

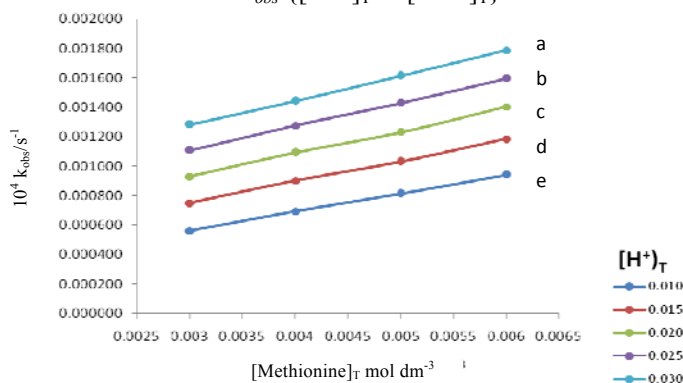


Figure 5(A). Plot of k_{obs} versus [methionine]; (Oxidant= ICC, T=25 $^{\circ}$ C where a: $[H^+]_T=0.010$ mol dm $^{-3}$, b: $[H^+]_T=0.015$ mol dm $^{-3}$, c: $[H^+]_T=0.020$ mol dm $^{-3}$, d: $[H^+]_T=0.025$ mol dm $^{-3}$, e: $[H^+]_T=0.030$ mol dm $^{-3}$)

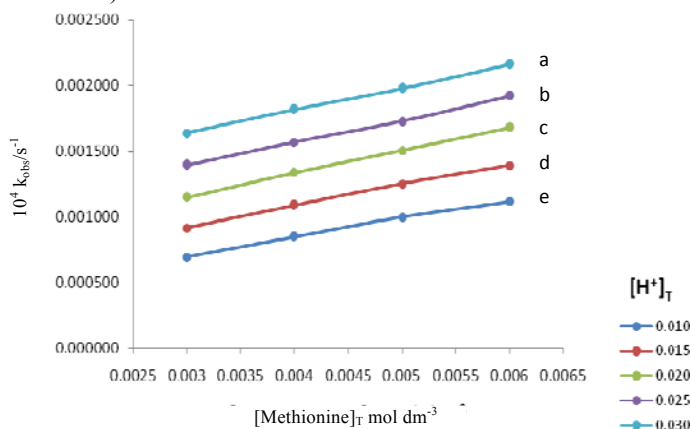


Figure 5(B). Plot of k_{obs} versus [methionine]; (Oxidant= BCC, T=25 $^{\circ}$ C where a: $[H^+]_T=0.010$ mol dm $^{-3}$, b: $[H^+]_T=0.015$ mol dm $^{-3}$, c: $[H^+]_T=0.020$ mol dm $^{-3}$, d: $[H^+]_T=0.025$ mol dm $^{-3}$, e: $[H^+]_T=0.030$ mol dm $^{-3}$)

With $[ICC]$ or $[BCC] = 4 \times 10^{-4} \text{ mol dm}^{-3}$ and $[\text{methionine}] = 3 \times 10^{-3} \text{ mol dm}^{-3}$, $10^4 k_{obs}$ at (25 °C) changed from 5.60 to 12.83 in case of ICC and 6.95 to 16.38 in case of BCC respectively as $[H^+]$ was changed from 0.01 to 0.03 mol dm^{-3} . This behavior was repeated for the entire $[\text{methionine}]$ range 0.003 to 0.006 mol dm^{-3} (Figure 6(A) for ICC and 6(B) for BCC).

