

Kinetics and Mechanism of Chromium (VI) Oxidation of Threonine in Aqueous Perchloric Acid Medium

Shanu Mathur¹, Dhan Raj², Manju Bala Yadav³, Vijay Devra⁴

Lecturer, Department of Chemistry, Maa Bharti P.G. College, Kota, India¹

Lecturer, P. G. Department of Chemistry, Govt. College, Kota, Kota, India²

Associate Professor, P. G. Department of Chemistry, Govt. College, Kota, Kota, India³.

Associate Professor, P. G. Department of Chemistry, Govt. J. D. B. P. G. Girls College, Kota, India⁴

ABSTRACT: The present paper describes the kinetics and mechanism of oxidation of threonine by chromium (VI) in aqueous perchloric acid medium at 45°C. The reaction is first order with respect to oxidant, substrate and acid concentration. The effect of chloride ion and ionic strength were found to be negligible. The dependence of rate on temperature has been studied and activation parameters have been evaluated and tend further support to the proposed mechanism. 2-Hydroxy propanaldehyde was identified as the oxidation product

KEYWORDS: Kinetics, mechanism, oxidation, threonine, chromium (VI), perchloric acid.

I. INTRODUCTION

Chromium has frequently and extensively been employed as an oxidizing agent both for preparative as well as analytical methods in chemistry. Chromic acid, aqueous dichromate, chromyl chloride, chromyl acetate and other substituted chromates have been employed in oxidation of organic as well as inorganic compounds in aqueous acid and alkaline media. It is the reason for which the analytical chemists in general and kineticists in particular are attracted to know more about such an interesting chemistry of this reagent¹⁻¹⁰. To understand the mechanistic aspect of reduction of Cr (VI) to Cr (III), several kinetics studies of chromic acid oxidation of different types of organic substrates have been carried out by different workers¹¹⁻¹³. In general, the reduction of chromate is assumed to occur via the initial formation of an intermediate complex. In acidic solution the intermediate may decompose by an acid-catalyzed pathway where the initial process in the reduction of chromate is likely to be a one electron step to chromium (V). In neutral solution the intermediate reacts with a second molecule of substrate in which a two electron step to chromium (IV) predominates. The 3-electron reduction of Cr (VI) to Cr(III) may proceed in different possible way through the formation of different intermediate like Cr(V), Cr(IV) and Cr(III). The mechanism path of this reduction depends upon the nature of the reductant and reaction conditions¹⁴. This paper discusses the importance of redox process. Threonine is an essential amino acid classified as non-polar and forms active sites of enzymes and helps in maintaining proper conformation by keeping them in proper ionic states. Amino acids can undergo many kinds of reactions, depending upon whether a particular amino acid contains non-polar substituent. Hence oxidation of threonine may help in understanding reactivity towards chromium (VI) in acid medium^{15, 16}. In this paper, efforts have been made to determine the kinetic orders with respect to each reactant and to propose a suitable reaction path for the oxidation of Threonine.

II. MATERIAL AND METHOD

All chemicals were commercially available and used directly as received from manufacturer. The stock solution of chromium (VI) was obtained by dissolving a known weight of potassium dichromate (AR) in double distilled water and its concentration was checked iodometrically. The standard solution of Threonine (AR) was freshly prepared with

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 3, Issue 11, November 2014

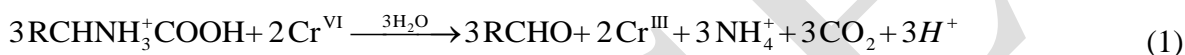
double distilled water. The ionic strength was kept constant with NaClO₄ (AR). The standard solution of NaClO₄ (AR) was used to maintain the required acidity. The Cr(III) solution was prepared by dissolving Cr₂(SO₄)₃·K₂SO₄·24H₂O (BDH) in double distilled water.

