

## Studies on in Situ Generation of Chromium(IV) and its Involvement in the Kinetics of Oxidation of L-methionine in Aqueous Medium

M. Jebastin Sonia Jas<sup>1</sup>, K. Margandan<sup>2</sup>, S. Parameswari<sup>3</sup>

<sup>1</sup>Chemistry, IFET College of Engineering, Villupuram, Tamilnadu, India

Research scholar, R&D centre, Bharathiyar University, Coimbatore

<sup>2,3</sup>Chemistry, IFET College of Engineering, Villupuram, Tamilnadu, India

**Abstract:** Chromium (IV) complex was prepared by the procedure reported in the literature and it was characterized by UV spectroscopy. Kinetics and mechanism of oxidation of methionine by Cr (IV) in water follows first order kinetics with respect to oxidant. There of the reaction with respect of substrate in different solvent was found to be first order. Thermodynamic parameters were calculated. The increase in the acetic acid content of the medium was increased the rate of the reaction. The rate of the reaction was increased by increasing the ionic strength of the reaction.

**Keywords:** Chromium (IV) complex, methionine, kinetics, acetic acid, Ionic Strength.

### 1. Introduction

The studies on kinetics have been highly useful in determining the factors which influence the rate of reaction as well as in understanding the mechanism of number of chemical reactions. Further more, the effect of ionic strength, polymerization test, and kinetic isotopes test will provide support for the proposed mechanism. One class of reaction study is concerned with oxidation and reduction refers to the loss and gain of electron respectively at an atom, ion (or) molecule and the consequent changes in molecular identity. A variety of oxidizing agents have been used in experimental studies.

Halogens, metal ion in higher oxidation states such as Co(III), Ce(IV), Mn(III), Ni(III), Fe(IV), V(V), Mn(VII), Os(VIII), Fe(III),. Using these oxidants, the behavior of the organic compound such as Aliphatic, aromatic carbons, aliphatic alcohols, glycols, phenols, amino phenols, aliphatic and aromatic acetones, acids, saturated and unsaturated organic compounds, hydroxyl acids, dicarboxylic acids, esters, and sugars have been studied extensively. Oxidation of L-methionine by Cr (VI) in acidic medium was studied by L.F.Salatal<sup>1</sup> during the year of 1993. They have reported that methionine sulphoxide and methional were the products formed by two parallel redox steps. P.Vani et al<sup>2</sup> during the year of 1994, studied the oxidation of DL-Methionine by manganese (III) in sulphuric acid medium. The reaction is first order in Mn(III) and methionine. The suitable rate law proposed was,

$$\frac{d[\text{Mn(III)}]}{dt} = \frac{K_1[\text{H}^+][\text{Mn(III)}][\text{MET}]}{[\text{H}^+] + K_h}$$

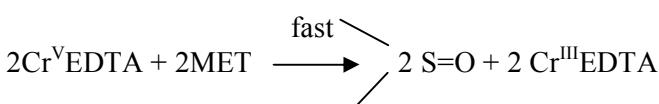
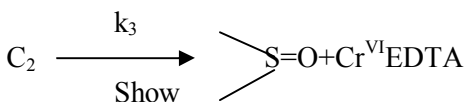
Mechanism of oxidation of seleno-DL-Methionine by potassium ferrate was studied by Read.J.F *et al*<sup>3</sup> during the year of 1998. In this kinetics the reaction follows first order with respect to hydrogen ion, selenomethionine and ferrate ion concentration over a pH of 8.53 to 10.13, but zeroth order in hydrogen ion concentration at low pH.

The proposed mechanism involves a rate determining step between seleno methionine and protonated ferrate ion.

A kinetic study of oxidation of methionine to methionine sulphoxide by peroxyxynitrite was studied by Daniel Perrin *et al*<sup>4</sup> during the year of 1999. They found that for every two sulphoxides formed, one peroxyxynitrite is converted to nitrate. Neither the pH nor the concentration of methionine affected the distribution of the yields of nitrite, nitrate and methionine sulphoxide. P.Vani *et al*<sup>5</sup> during the year 2001, had studied the oxidation of L-methionine by iron (III)1,10-phenanthroline complex in perchloric acid medium. The reaction is first order in Fe (III) and methionine. The proposed mechanism leads to the rate law.

$$\frac{d[\text{Fe}(\text{phen})_3^{2+}]}{dt} = \frac{k_2 k_4 k_3 k_2^2 [\text{Fe}^{\text{III}}][\text{phen}]^2 [\text{MET}]}{(1 + K_1 [\text{H}^+])([\text{H}^+]^2 + K_4 K_3 K_2^2 [\text{phen}]^2)}$$

Kinetics and mechanism of oxidation of methionine by Cr (VI): Edta catalysis was studied by S. Meenakshi *et al*<sup>6</sup> during the year 2003. The reaction exhibits first order dependence on the concentration of Cr<sup>VI</sup>. The mechanism proposed is