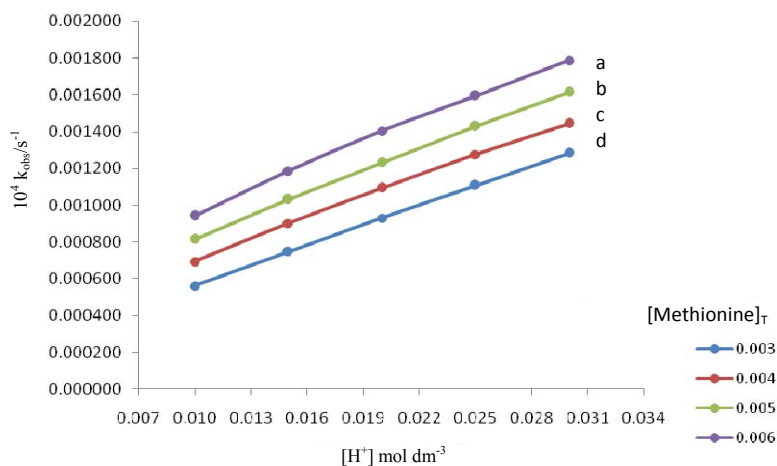


Figure 6(A). Plot of k_{obs} versus $[H^+]$; (Oxidant= ICC, $T=25$ °C where a: $[\text{Met}]_T=0.003 \text{ mol}^{-1} \text{ dm}^3$, b: $[\text{Met}]_T=0.004 \text{ mol}^{-1} \text{ dm}^3$, c: $[\text{Met}]_T=0.005 \text{ mol}^{-1} \text{ dm}^3$, d: $[\text{Met}]_T=0.006 \text{ mol}^{-1} \text{ dm}^3$)

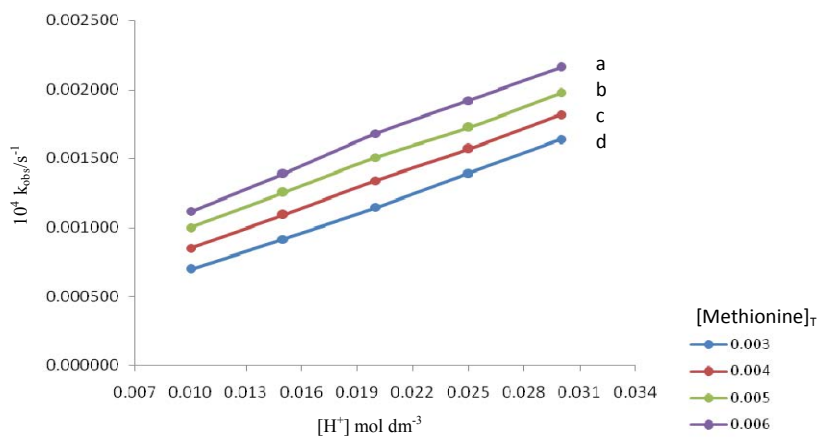
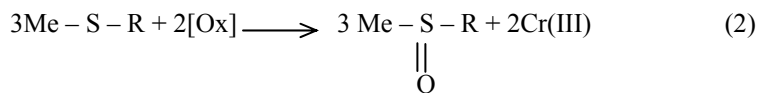


Figure 6(B). Plot of k_{obs} versus $[H^+]$; (Oxidant= BCC, $T=25$ °C where a: $[\text{Met}]_T=0.003 \text{ mol}^{-1} \text{ dm}^3$, b: $[\text{Met}]_T=0.004 \text{ mol}^{-1} \text{ dm}^3$, c: $[\text{Met}]_T=0.005 \text{ mol}^{-1} \text{ dm}^3$, d: $[\text{Met}]_T=0.006 \text{ mol}^{-1} \text{ dm}^3$)

The effect of temperature was studied in the range 20 to 40 °C. With the increase in temperature, k_{obs} was found to increase. With $[\text{methionine}] = 3 \times 10^{-3} \text{ mol dm}^{-3}$ $[ICC]$ or $[BCC] = 4 \times 10^{-4} \text{ mol dm}^{-3}$, $[H^+] = 0.01 \text{ mol dm}^{-3}$, $10^4 k_{obs}/s^{-1}$ changed from 3.09 to 7.59 in case of ICC and 4.24 to 10.35 in case of BCC (Table 1(A) for ICC and 1(B) for BCC).