Reactions were carried out taking all other ingredients except chromium (VI) in glass stoppered Erlenmeyer flasks immersed in water bath at 45±0.1°C. The reaction was initiated by adding a known volume of pre-equilibrated chromium(VI) solution. The kinetics of the reaction was monitored at 360 nm in a 1 cm cell placed in the thermostated compartment of a UV-visible spectrophotometer (UV win 2000⁺). The kinetics was studied under pseudo first order conditions. Triplicate rate measurements were reproducible within ± 5%

III.RESULT AND DISCUSSION

Stoichiometry and product analysis

The stoichiometric reactions of different sets of concentration of reactants with fixed concentration of other reaction ingredients were allowed to occur in thermostatic water bath at 45±1°C. The remaining chromium(VI) was analysed by measuring absorbance at 360 nm. The results indicated that two moles of chromium(VI) were consumed to oxidise three moles of threonine to produce 2-hydroxy propanaldehyde, carbon dioxide, ammonia and chromium(III). The observed stoichiometry may be represented by equation (1).



Threonine R= CH(OH)CH₃

The product chromium(III) was identified by recording its absorbance at 570 nm and aldehyde was detected quantitatively by 2,4 DNP test¹⁷. The yellow precipitate of 2,4-dinitrophenylhydrazone of aldehyde product was obtained. Ammonia and carbon dioxide were detected by the conventional tests. However, it was also observed that aldehyde does not undergo further oxidation in the same experimental conditions and the test for the corresponding acid was negative.

The reaction orders have been determined from the slope of log k' versus log concentration plots by different concentrations of oxidant, substrate and acid in turn while keeping others constant. The chromium (VI) concentration was varied from 1.0 × 10⁻⁴ - 1.0 × 10⁻³ at fixed concentration of perchloric acid 0.5 mol dm⁻³, ionic strength 1.5 mol dm⁻³ at three concentration of threonine 1.0 × 10⁻², 2.0 × 10⁻², 3 × 10⁻² at 45°C. Pseudo first order plots for the variation of chromium (VI) at 2.0 × 10⁻² mol dm⁻³ concentration of threonine are given in (Fig. 1).

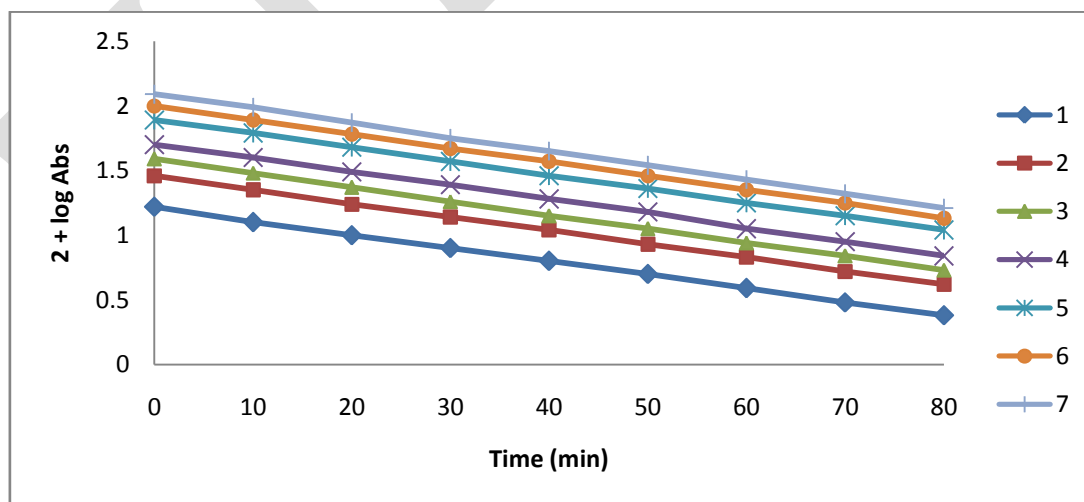


Fig. 1 Pseudo First Order Plots For The Variation Of Chromium(VI)