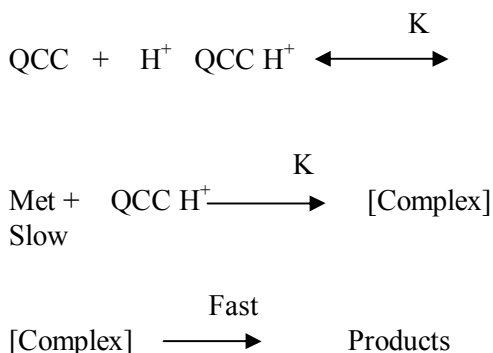


$$[\text{Cr}^{\text{VI}}]_t = [\text{Cr}^{\text{VI}}] + [\text{C}_1] + [\text{C}_2]$$

Total Cr<sup>VI</sup> concentration, Applying equilibrium treatment, [Cr (VI)] can be determined.

$$\begin{aligned} \frac{-d[\text{Cr}^{\text{VI}}]}{dt} &= k_3 [\text{C}_2] \\ &= k_3 k_1 [\text{MET}][\text{Cr}^{\text{VI}}][\text{EDTA}] \end{aligned}$$

M.Pandeeswaran *et al*<sup>7</sup> during the year of 2006 studied the kinetics and mechanism of the oxidation of methionine by quinoliniumchlorochromate. The reaction is first order with respect of methionine, QCC and acid. A solution model and suitable mechanism are postulate. The proposed scheme envisages an oxygen atom transfer from the oxidant.

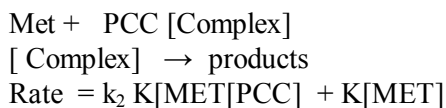


Under experimental conditions, methionine was oxidized to the sulfoxide stage only. In addition, oxidation of methionines by oxochromium (V) cation was studied by N.S.Venkataramanan *et al*<sup>8</sup> during the year of 2007. The oxidation of methionine and substituted methionine with five oxo(salen)chromium (V) complexes in aqueous acetonitrile was investigated by spectrophotometric method. Although Cr(IV) was generally considered to be an typical oxidation state, awareness is increasing as to its role in a redox chemistry of that element. Sodium(2-ethyl-hydroxybutanoate(2-))oxochromate(V) is sufficiently stable in aqueous solutions in the pH range 3-4 to allow the study of the oxidation of a series of organic substrates. Oxalic acid, secondary and primary 2-hydroxyl acids, and 2-oxoacids temperature (60°C) was required. The rates of chromium (V) relative to react readily at 25°C while for tertiary 2- hydroxyl acids, alcohols, aldehydes, and diols a higher chromium(VI) oxidations ranges from 0.08 to over 400. It was studied by Rocek *et al*<sup>9</sup> during the year of 1985.

The kinetics of reaction of sodium bis(2-ethyl-2-hydroxybutyrate), oxochromate(V) with triphenylphosphine (TPP) have been studied in 100% acetone. The reaction exhibits total second order kinetics, first order with respect to each reactant. To account for the quantitative yield of triphenylphosphine oxide as one of the product of these reactions. Suitable mechanistic scheme, involving a precursor complex between oxochromate (V) and TPP with a subsequent oxygen atom transfer to TPP, has been proposed. The presence of Cu (II) salts enhances the rate of oxygen atom transfer by oxochromate (V), it was studied by A.Rajavelu, *et al*<sup>10</sup> during the year of 1989. The selective oxidation of alkylarylsulfides to sulfoxide with three oxochromium (V) complexes in an acetonitrile – water mixture is over all second order, first order in the oxidant and in the substrate. Sulfides containing electron – attracting substituents retard the rate while those containing electron realizing substituent accelerate the rate of oxidation. The rate constant for the oxygenation reaction,  $k_2$  is better correlated with  $\rho^+$  than Hammett constants. The reactivity of different alkyl phenyl sulfides  $\text{C}_6\text{H}_5\text{SR}$  ( $\text{R} = \text{Me, Et, N-Pr, i-Pe, n-Bu}$  and  $\text{t-Bu}$ ) is accounted for all terms of Taft's polar,  $\sigma^*$  and steric,  $E_s$ , substituent constants. These kinetic results are interpreted in terms of a mechanism involving outer sphere electron transfer from sulphide to Cr(V) as the rate determining step. The results of Cr(V) oxidation are compared with those of Cr (VI) oxidant. It was studied by .J. BoscoBharathi *et al*<sup>11</sup> during the year of 1988. The Cr(V) chelatebis(2-ethylhydroxybutanoate)oxochromate(V) oxidizes the adenoidal budroquinone and 2,3-dihydroxybenzoic acid in solutions buffered with the ligand acid,2-ethyl-hydroxybutanoic acid, and its anion. The observed 1:1 stoichiometry of these reactions corresponds to the formation of the related quinone and Cr (III). The Cr (III) product from the reaction excess hydroquinone is a bis chelate derived from the ligand anion, having, in addition, a ligand derive from the diol with 2,3, - dihydroxybenzoic acid, the diol appears to have coordinated to Cr(III) as a bidentate ligand. Both reactions are catalyzed by Cr(IV) and pass through semiquinone radicals,  $\text{ArO}_2\text{H}$ ; for which Cr(IV) and Cr (V) complete. Suggested reaction. Sequence for the two reductions ligature bimolecular steps involving  $\text{Cr(V)} + \text{Ar(OH)}_2$ ,  $\text{Cr(V)} + \text{ArO}_2\text{H}$ ;  $\text{Cr(IV)} + \text{ArO}_2\text{H}$ , but differ in the reaction of Cr(IV) with  $\text{Ar(OH)}_2$  which is bimolecular with hydroquinone but exhibits kinetic saturation with 2,3-dihydroxybenzoic acid, indicating the formation of a strongly associated complex with Cr(IV). It was studied by S.K.Ghosh *et al*<sup>12</sup> during the year 1988. The kinetics of oxidation of unsaturated alcohol by Sodium bis(2-ethyl-2 Hydroxybutanoate (2-1) oxochromate (V) has been investigated in 25% (v/v) aqueous HOAC :  $\text{HClO}_4$ . The order in (oxidant) and (substrate) was 1.0 and 0.7 respectively. The oxidation rate increased with increase in 2-ethyl-2-hydroxybutyric acid (EHBA) and decreased with increase in the percentage of HOAC. The rate decreases slightly with increase in  $(\text{H}^+)$ . The unsaturated alcohols exhibited higher reactivity compared to their saturated analogues. A mechanism involving the formation of a complex between Cr(V) and alcohol which in turn disproportionate in to