Stoichiometry and mechanism

The stoichiometry of the reaction was studied at 30 °C where $[ICC]$ or $[BCC]$ was kept constant at $4.00 \times 10^{-4} \text{ mol dm}^{-3}$ and $[\text{methionine}] = 6.00 \times 10^{-3} \text{ mol dm}^{-3}$, the $[H^+] = 0.01 \text{ mol dm}^{-3}$. From the decrease in $[ICC]$ or $[BCC]$ and $[\text{methionine}]$ the stoichiometry of the reaction can be written as;



Where R = $-\text{CH}_2-\text{CH}_2-\underset{\substack{| \\ \text{NH}_2}}{\text{CH}}-\text{COOH}$

and [Ox] means oxidants *i.e.* ICC or BCC.

Table 1(A). Effect of temperature (ICC)

Temp, °C	$10^3[\text{Meth}]_{\text{T}}$ mol dm ⁻³	$10^4 k_{\text{obs}}, \text{ s}^{-1}$				
		[H ⁺], mol dm ⁻³				
		0.010	0.015	0.020	0.025	0.030
20	3.0	4.46	6.35	8.17	9.94	11.69
25	3.0	5.60	7.49	9.31	11.08	12.83
30	3.0	6.49	8.38	10.20	11.97	13.72
35	3.0	7.64	9.53	11.35	13.12	14.87
40	3.0	8.96	10.85	12.67	14.44	16.19
20	4.0	5.79	7.88	9.80	11.61	13.30
25	4.0	6.93	9.02	10.94	12.75	14.44
30	4.0	7.82	9.91	11.83	13.64	15.33
35	4.0	8.97	11.06	12.98	14.79	16.48
40	4.0	10.29	12.38	14.30	16.11	17.80
20	5.0	6.99	9.18	11.16	13.16	15.00
25	5.0	8.13	10.32	12.30	14.30	16.14
30	5.0	9.02	11.21	13.19	15.19	17.03
35	5.0	10.17	12.36	14.34	16.34	18.18
40	5.0	11.49	13.68	15.66	17.66	19.50
20	6.0	8.27	10.72	12.90	14.80	16.72
25	6.0	9.41	11.86	14.04	15.94	17.86
30	6.0	10.30	12.75	14.93	16.83	18.75
35	6.0	11.45	13.90	16.08	17.98	19.90
40	6.0	12.77	15.22	17.40	19.30	21.22

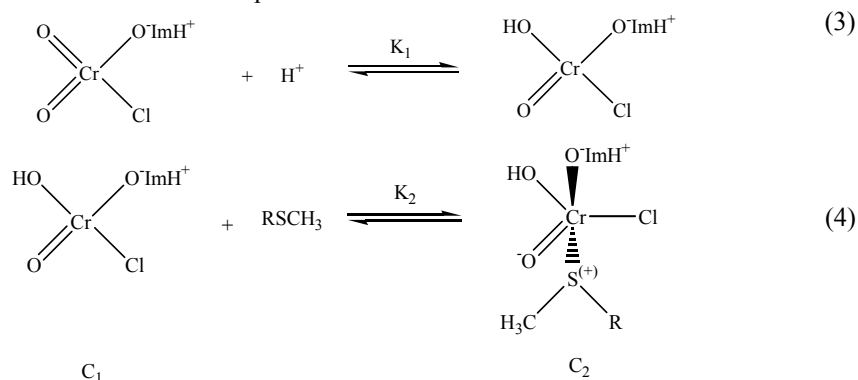
Table 1(B). Effect of temperature (BCC)