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 3, Issue 11, November 2014

Thr] = $2.0 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{H}^+] = 0.5 \text{ mol dm}^{-3}$, Temp. = 45°C , $[\text{Cr(VI)}] = (1) 1.0 \times 10^{-4} \text{ mol dm}^{-3}$, (2) $2.0 \times 10^{-4} \text{ mol dm}^{-3}$, (3) $3.0 \times 10^{-4} \text{ mol dm}^{-3}$, (4) $4.0 \times 10^{-4} \text{ mol dm}^{-3}$, (5) $6.0 \times 10^{-4} \text{ mol dm}^{-3}$, (6) $8.0 \times 10^{-4} \text{ mol dm}^{-3}$, (7) $10.0 \times 10^{-4} \text{ mol dm}^{-3}$

The order with respect to chromium(VI) was found to be unity (Table-1). The substrate (threonine) concentration was varied from 1.0×10^{-2} to $7.5 \times 10^{-2} \text{ mol dm}^{-3}$ at three concentration of Cr(VI) viz 6.0×10^{-4} , 8.0×10^{-4} , $10.0 \times 10^{-4} \text{ mol dm}^{-3}$ at 45°C keeping all other conditions constant. The order with respect to threonine was found to be unity (Table-1). At constant ionic strength $I = 1.5 \text{ mol dm}^{-3}$ and other conditions remaining constant, the rate was found to increase with increasing perchloric acid concentration (Table-1). The order with respect to perchloric acid concentration was found to be unity.

Table-1: Effect of variation of chromium(VI), threonine and perchloric acid in the reaction of chromium(VI) and threonine in acid medium at $I = 1.5 \text{ mol dm}^{-3}$ at 45°C .

$10^4[\text{Cr(VI)}], \text{mol dm}^{-3}$	$10^2[\text{Thr}], \text{mol dm}^{-3}$	$[\text{HClO}_4], \text{mol dm}^{-3}$	$10^4(k_{\text{obs}}), \text{sec}^{-1}$
1.0	1.0	0.5	2.22
2.0	1.0	0.5	2.21
3.0	1.0	0.5	2.20
4.0	1.0	0.5	2.24
6.0	1.0	0.5	2.20
8.0	1.0	0.5	2.27
10.0	1.0	0.5	2.20
1.0	2.0	0.5	4.00
2.0	2.0	0.5	4.04
3.0	2.0	0.5	4.08
4.0	2.0	0.5	4.03
6.0	2.0	0.5	4.05
8.0	2.0	0.5	4.07
10.0	2.0	0.5	4.05
1.0	3.0	0.5	6.07
2.0	3.0	0.5	6.05
3.0	3.0	0.5	6.04
4.0	3.0	0.5	6.00
6.0	3.0	0.5	6.06
8.0	3.0	0.5	6.04
10.0	3.0	0.5	6.07
6.0	1.0	0.5	2.20
6.0	2.0	0.5	4.05
6.0	3.0	0.5	6.06
6.0	4.0	0.5	8.45
6.0	5.0	0.5	10.4
6.0	7.5	0.5	15.8
8.0	1.0	0.5	2.20
8.0	2.0	0.5	4.07
8.0	3.0	0.5	6.04
8.0	4.0	0.5	8.45
8.0	5.0	0.5	10.4
8.0	7.5	0.5	15.8
10.0	1.0	0.5	2.20
10.0	2.0	0.5	4.05
10.0	3.0	0.5	6.07

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 3, Issue 11, November 2014

10.0	4.0	0.5	8.44
10.0	5.0	0.5	10.4
10.0	7.5	0.5	15.8
10.0	2.0	0.25	2.01
10.0	2.0	0.5	4.09
10.0	2.0	0.75	6.6
10.0	2.0	1.0	8.9
10.0	2.0	1.25	10.9
10.0	2.0	1.50	13.1