products in a slow step is advanced to explain the kinetic results. It was studied by G. Sreelatha et al<sup>13</sup> in the year 1987.

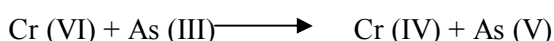
The oxidation of methionine by pyridiniumchlorochromate (PCC) leads to the formation of the corresponding sulphoxide. The reaction is first order with respect to PCC. Michaelis-Menten type kinetics has been observed with respect to methionine. The reaction has been studied in organic solvents and the solvent effect has been analyzed using multiparametric equations. A suitable mechanism has been proposed. It was studied by K. Sharma et al<sup>14</sup> in the year 1997.



The reaction of Cr(VI) with hydrogen peroxide was studied in the presence of glutathione. In vitro, reaction of chromium (VI) with H<sub>2</sub>O<sub>2</sub> led to production of hydroxyl radical as the significant reaction intermediate, while reaction of chromium (V) with glutathione led to formation of two chromium (V)-glutathione complexes and the glutathione ethyl radical. Incubation of chromium (VI) with glutathione prior to addition of H<sub>2</sub>O<sub>2</sub> led to formation of peroxochromium (v) species and a dramatic increase in hydroxyl radical production over the detected in the reaction of chromium (VI) with hydrogen peroxide alone. It was studied by J. A. Aiyar et al<sup>15</sup> in the year 1990. Reduction of HCrO<sub>4</sub><sup>-</sup> with the bridged dimer of Mo (V) in aqueous solutions buffered by 2-ethyl-2-hydroxybutanoic acids and its salt yield pink Cr (IV) complexes. There are two keys to this improve stability.

1. The complex must be formed by a two electrons reduction of Cr (VI) rather than a one electron reduction of Cr (V) to avoid the rapid one electron reduction of the Cr(IV) following its generation.
2. The carboxyl ligand used to stabilize Cr (IV) must be attached to the Cr (VI) reagent prior to the redox process.

It was studied by M.C.Ghosh et al<sup>16</sup> during the year of 1990. Reduction of HCrO<sub>4</sub><sup>-</sup> with H<sub>3</sub>AsO<sub>3</sub> in solution buffered by 2-ethyl-2-hydroxybutanoic acid and its salt yield stabilized pink solution of Cr (IV). The Cr (IV) solutions so produced are sufficiently stable to allow examination of ligation equilibria by static methods.



It was done by C. Ghose et al<sup>17</sup> in the year 1991. Tetrapositive chromium Cr (IV), a state stabilized in aqueous solution through ligation by anions of branched  $\alpha$ -hydroxyl acids, undergo decay by a combination of disproportionation (2 Cr (IV)  $\rightarrow$  Cr (III) + Cr (VI) and ligand oxidation. It was studied by C. Ghose et al<sup>18</sup> in the year 1992. The review discusses different possible routes of reduction of Cr (VI) to Cr (III) by several types of organic reducing agents with special emphasis to those occurring in aqueous micelle systems. The micelle media can influence the mechanistic paths of reduction of Cr(VI) to Cr(III) by several types of organic reducing agents with special emphasis to those occurring in aqueous micelle systems. The micelle media can influence the mechanistic paths of reduction of Cr (VI) to Cr (III). Such studies in micro heterogeneous systems are important from the standard point of understanding the mechanism of redox activity and toxicity of Cr (VI). The possible use of suitable surfactants in the two-phase oxidation of organic substance by chromic acid was discussed. It was studied by Asim K. Das<sup>19</sup> in the year of 2004. Carboxylato bound Cr(V) oxidation of aryl Methyl Sulphides (ArSMe), produces through a complex formation between the oxidant and substrate. The peculiar substituent effect observed was attributed to the reaction being carried out at a temperature close to the isokinetic temperature. Comparisons of the kinetic results observed with Cr(V) and Cr(VI) oxidations points out the operation of different mechanisms-single electron transfer in Cr (VI) oxidation and complex formation followed by ligand and coupling in Cr(V) oxidation<sup>20</sup>. This work was carried out by S.S.Mitic in the year 2004.