Temp / °C	$10^3[\text{Meth}]_{\text{T}}$ /mol dm ⁻³	$10^4 k_{\text{obs}} / \text{ s}^{-1}$				
		[H ⁺] / mol dm ⁻³				
		0.010	0.015	0.020	0.025	0.030
20	3.0	5.41	7.60	9.92	12.39	14.84
25	3.0	6.95	9.14	11.46	13.93	16.38
30	3.0	8.08	10.27	12.59	15.06	17.51
35	3.0	9.90	12.09	14.41	16.88	19.33
40	3.0	11.52	13.71	16.03	18.50	20.95
20	4.0	6.94	9.36	11.84	14.15	16.64
25	4.0	8.48	10.90	13.38	15.69	18.18
30	4.0	9.61	12.03	14.51	16.82	19.31
35	4.0	11.43	13.85	16.33	18.64	21.13
40	4.0	13.05	15.47	17.95	20.26	22.75

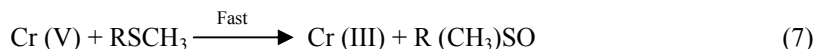
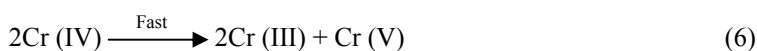
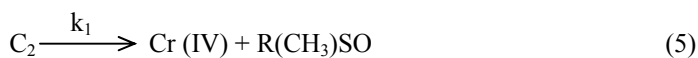
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20	5.0	8.44	10.98	13.51	15.71	18.23
25	5.0	9.98	12.52	15.05	17.25	19.77
30	5.0	11.11	13.65	16.18	18.38	20.90
35	5.0	12.93	15.47	18.00	20.20	22.72
40	5.0	14.55	17.09	19.62	21.82	24.34
20	6.0	9.62	12.37	15.25	17.65	20.07
25	6.0	11.16	13.91	16.79	19.19	21.61
30	6.0	12.29	15.04	17.92	20.32	22.74
35	6.0	14.11	16.86	19.74	22.14	24.56
40	6.0	15.73	18.48	21.36	23.76	26.18

At higher concentration of the acid 0.03 mol dm^{-3} , the undissociated form of methionine will participate in the electron transfer reaction. The reaction sequence presented below (Scheme 1) is consistent with the experimental data.



Scheme 1. The above scheme for ICC (same in case of BCC)



The rate of law for the electron transfer reaction can be derived in the following manner

$$\text{Rate} = k_1[\text{C}_2]_e \quad (8)$$

$$K_2 = [\text{C}_2]_e / [\text{C}_1]_e [\text{methionine}]$$

$$[\text{C}_2]_e = K_2 [\text{C}_1]_e [\text{methionine}] \quad (9)$$

Substituting the value of $[\text{C}_2]_e$ in Equation 8

$$\text{Rate} = k_1 K_2 [\text{C}_1]_e [\text{methionine}]_e \quad (10)$$

$$K_1 = [\text{C}_1]_e / [\text{Ox}]_e [\text{H}^+]_e$$

$$[\text{C}_1]_e = K_1 [\text{Ox}]_e [\text{H}^+]_e \quad (11)$$

Substituting the value of $[\text{C}_1]_e$ in the Equation 10

$$\text{Rate} = k_1 K_1 K_2 [\text{H}^+]_e [\text{Ox}]_e [\text{methionine}]_e \quad (12)$$

$$[\text{Ox}]_T = [\text{Ox}]_e + [\text{C}_1]_e$$

$$= [\text{Ox}]_e + K_1 [\text{Ox}]_e [\text{H}^+]_e$$

$$= [\text{Ox}]_e \{1 + K_1 [\text{H}^+]_e\}$$

$$[\text{Ox}]_e = \frac{[\text{Ox}]_T}{1 + K_I[\text{H}^+]_e} \quad (13)$$

$$\text{Rate} = \frac{k_I K_I K_2 [\text{Ox}]_T [\text{H}^+]_e [\text{methionine}]_e}{1 + K_I[\text{H}^+]_e} \quad (13)$$

$$\text{Since rate} = k_{obs} [\text{Ox}]_T \quad (14)$$

$$k_{obs} = \frac{k_I K_I K_2 [\text{Methionine}]_e [\text{H}^+]_e}{1 + K_I[\text{H}^+]_e} \quad (15)$$