At constant concentration of reactants and other conditions remaining constant, ionic strength was varied between 1.5 to 2.5 mol dm⁻³. The ionic strength was adjusted by the different concentration of NaClO₄. The rate of reaction remains unaffected indicating that the interaction in the rate determining step is not an ion-ion type. The effect of initially added

products Cr(III) was studied in the concentration 0.5×10^{-4} - 4.0×10^{-4} mol dm⁻³, keeping the reactant concentration and all other conditions constant. The rate of reaction is not affected by the reaction product Cr(III), which indicates that the product is not involved in a pre-equilibrium step.

When the reactant concentration and other conditions were kept constant, ions such as Na⁺, NO₃⁻, Cl⁻ did not have any effect on the rate of reaction whereas Mn²⁺ decreases the rate of reaction.

The effect of temperature from 40°C to 50°C on the rate of reaction was studied at fixed concentration of components viz. [Cr(VI)] = 1.0×10^{-3} mol dm⁻³, [Thr] = 2.0×10^{-2} mol dm⁻³, [H⁺] = 0.5 mol dm⁻³, I = 1.5 mol dm⁻³. A plot of log k_{obs} versus 1/T was made that yielded a straight line with negative slope (**Fig. II**).

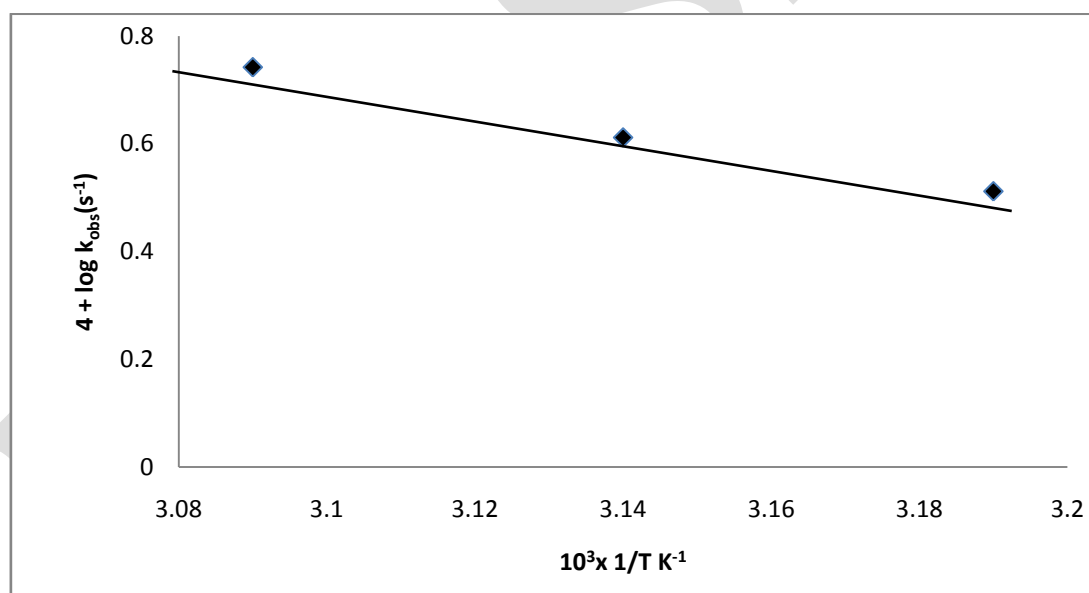


Fig. II. Plot of log k_{obs} versus 1/T

[Cr(VI)] = 1.0×10^{-3} mol dm⁻³; [Thr] = 2.0×10^{-2} mol dm⁻³; [H⁺] = 0.5 mol dm⁻³; (I) = 1.5 mol dm⁻³

From the slope of graph obtained, the value of energy of activation and other activation parameters have been evaluated.