## 2. Experimental

### 2.1 Preparation of Cr (IV) complex:

A solution of 0.1M of  $K_2Cr_2O_7$  in water was added with 0.1M of 30% of  $H_2O_2$ . After 20 minutes, Cr (IV) species was formed in solution. The formation of Cr (IV) is confirmed by adding  $MnSO_4$ , to the mixture of Cr (IV) and  $H_2O_2$ . The formation of Cr (V) was observed from the following changes. Absorbance was decreased and the color of the mixture was turned to pink color well after 20 minutes.

### 2.2 Characterization

The freshly prepared Cr(IV) complex was characterized using UV-visible spectrophotometer. The kinetics and mechanism of Cr (IV) oxidation of L-methonine in water medium was studied at 510nm using Agilent 8453 diode array spectrophotometer attached with a thermometer. The preparation of reagents used and the kinetic procedure were presented below.

### 2.3 Chemicals and Reagents:

#### Methionine:

AR grade methionine was used. 0.1 M methionine in water was prepared as the stock solution.

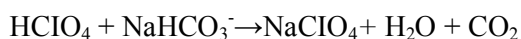
Solution of 0.1M of  $K_2Cr_2O_7$  in water added with 0.1M of 30% of  $H_2O_2$ . After 30 minutes, Cr (IV) species was formed in solution.

#### Water:

Double distilled water was used.

#### Sodium Perchlorate:

0.1M Sodiumperchlorate was prepared by reacting 0.1M  $HClO_4$  with 0.1M  $NaHCO_3$  and it was used to study the effect of ionic strength on the reaction rate.



#### Methyl methacrylate:

0.1% solution of distilled methylmethacrylate in  $H_2O$  was prepared and it was used to study whether the reaction mechanism involved radicals or not.

### 2.4 Kinetic procedure:

Kinetic measurements were carried out at room temperature under pseudo-first order conditions by taking the substrate concentration to be at least ten times greater than that of the oxidant. The concentrations of all the reagents except the one that was varied were maintained constant. The kinetics oxidation reactions were followed by using diode array spectrophotometer at 510 nm. In all the kinetic runs, the total volume of the reaction was kept constant. The instrument was switched on the warmed up for fifteen minutes, to get stabilized. The reaction was initiated by the rapid addition of the oxidant from a pipette into the standard flask containing the reaction mixture. The solution was immediately transferred into cuvette and the progress of the reaction was monitored by noting the decrease in optional density. In almost all the variations, reaction was followed by initial rate method for a maximum of 300 sec. A linear plot of  $(A_\infty - At)$  versus time was made for each run using linear regression and the pseudo first order rate constant was calculated from the slope of the plot.

## 2. 5 Kinetic variations:

### Substrate variation:

The substrate variation was done by varying the concentration of the substrate in water ranging from 0.01 to 0.1M with different solvents.

### Oxidant variation:

The oxidant variation was carried out by varying the concentrations ranging from 0.001M to 0.008M.

### Salt effect:

Salt effect was carried out by adding 0.001M TO 0.008M of NaClO<sub>4</sub> to the reaction mixture.

### Solvent variation:

The solvent variation was done for four different compositions ranging from 80% H<sub>2</sub>O-20% Acetic acid to 60% H<sub>2</sub>O-40% Acetic acid.

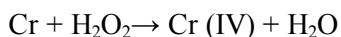
### Temperature variation:

The temperature variation was carried out by varying the temperature of the reaction at 313K, 303K and 293K.

## 3. Result and Discussion

### 3.1 In Situ Generation of Chromium (IV):

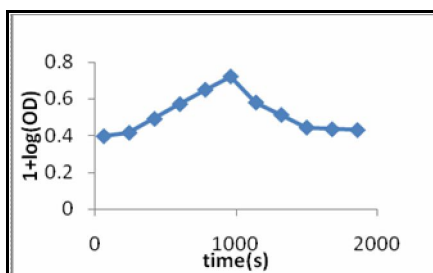
When Cr(VI) is added with H<sub>2</sub>O<sub>2</sub> Cr(VI) is being reduced to Cr(IV), we found this reduction process was slow, with the appearance of pink color found to be maximum after 20 minutes. It indicated that Cr(IV) was maximum after 20 minutes. Then the pink color vanished after 1 hour. We proposed to carry out the oxidation reaction with Cr(IV). Hence we prepared the Cr(IV) Species in situ by mixing Cr(VI) with H<sub>2</sub>O<sub>2</sub> and waited for 20 minutes, After 20 minutes pink color solution of Cr (IV) was obtained.