The plot of k_{obs}^{-1} versus $[\text{H}^+]^{-1}$ should be linear for every $[\text{methionine}]$ changing from 3.00×10^{-3} to 6.00×10^{-3} mol dm⁻³ (Figure 7(A) for ICC and 7(B) for BCC). The slope of this plot is $\{1/k_I K_I K_2 [\text{methionine}]\}$ and intercept is $\{1/k_I K_2 [\text{methionine}]\}$. Now from this value of K_I can be calculated *i.e.* intercept/slope = K_I . The values of K_I were determined for five different temperatures ranging from 20^o to 40^o C and found to be 22.32, 33.14, 41.50, 52.25, 64.51 respectively in case of ICC and 20.10, 31.77, 40.26, 53.82, 65.81 respectively in case of BCC.

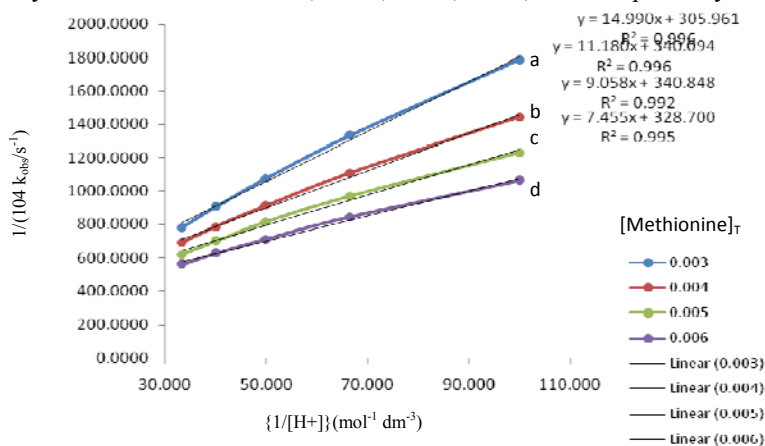


Figure 7(A). Plot of k_{obs}^{-1} versus $[\text{H}^+]^{-1}$ (Oxidant : ICC, T=25^oC where a: $[\text{Met}]_T = 0.003$ mol⁻¹ dm³, b: $[\text{Met}]_T = 0.004$ mol⁻¹ dm³, c: $[\text{Met}]_T = 0.005$ mol⁻¹ dm³, d: $[\text{Met}]_T = 0.006$ mol⁻¹ dm³)

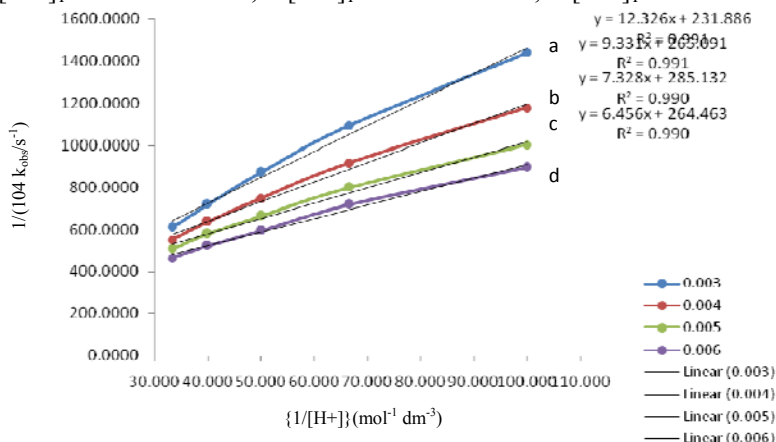


Figure 7(B). Plot of k_{obs}^{-1} versus $[\text{H}^+]^{-1}$ (Oxidant : BCC, T=25^oC where a: $[\text{Met}]_T = 0.003$ mol⁻¹ dm³, b: $[\text{Met}]_T = 0.004$ mol⁻¹ dm³, c: $[\text{Met}]_T = 0.005$ mol⁻¹ dm³, d: $[\text{Met}]_T = 0.006$ mol⁻¹ dm³)