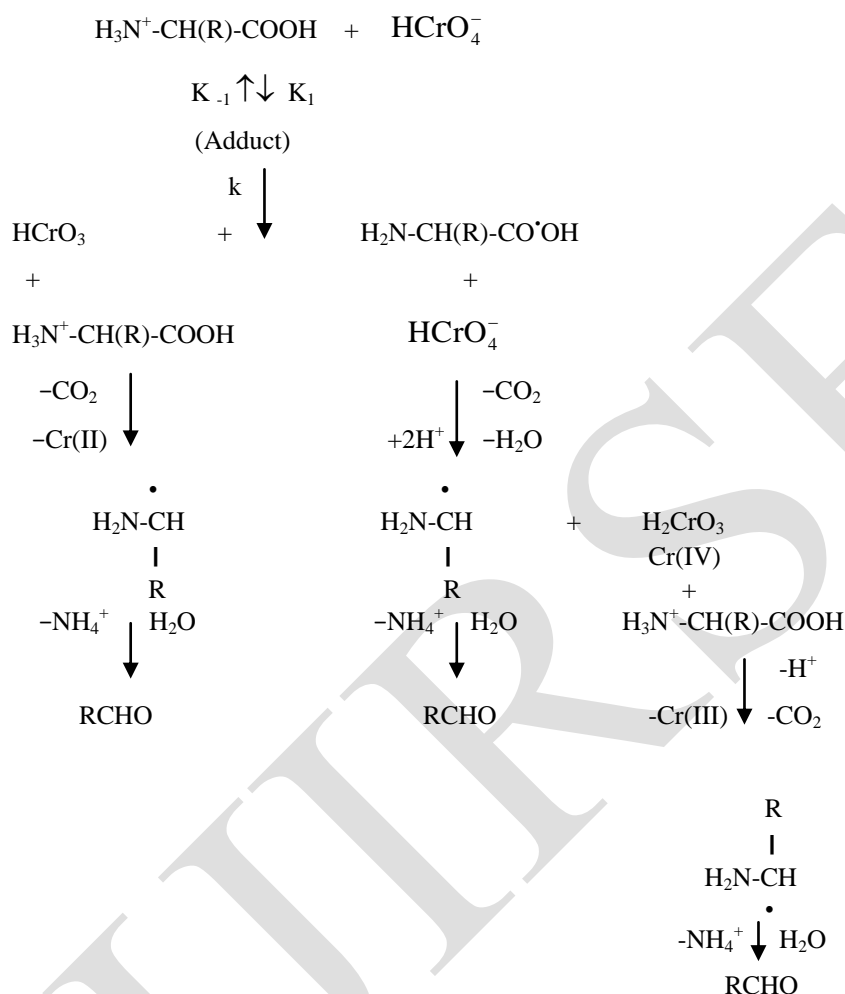
The stoichiometry of the oxidation of threonine by Cr(VI) is found to be 3:2. It has been emphasised in the reactions of chromium (VI) that the recognition of the effective oxidant species is necessary. Cr(VI) is known to participate in acid base equilibria and exist in aqueous acid solution in a variety of forms such as CrO₄²⁻, HCrO₄⁻, HCrO₃⁺, and dimeric

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 3, Issue 11, November 2014

species $\text{Cr}_2\text{O}_7^{10}$. Under the present experimental conditions, the chromium (VI) species involved in the reaction seems to be HCrO_4^- . The results suggest that first order dependence with threonine and Cr(VI) and linear increase in oxidation rate with acidity, suggested the involvement of HCrO_4^- in the prior equilibrium step. There have been earlier reports of the involvement of such species in chromic acid oxidation⁹. HCrO_4^- react with threonine to form a complex. Then complex decompose in a rate determining step to form the free radical of amino acid and intermediate Cr(V). This step further followed by subsequent fast steps leads to the products.