Similarly the pink solution of Cr (IV) was prepared by reduction of HCrO<sub>4</sub> with H<sub>2</sub>AsO<sub>3</sub> in solutions buffered by 2-ethyl 2- hydroxyl butanoic acid (LigH). After 30 minutes only the pink color solution of Cr (IV) was formed it was studied by C.,Ghosh et al<sup>17</sup> during the year of 1991. We prepared Cr(IV) by conventional mixing experiment. Similarly, C.Ghosh<sup>16</sup> prepared Cr (IV) in conventional mixing experiment during the year 1990. In our work, equal molar quantities of the two-redox centers, react, yielding the characteristic of Cr (IV) species. Similarly, C.Ghosh et al<sup>17</sup> was studied the preparation of Cr (IV) with equimolar quantities of the two-redox centers during the year of 1991

**Table 1: Rate of formation and decomposition of Cr(VI)**

Time	OD	1+log(OD)
60	0.249	0.397
240	0.260	0.416
420	0.310	0.491
600	0.372	0.571
780	0.445	0.648
960	0.525	0.720
1140	0.379	0.579
1320	0.325	0.512
1500	0.278	0.444
1680	0.272	0.435
1860	0.269	0.430

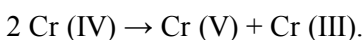


Rate of formation of Cr (IV)  $k_f = 8.7 \times 10^{-4} \text{ S}^{-1}$

Rate of decomposition of Cr (IV)  $k_d = 4.8 \times 10^{-1} \text{ S}^{-1}$

From the data, the rate of formation of Cr(IV) was found to be  $10^{-4}$ , the rate of decomposition Cr(IV) was found to be  $10^{-4}$ , it implied that  $k_f$  approximately equal to  $k_d$ . Hence, Cr (IV) is supposed to be present in least amount after the particular period (Table 1). The principal catalytic species to be a Cr(IV) complex, as it is present throughout the reaction but it was destroyed the end of each run via reduction by sulphite. It was studied by N.Bose *et al*<sup>21</sup> during the year of 1986. The rate of reaction of Cr (IV) with L-Methionine was  $10^2 \text{ S}^{-1}$ . Therefore; the rate of decomposition was insignificant during rate measurements. Similarly, the rate of reaction of Cr (IV) with dimer of molybdenum was  $10^2 \text{ S}^{-1}$ . It was studied by C.Ghose *et al*<sup>16</sup> during the year of 1990.

All the above data conformed that Cr (IV) could be involved in the reaction with methionine. The reaction was initiated by adding the formed Cr (IV) with methionine. The decrease in absorbance was noted as 510nm, the molar absorbance of Cr (IV) associated with the peak at 510nm. It was studied by C.Ghose *et al*<sup>17</sup> during the year of 1991. However, the decrease was found to be regular up to 20s after fixing. But intervention of various side reactions, such as disproportionation reaction of Cr(IV), Cr(V) yielding Cr(IV) and Cr (III). In other words, disproportionate of Cr (IV) was present.



Since we would not identify the absorbance due to Cr (V) and other intermediate complexes that may possibly absorb at this wavelength. Since we employ initial rate method, we neglect the date beyond 20s. The date constants that we have calculated was found to be in the order of  $10^2 \text{ S}^{-1}$  is in consistent with various work done with Cr(IV). Similarly the rate of reaction of Cr (IV) with tin (II) and cerium (III) was found to be  $10^{-2} \text{ S}^{-1}$ . It was studied by C. Ghose *et al*<sup>22</sup> during the year of 1992.

### 3.2 Kinetic studies of Cr(IV) with methionine:

Agilent 8453 Diode Array UV-Visible spectrophotometer was standardized by taking the spectrum of water and then electronic spectrum of Mo (VI) in water recorded using the same instrument from 1100nm to 190nm. The reported max of 510 nm was obtained. Kinetics and mechanism of Mo(VI) oxidation of L – methionine in 100%  $\text{H}_2\text{O}$  medium has been studied.

**Table 2: Dependence of Rate on Oxidant Concentration**

[MET]=0.01      100% water      Temp=303 K

$[\text{Cr}]_t$	K
0.001	0.0101
0.002	0.0117
0.004	0.0122
0.006	0.0148
0.008	0.0150

#### 3.2.1 Effect of varying oxidant concentration:

The reaction rate remained almost constant with an increased Cr(VI) concentration. This showed that the order with respect to Cr(IV) is one (Table 2)

### 3.2.2 Effect of varying substrate concentration:

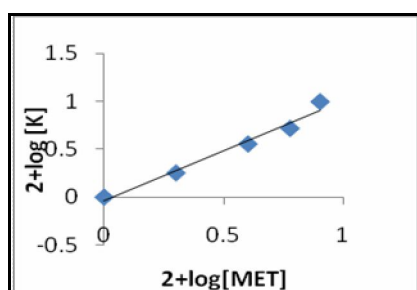
The reaction rate was increased with increase in the concentration of L-methionine. The plot of log k versus log [Met] was linear with a slope of 1.04, which revealed that the order with respect to [Met] is first order. (Table 3-Table 9)

**Table 3: Dependence of Rate on Substrate Concentration**

[Cr]<sub>t</sub>=0.001    100% water    Temp=303 K

[MET]	k	2+log[MET]	2+log[k]
0.01	0.0101	0	0.00432
0.02	0.0018	0.30103	0.2555
0.04	0.036	0.60206	0.5566
0.06	0.0522	0.77518	0.7176
0.08	0.099	0.90309	0.9956