The slope of each $[H^+]$ was plotted against $[\text{methionine}]^{-1}$. The plots are found to be linear (Figure 8(A) for ICC and 8(B) for BCC). The slope of Figure 8 (A) and (B) will be equal to $\{1/k_1K_1K_2\}$. The value of $k_1K_1K_2$ will be equal to reciprocal of the new slope. The values of $k_1K_1K_2$ were determined for four different temperatures ranging from 20 °C to 40 °C. The activation parameters were determined from the composite rate constants by using Eyring equation. The value of the ΔH^\ddagger and ΔS^\ddagger were found to be 12.5 (kJ/mol) and -154.1 ($\text{JK}^{-1}\text{mol}^{-1}$) in case of ICC and 17.5 (kJ/mol) and -136.9 ($\text{JK}^{-1}\text{mol}^{-1}$) in case of BCC respectively. The negative value of activation parameters favors the formation order transition states.

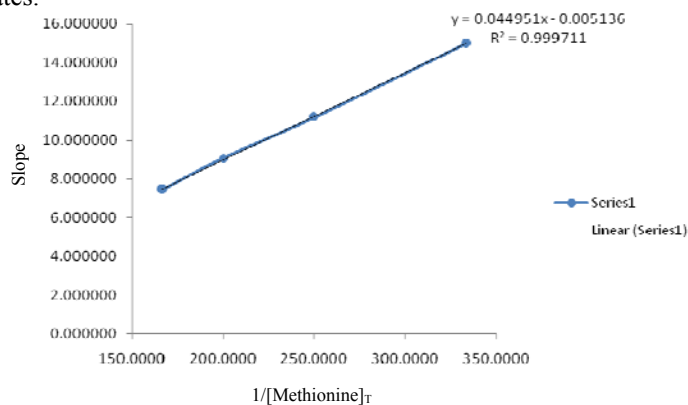


Figure 8(A). Plot of $[H^+]$ versus $[\text{methionine}]^{-1}$ (ICC)

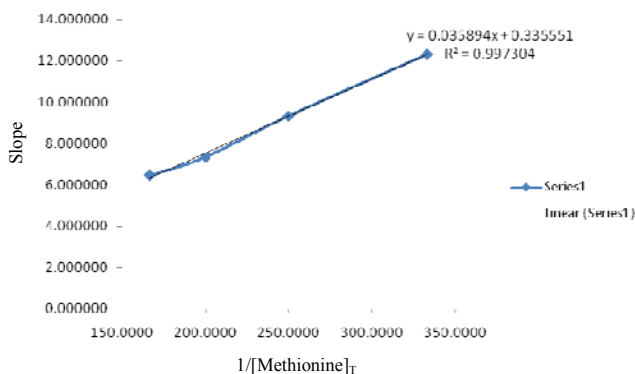


Figure 8(B). Plot of $[H^+]$ versus $[\text{methionine}]^{-1}$ (BCC)

Product analysis

In a typical experiment for the product analysis of ICC or BCC [0.2 m mol] mixed with 0.3 m mol of methionine at $[H^+]$ 0.01 mol dm^{-3} . The mixture was kept for 3 hour in a thermostat at 50 °C. The total volume of the solution was initially 50 mL. The concentrated solution was slowly evaporated to dryness in a desiccator. The IR spectra of methionine and the dried product were recorded in a SHIMADZU FTIR – 8000 spectrophotometer. In the product (Figure No 10(A) & 10(B)) most of the peaks of DL – methionine were retained. A broad strong NH_3^+ stretching band appears at 3200 cm^{-1} in the product compared to that at 2900 cm^{-1} in DL – methionine (Figure 9). The shift to higher frequency is probably due to association of water with the product. A strong peak at 1600 cm^{-1} and a weak peak at 1400 cm^{-1} are obtained

in the product^{19,20} due to the absorption of carboxylate group. The corresponding peaks in DL – methionine are obtained at 1500 cm^{-1} and 1400 cm^{-1} respectively. A new strong peak at 1100 cm^{-1} in the product is probably due to S=O stretching vibration. The corresponding peak of the sulfoxide is obtained in 1070 to 1030 cm^{-1} region. From the individual assignment of different peaks it can be inferred that the product is methioninesulfoxide.