Scheme I

Since oxidation of threonine by Cr (VI) is a non complementary reaction, It may occur by the intervention of reactive chromium and chromium(IV) species. The intervention of chromium(V) is evident from the induction experiment with iodide¹⁸. The induced oxidation of iodide yields two equivalent of iodine for each equivalent of the inductor oxidized. The induction factor for iodide oxidation is nearly two, which indicates that the active oxidizing agent is pentavalent chromium. The intervention of chromium(IV) is evident from the progressive rate decrease in the presence of increasing amount of added manganese(II). Addition of reaction mixture to aqueous acrylonitrile threonine solution initiates polymerization indicating the possibility of formation of free radical species during the reaction. Scheme I accounts for the observed experimental results which leads to rate law (2) to (8)

$$\text{Rate} = k[\text{C}] \quad (2)$$

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 3, Issue 11, November 2014

Applying steady state approximation to the complex C

$$\frac{-d[\text{Cr}^{\text{IV}}]}{dt} = K_1[\text{Cr(VI)}][\text{Thr}][\text{H}^+] - K_{-1}[\text{C}] - k[\text{C}] = 0 \quad (3)$$

$$K_1[\text{Cr(VI)}][\text{Thr}][\text{H}^+] = [\text{C}][K_{-1} + k] \quad (4)$$

$$[\text{C}] = \frac{K_1[\text{Cr(VI)}][\text{Thr}][\text{H}^+]}{K_{-1} + k} \quad (5)$$

$$\text{Rate} = \frac{k K_1[\text{Cr(VI)}][\text{Thr}][\text{H}^+]}{K_{-1} + k} \quad (6)$$

$$k_{\text{obs}} = \frac{\text{Rate}}{[\text{Cr(VI)}]} = \frac{k K_1[\text{Thr}][\text{H}^+]}{K_{-1} + k} \quad (7)$$

Equation (7) can be rearranged as

$$\frac{1}{k_{\text{obs}}} = \frac{K_{-1}}{k K_1[\text{Thr}][\text{H}^+]} + \frac{1}{K_1[\text{Thr}][\text{H}^+]} \quad (8)$$

The rate law (8) is in consistent with the experiment results. From the Arrhenious plots, activation energy 44.61 kJ mol⁻¹, entropy = -175.38JK⁻¹ mol⁻¹ and free energy 108.31 kJ mol⁻¹ were calculated. The negative entropy of activation (ΔS^\ddagger) indicates that involvement of rigid associates species in the transition state, which might form due to solvation, lowering the entropy of activation. Further threonine react with Cr(IV) through proposed mechanism, this is clearly indicated by the positive value of ΔH^\ddagger and ΔG^\ddagger .

IV. CONCLUSION

From the above study we concluded that the chromium (VI) oxidation of threonine in perchloric has the stoichiometry 2:3 in oxidant to reductant. The reaction is very slow at room temperature. However the reaction occurs in measureable quantities at 45°C. The order with respect oxidant, substrate, and acid are found to unity. The oxidant chromium(VI) exist in acid media as HCrO_4^- , which takes part in the reaction. The decomposition of complex is the slow step followed by fast steps to give the products. The derived mechanism is consistent with all experimental results.