SLOPE = 1.0439    r = 0.98



**Table 4: Effects of Substrate Concentration on Reaction Rate.**

[MET]	[Cr] <sub>t</sub>	Solvent	K	r
0.06	0.001	50% acetone: 50%H <sub>2</sub> O	1.2 X 10 <sup>-2</sup> s <sup>-1</sup>	0.95
0.08	0.001	50% acetone: 50%H <sub>2</sub> O	1.9 X 10 <sup>-2</sup> s <sup>-1</sup>	0.92
0.06	0.001	50% acetonitrile: 50%H <sub>2</sub> O	2.2 X 10 <sup>-2</sup> s <sup>-1</sup>	0.95
0.08	0.001	50% acetonitrile: 50%H <sub>2</sub> O	5.9 X 10 <sup>-2</sup> s <sup>-1</sup>	0.97
0.02	0.001	50% acetic acid: 50%H <sub>2</sub> O	2.3 X 10 <sup>-2</sup> s <sup>-1</sup>	0.92
0.04	0.001	50% acetic acid: 50%H <sub>2</sub> O	3.6 X 10 <sup>-2</sup> s <sup>-1</sup>	0.98
0.06	0.001	50% acetic acid: 50%H <sub>2</sub> O	5.9 X 10 <sup>-2</sup> s <sup>-1</sup>	0.97
0.08	0.001	50% acetic acid: 50%H <sub>2</sub> O	6.5 X 10 <sup>-2</sup> s <sup>-1</sup>	0.96
0.08	0.001	50% DMSO: 50%H <sub>2</sub> O	9.7 X 10 <sup>-2</sup> s <sup>-1</sup>	0.91
0.02	0.001	50% Ethanol : 50%H <sub>2</sub> O	2.1 X 10 <sup>-2</sup> s <sup>-1</sup>	0.97
0.04	0.001	50% Ethanol : 50%H <sub>2</sub> O	1.04 X 10 <sup>-2</sup> s <sup>-1</sup>	0.99
0.06	0.001	50% Ethanol : 50%H <sub>2</sub> O	3.4 X 10 <sup>-2</sup> s <sup>-1</sup>	0.95
0.08	0.001	50% Methanol : 50%H <sub>2</sub> O	4.2 X 10 <sup>-2</sup> s <sup>-1</sup>	0.91

**Table 5: Dependence of Rate on Substrate Concentration**

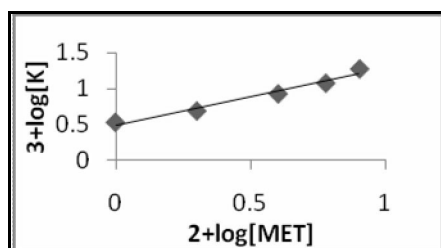
[Cr]<sub>t</sub>=0.001    50% acetone: 50%H<sub>2</sub>O    Temp=303 K

[MET]	k	2+log[MET]	3+log[k]
0.01	0.0034	0	0.53147
0.02	0.0049	0.30103	0.69019
0.04	0.0085	0.60206	0.9294
0.06	0.012	0.77518	1.0791
0.08	0.019	0.90309	1.278



Slope = 0.8011

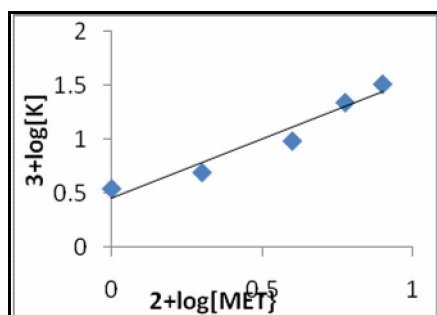
r = 0.98



**Table 6: Dependence of Rate on Substrate Concentration**  
 $[Cr]_i=0.001$  50% aceto Nitrile: 50%  $H_2O$  Temp=303 K

[MET]	k	2+log[MET]	3+log[k]
0.01	0.0035	0	0.544
0.02	0.0049	0.30103	0.694
0.04	0.0080	0.60206	0.985
0.06	0.0221	0.778	1.342
0.08	0.059	0.90309	1.512

Slope = 0.9814 r = 0.96



**Table 7: Dependence of Rate on Substrate Concentration**  
 $[Cr]_i=0.001$  50% acetic acid: 50%  $H_2O$  Temp=303

[MET]	k	2+log[MET]	3+log[k]
0.01	0.011	0	0.0413
0.02	0.021	0.30103	0.0791
0.04	0.023	0.60206	0.3617
0.06	0.034	0.77581	0.5314
0.08	0.042	0.90309	0.6232

Slope = 0.824 r = 0.99

**Table 8: Dependence of Rate on Substrate Concentration**  
 $[Cr]=0.001$  50% DMSO: 50%  $H_2O$  Temp=303 K

[MET]	k	2+log[MET]	3+log[k]
0.01	0.003	0	0.491
0.02	0.004	0.30103	0.672
0.04	0.004	0.60206	0.681
0.06	0.012	0.778	1.079
0.08	0.097	0.90309	1.278

Slope = 0.807, r = 0.90

**Table 9:Dependence of Rate on Substrate Concentration**  
[Cr]<sub>i</sub>=0.001 50% Methanol: 50%H<sub>2</sub>O Temp=303 K