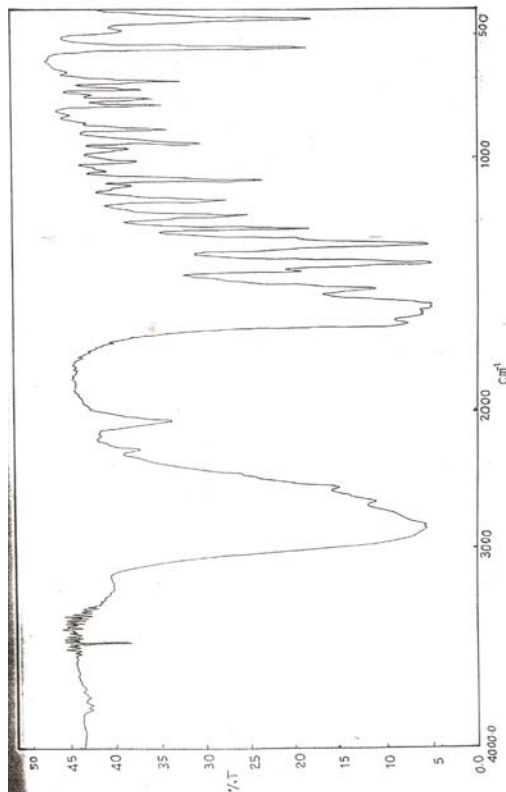


Figure 9. IR spectra of DL – Methionine

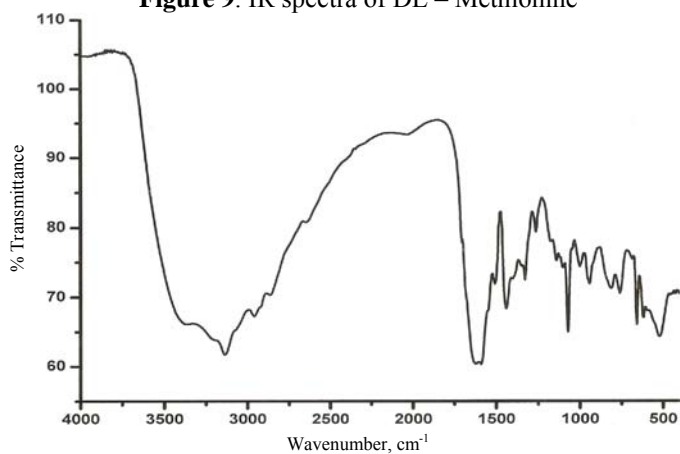


Figure 10(A). IR spectra of ICC oxidation product of methionine

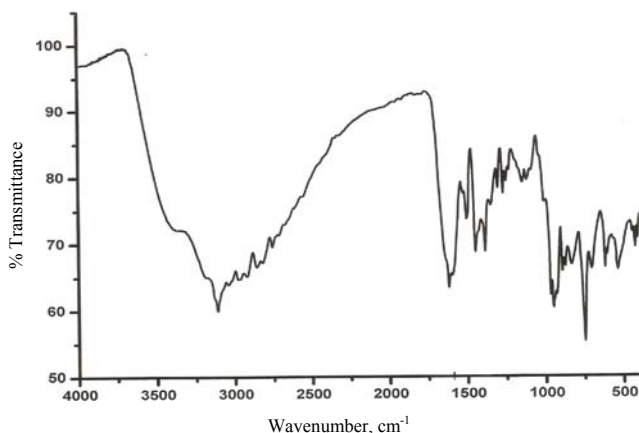


Figure 10(B). IR spectra of BCC oxidation product of methionine

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