REFERENCES

- Chellamni, A. and Rajarajeswari, "Mechanisms of Picolinic Acid Catalyse Chromium (VI) Oxidation of Phenoxyacetic acid", *Afinidad*, Vol. 56, pp. 322-324, 1999.
- Karunakaran, C. and Suresh, S., "Oxidation of Organic sulphides with Nicotinium Dichromate", *Chem. J. Res.*, Vol. 5, pp. 114-115, 2000.
- Signorella, S.R., Santoro, M.L., Mulero, M.N., and Sela, L.F., "Kinetics and Mechanisms of the reduction of Cr (VI) and Cr (V) by lactobionic Acid", *Can. J. Chem.*, Vol. 72, pp. 398-402 1994.
- Abid, M., and Khan, Z., "The effect of Complexing agent on the DMF-Chromium (VI) reaction, A Kinetic Study", Vol. 28, pp. 79-84, 2003.
- Chimatadar, S.A., Basavaraj, T. and Nandibewoor, S.T., "Kinetics and Mechanism of Chromium (VI) Oxidation of mercury (I) in aqueous sulphuric acid", *Oxid. Comm.*, Vol. 26, pp. 88-94, 2003.
- Kabir- Ud- din, Marshad, A. M. A., and Khan, Z., "Role of Manganese (II), micelles and inorganic salts on the Kinetics of the redox reaction of L-Sorbose and Chromium (VI)", *J. Chem. Kinet* Vol. 35, pp.543-544, 2003
- Levina, L., and Lay, P.A., "Zero field splitting in metal complexes", *Cood. Chem. Rev.*, Vol.249, pp. 281-298, 2005.
- Santoro, M., Caffaratti, E., Salas pelegrin, J.M., Koreez, L., Rockenbauet, A., Sala, L.F., and Signorella, S., "Kinetics and Mechanism of the chromic Oxidation of myo-inositol", *Polyhedron*, Vol. 26, pp. 169-177, 2007.
- Naik, P.N., Chimatadar, S.A. and Nandibewoor, S.T., "A Kinetic and Mechanistic study of oxidation of tyrosine by Chromium (VI) in acid perchloric medium", *Trans. Met. Chem.*, Vol.33, pp. 405-410, 2008.
- Sharma, S., Sailani, R., Khandelwal, C.L. and Sharma, P.D., "Kinetics and Mechanisms of electron transfer reaction oxidation of dimethyl sulphoxide by Chromium (VI) in acid medium", *Indian Chem. Soc.*, Vol.89, pp. 393-399, 2012.
- Gonzalaz, J.C., Garvia, S., Mamana, N., Sala, L.F. and Sinorella, S.J., "Evidence for the involvement of Cr(II) and free radicals as

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 3, Issue 11, November 2014

- intermediates in the reduction of HCrO_4^- by saccharides, alcohols and hydroxyacids," *Inorg. Chem. Commun.*, Vol. 9, pp. 437-440, 2006.
12. Chimatadar, S.A, Koujalagi, S.B. and Nandibewoor, S.T., "Kinetics and Mechanism of Palladium (II) Catalysed Chromium (VI) Oxidation of mercury (I) in aqueous sulphuric acid", *Trans. Met. Chem.*, Vol.26, pp.662-667, 2001.
 13. Bayer Ruhidas and Das Asim K., "Kinetics and Mechanisms of Oxidation of D-Galactose by Chromium (VI) in presence of 2,2 bipyridine catalyst in aqueous micellar media", *The Open Catalysis Journal*, Vol.2, pp.71-78, 2009.
 14. Mahanti, M.K, Banerji, K.K, "Synthetic and mechanistic aspects of reactions of complexed Chromium(VI) compounds", *J. Indian Chem. Soc.*, Vol. 79, pp. 31-44, 2002.
 15. Mahanti, M.K. and Laloo, D., "Kinetics and Oxidation of amino acid by alkaline hexocyanoferrate (III)", *J. Chem. Soc. Dalton Trans.*, pp. 311-314, 1990.
 16. Choregale, R.B., Hiremath, G.A. and Nandibewoor, S.T., "Kinetics and Mechanism of oxidation of L-alanine by alkaline permanganate", *Polish Journal Chem.*, Vol.71, pp. 471-478, 1997.
 17. Jeffery, G.H., Bassett, J.J., Mendham, J. and Danney, R.C., "Vogels text book of quantitative chemical analysis", 5th ed., ELB, Longman, Essex England, pp. 375, 1996.
 18. Wiberg, K.B., *Oxidation in organic chemistry*, Academic press, Newyork, part A, pp. 69, 1965.