[MET]	K	2+log[MET]	4+log[k]
0.01	0.0030	0	0.796
0.02	0.0039	0.30103	0.5910
0.04	0.027	0.60206	0.6901
0.06	0.0069	0.77581	0.8388
0.08	0.0421	0.90309	1.6242

Slope = 0.761, r = 0.94

**3.2.3Effect of dielectric constant:**

The reaction rate was decreased with an increase in the dielectric constant of the solvent. Reaction was profoundly influenced by the change in solvent composition. The increase in acetic acid content of the medium increased the rate. The decrease in polarity of the solvent facilitates the reaction between Cr(IV) and methionine. A plot of log k versus 1/D is linear with a positive slope pointing to an interaction between a ion and a dipole. The observed solvent effects in favor of an electron transfer process are in the rate-determining step. As the increase in acetic acid, content of the medium increases the viscosity and dielectric constant of the medium, the formation of encounter complex is more facile by increasing the rate of electron transfer (Table 10).

**Table 10: Effect of Dielectric Constant**  
[MET]=0.01 [Cr]<sub>i</sub>=0.001 T=303K r=0.97

D	K	1/D	2+log[k]
65.4	0.021	0.015	1.32
58	0.026	0.017	1.41
50.54	0.049	0.019	1.69

**3.2.4 Effect of sodium perchlorate:**

The reaction rate was increased with an increase in the ionic strength of the reaction. It indicated that the participation of an ionic species in the rate determining step (Table 11)

**Table 11 Dependence of Rate O Ionic Strength Variation**  
[MET]=0.01 [Cr]<sub>i</sub>=0.001 100% H<sub>2</sub>O

I	K0.015	2+log[k]	I <sup>1/2</sup>
0.001	0.015	0.1760	0.0316
0.002	0.016	0.20412	0.0447
0.04	0.14	1.14612	0.0632
0.006	0.16	1.20412	0.0774
0.08	0.44	1.643	0.0890

**3.2.5 Effect of solvent studies:**

In all the solvents, the order with respect to substrate was found to be first order reaction. In indicated the least influence of the solvent in the reacting system. Since free H<sup>+</sup> is present in acetic acid and ethanol, the rate enhanced compared with other solvents (Table 12).

**Table 12: Effect of solvent on reaction rate**

[MET]	[Cr] <sub>t</sub>	T	Solvent	K	R
0.01	0.001	303K	30% acetic acid : 70%H <sub>2</sub> O	2.1X 10 <sup>-2</sup> s <sup>-1</sup>	0.93
0.01	0.001	303K	40% acetic acid : 60%H <sub>2</sub> O	2.6 X 10 <sup>-2</sup> s <sup>-1</sup>	0.98
0.01	0.001	303K	20% acetic acid : 80%H <sub>2</sub> O	4.9 X 10 <sup>-2</sup> s <sup>-1</sup>	0.98

**3.2.6 Effect of monomer:**

While adding methylmethacrylate to the reaction mixture, polymerization of monomer was induced and turbidity appeared in the reaction mixture. Hence, presence of radical intermediates in the reaction scheme was proposed.

**3.2.7 Temperature Studies:**

The reaction rate was increased with an increase in the temperature of the reaction. Thermodynamic parameters could be calculated from the temperature studies, (Table 13, 14)

$$\Delta G^* = 89.16 \text{ k J mol}^{-1}$$

$$\Delta H^* = 86.66 \text{ k J mol}^{-1}$$

$$\Delta S^* = 123.19 \text{ JK}^{-1}$$

$$E_a = 89.16 \text{ k J mol}^{-1}$$

G\*, H\* values were low compared to the oxidation of organic sulphides by Cr(V)<sup>23</sup>. It indicated the fastness of the reaction. The positive value of ΔS\* also indicated the fastness of the reaction.

**Table13:Dependence of Rate on Temperature**

[MET]=0.01 [Cr]<sub>t</sub>=0.001 100%H<sub>2</sub>O R=0.98

T	K	1/T	4+ log[k]
313	0.00701	0.0031	1.8457
303	0.010	0.0033	1.176
293	0.006	0.00341	0.826

**Table14:Dependence of Rate on Temperature**

[MET]=0.01 [Cr]<sub>t</sub>=0.001 100%H<sub>2</sub>O r = 0.97

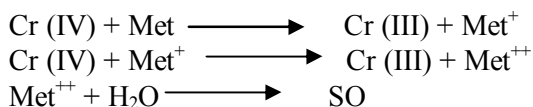
T	k	1/T	k/T	7+ log[k/T]
313	0.00701	0.0031	2.24E-05	2.35
303	0.010	0.0033	4.9E-06	1.694
293	0.006	0.00341	2.29E-06	1.359

**3.2 Stoichiometric Studies and Mechanism**

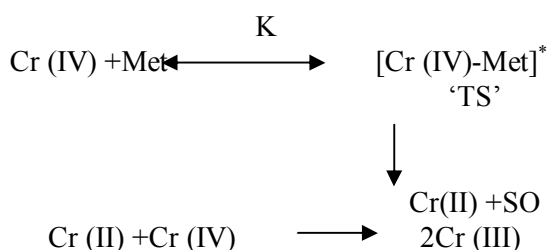
During the stoichiometric studies, when equimolar concentration of methionine(0.01M) and Cr(IV)(0.01M) were used, the initial absorbance was found to be 0.06. But when the concentration of

methionine(0.01M) and Cr(IV)(0.01M) were used, the initial absorbance was found to be 0.234. The stoichiometry of the reaction was found by 2:1(Table, 15, 16, 17)

This indicates that two molecules of Cr (IV) with the one molecule of methionine. This suggests the following scheme:



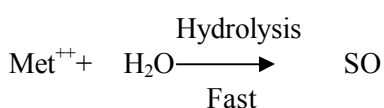
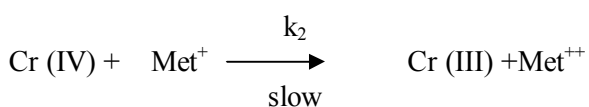
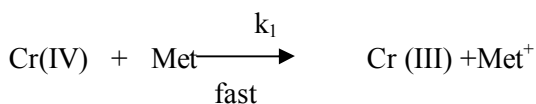
Since the temperature studies gave positive  $\Delta S^*$ , we propose the following mechanism scheme with indicates the formation of transition species is very unlikely,



In stoichiometric studies increase in Cr(IV) (0.02M) and methionine (0.01M) increases the absorbance at 510 nm indicate two possibilities.

1. Increase in Cr (IV) – Met complex.
2. Disproportion of CR (IV) into Cr(V) and Cr(III) in which Cr(V) also absorbs at 510 nm.

Based on the observations, we could be proposed the following mechanism,



Rate law:

$$\text{Rate} = k_2[\text{Cr (IV)}] [\text{Met}^+]$$

$$-\frac{d[\text{Met}^+]}{dt} = k_1[\text{Cr(IV)}] [\text{Met}] - k_2[\text{Cr(IV)}][\text{Met}^+] = 0$$

$$[\text{Met}^+] = \frac{k_1 [\text{Cr (IV)}][\text{Met}]}{k_2 [\text{Cr (IV)}]}$$

$$\text{Rate} = k_2[\text{Cr(IV)}]k_1 [\text{Met}]$$

$$\text{Rate} = k_1k_2[\text{Cr(IV)}][\text{Met}]$$

**Table 15: Stoichiometric Variation**[Cr]<sub>t</sub>=0.02 [MET]=0.01 100%water 2: 1

Time(s)	OD	1+og(OD)
1	0.234	0.369
3	0.233	0.367
5	0.232	0.365
9	0.229	0.359
11	0.228	0.357
13	0.222	0.346
15	0.218	0.338
17	0.217	0.336

**Table 16: [Cr]<sub>t</sub>=0.01 [MET]=0.02 100%water 1:2**

Time(s)	OD	1+og(OD)
1	0.14	0.146
3	0.139	0.143
5	0.137	0.136
9	0.135	0.130

**Table 17: [Cr]<sub>t</sub>=0.01 [MET]=0.01 100%water 1:1**

Time(s)	OD	1+og(OD)
1	6.05E-02	1.78
3	6.05E-02	1.78
5	6.05E-02	1.78
9	6.05E-02	1.78

### 3.3 Product Analysis

Equimolar solution of Cr (IV) and methionine was mixed in 100% H<sub>2</sub>O solvent mixture and it was left alone for 2 hours at 50°C. There after sodium bicarbonate was added and the solution was stirred vigorously followed by drop wise addition of benzoyl chloride solution until precipitation was complete. The precipitate obtained was identified as N-benzoyl methionine sulphoxide (m.pt.183°C) a derivative of methionine sulphoxide. In addition, the IR spectra for the substrate methionine and the produce was taken using the SHIMADZU IR – 480 Infrared spectrometer ranging from 4500 – 500 cm<sup>-1</sup>:

#### Methionine:

No. of vibration modes	Wave number (cm <sup>-1</sup> )
NH <sub>3</sub> <sup>+</sup> (ν – stretch) (b)	3155.65
COO <sup>-</sup> (s)	1613.51
C – S (ν – stretch)	6739.93

#### Product:

No. of vibration modes	Wave number cm <sup>-1</sup>
NH <sub>3</sub> <sup>+</sup> (ν – stretch) (b)	3170.11

S = O (b) (v-stretch)	1030.02
C— S (v-stretch)	655.82

The shift in the  $\text{NH}_3^+$ , C—S bands and appearance of a new peak at  $1312\text{ cm}^{-1}$  which is characteristic for S = O. Hence the product was formed.

#### 4. Conclusion

Chromium (IV) complex was prepared by the procedure reported in the literature and it was characterized by UV spectroscopy. Kinetics and mechanism of oxidation of methionine by Cr (IV) in water follows first order kinetics with respect of oxidant. There of the reaction with respect of substrate in different solvent was found to be first order. Thermodynamic parameters were calculated. The increase in the acetic acid content of the medium was increased the rate of the reaction. The rate of the reaction was increased by increasing the ionic strength of the reaction. Stoichiometry of the reaction was found to be 2:1 ((Chromium (IV): Methionine)).

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