Kinetic Study of Oxidation of Some Amino Acids by Various Oxidants of Chromium: A Review

Dhan Raj
Assistant Professor,
Department of Chemistry, Government College Kota, Rajasthan, India.

Abstract

Oxidation of amino acids is of great importance both from a chemical viewpoint and from its bearing on the mechanisms of amino acid metabolism. The reagent hexavalent chromium is one of the most strongly oxidizing agents in chemistry and industry and immensely useful. The main aim of this paper is to briefly summarize and explore the available literature on oxidation of amino acids by chromium (VI) reagents and encourage its various contributions to the importance and exciting field of oxidation of amino acids in organic chemistry.

Keywords: Oxidation, Chromium (VI), Amino Acids, Chemical Kinetics.

Introduction:

Chemical kinetics is a branch of physical chemistry that deals with the study of rate of the reaction and therefore the varied factors which may hamper the yield of overall reaction. It includes empirical studies of the impact of the concentration, temperature and hydrostatic pressure on reaction of various types. Such studies may be much vital in concentration with technical processes. The rate of reaction always depends on the temperature at which it is run and usually depends on the concentrations of the reactants. Because of this latter fact, the rate of a reaction will usually change during the course of the reaction, the reactants get used up and their concentrations fall. The rate of a reaction at a particular temperature often depends solely on the concentrations of the reactants present.

Amino acids are the building blocks in protein synthesis. In metabolism, amino acids are subjected to many reactions, and can supply precursors for various endogenous substances, as for example, hemoglobin in blood. Amino acids undergo various kinds of reaction, depending on whether the particular amino acids contain non-polar groups, polar substituent, acidic or basic substituent.

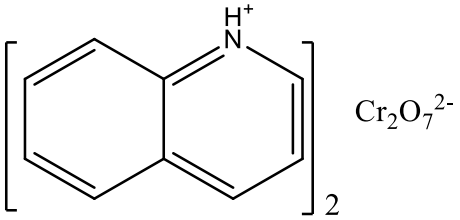
The study of amino acids is one of the most exciting fields of organic chemistry. They play a significant role in a number of metabolic reactions like biosynthesis of polypeptide, protein and nucleotides. Thus, the mechanism of analogous non enzymatic chemical processes in the oxidation of amino acids is a potential area for intensive investigation[1] in order to understand some aspects of enzyme kinetics.

The oxidation of amino acids is of interest as the oxidation products differ for different oxidants[2]. Amino acids have been oxidized by a variety of reagents under different experimental conditions [3-7]. Anajali Goel and coworker[8] studied the kinetic and mechanistic study on the oxidation of arginine and lysine by hexacynoferrate (III) catalysed by iridium (III) in aqueous alkaline medium. Kinetic studies and mechanism on the permanganic oxidation of L-Glutamine in strong medium in the presence and absence of sliver (I) has been stidied[9]. Mansoor et al.[10] has been reported the kinetics oxidation of methionine by tetra ethyl ammonium chlorochromate in non-aqueous media.

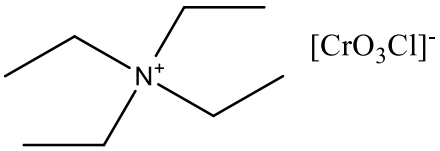
Chromium is one of the most widely distributed heavy metals and is the twenty-first most abundant element in the earth's crust. Chromium (VI) is considered as an important reagent in organic synthesis and has been used in aqueous and non aqueous medium for the oxidation of organic compounds[11-13]. It is difficult to study from mechanistic point of view that the oxidation reaction of Cr (VI) is a complex reaction that is influenced by the solvent used in the reaction, structure of the substrate, temperature and pH of the reaction medium and other factors. In various oxidation reaction reactions Cr (VI) reduced to Cr (V) and Cr (IV) intermediate species, the chemistry of these intermediate species attracted many researchers because of their involvement in the mechanism of chromium induced cancer[14]. Nowadays the development of newer chromium (VI) reagents [15-16] for the oxidation of organic substrates continues to be a subject of interest.

A number of new chromium (VI) containing compounds like quinolinium dichromate[17], pyridinium flourochromate[18], tetraethylammonium chlorochromate[19], morpholinium chlorochromate[20], cetyltrimethylammonium dichromate[21], quinolinium chlorochromate[22], quinolinium fluorochromate[23],

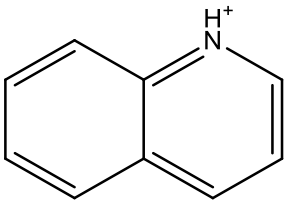
dipyridine chromium (VI) oxide[24], 2,2'-Bipyridinium Chlorochromate[25], 2,6-dicarboxypyridinium chlorochromate[26], tetramethylammoinium fluorochromate (VI)[27], cetyltrimethylammonium bromochromate[28]. The structure some of these oxidizing agents are given below:

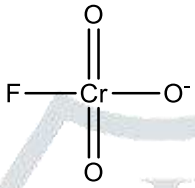


Quiloninium dichromate

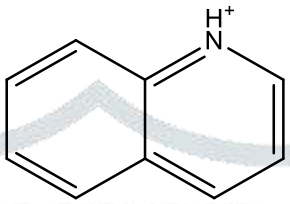


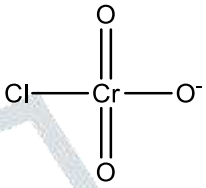
tetraethylammonium chlorochromate



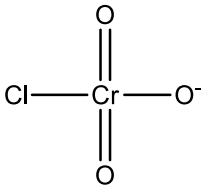


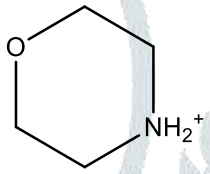
quinolinium fluorochromate



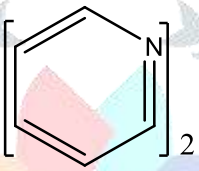


quinolinium chlorochromate

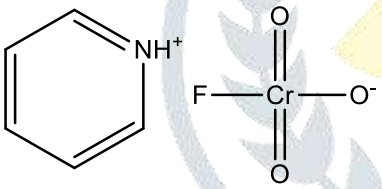




morpholinium chlorochromate



dipyridine chromium (VI) oxide



pyridinium fluorochromate

Mansoor et al[29] have investigated a kinetic and mechanistic study of oxidation of aliphatic alcohols by triethylammonium chlorochromate in non-aqueous medium. triethylammonium chlorochromate is more efficient and strong oxidizing reagent and more efficient for quantitative oxidation of several organic substrates and has certain advantages over similar oxidizing reagents in terms of the amount of oxidant and solvent required, short reaction times and high yield. Ghamami and coworker[30] has been reported the oxidation of organic substrates by tetraphenyl phosponium halochromate (IV).They reported that by tetraphenyl phosponium halochromate (IV) is efficient and mild reagent for the oxidation of organic substrates. The results obtained with tetraphenylphosphonium halochromates are very satisfactory and show the new reagents to be a valuable addition to the existing oxidizing agents. They concluded that the inequality between the Cr-O and the Cr-X bonds are responsible for the higher reactivity. They have also been found that these reagents have certain advantages over similar oxidizing agents in terms of the amounts of oxidants and solvent required, and especially in the short reaction times required and in the higher yields of the product.

Oxidation of Amino acids

A kinetic study of oxidative decarboxylation and deamination of essential amino acids like isoleucine, threonine, valine, phenylalanine, leucine and histidine by nicotinium dichromate in presence of perchloric acid medium at 313 K was reported by vivekanandan and Narayanan[31]. The reaction product was identified

corresponding aldehyde. The stoichiometry of the reaction showed that one mole of amino acid consumed by one mole of the oxidant. The pseudo first order conditions were maintained by a large excess of the substrates over nicotinium dichromate. They observed that the reaction was first order with respect to nicotinium dichromate, the order with respect to amino acids was less than unity and second order with respect to perchloric acid. There has no effect of ionic strength and addition of sodium perchlorate on rate constant. The reaction has been studied at different temperatures and a suitable mechanism is proposed by evaluating reaction constants and calculating activation parameters.

$$NDC+H^+ \overset{K_1}{\rightleftharpoons} NDCH^+$$

$$S+H^+ \overset{K_2}{\rightleftharpoons} SH^+$$

$$NDCH^+ + SH^+ \xrightarrow[\text{slow}]{K_3} [\text{complex}]$$

$$[\text{complex}] \xrightarrow[\text{fast}]{K_4} RCHO+Cr\ (IV)$$

Mathur and coworker[32] studied oxidation of lysine by chromium (VI) in acid perchlorate medium. They were used potassium dichromate as oxidant. The oxidation product was identified as chromium (III) and 5-aminopentanaldehyde. The reaction order with respect to chromium (VI) was followed first order kinetic and less than unit order in lysine concentration. The rate of reaction is accelerated with increase concentration of acid. The ionic strength and added products did not have any significance effect on the reaction. In the stoichiometry of the reaction the results indicated that two moles of chromium (VI) were consumed with three moles of lysine. The results of the reaction suggested that H_2CrO_4 react with lysine to form complex which decomposes in the rate determining step to give intermediate chromium (VI) species and product, in the next step acid chromate H_2CrO_4 react with lysine and form other moles of intermediate chromium (IV) and product. In the further step two moles of Cr (VI) reacts with one mole of lysine to give final product and Cr (III). A possible mechanism based on the kinetic results and product analysis has been proposed for the reaction.

$$HCrO_4^- + [H^+] \overset{K_1}{\rightleftharpoons} H_2CrO_4$$

$$H_2CrO_4 + RCHNH_2COOH \overset{K_2}{\rightleftharpoons} \text{Complex(C)}$$

$$\text{complex(C)} \xrightarrow[k]{\text{slow}} RCHO+H_3CrO_4^- + CO_2 + NH_3 + H^+$$

$$H_2CrO_4 + RCHNH_2COOH \xrightarrow{fast} RCHO+H_3CrO_4^- + CO_2 + NH_3 + H^+$$

$$2H_3CrO_4^- + RCHNH_2COOH \xrightarrow{fast} RCHO+CrO_2^- + CO_2 + NH_3$$

Kinetics and mechanism of the oxidation of DL-methionine by imidazolium dichromate in dimethyl sulfoxide has been investigated[33]. The reaction was found first order with respect to imidazolium dichromate and the reaction product was identified as corresponding sufoxides. In the mechanism of reaction the Michaelis-Menten type of kinetic observed with respect to methionine.

$$\text{Me-S-R+IDC} \overset{K}{\rightleftharpoons} [\text{Complex}]$$

$$[\text{Complex}] \xrightarrow{K_2} \text{Products}$$

$$\text{Rate} = k_2K\ (\text{Me-S-R})\ (\text{IDC})/\ 1+K\ ([\text{Me-S-R}])$$

Pandey and Khotari[34] also reported the kinetics and mechanism of the oxidation of DL-methionine by benzimidazolium dichromate in dimethyl sulfoxide. The order of the reaction was found to be first order with respect to benzimidazolium and the order with respect to methionine less than one. Michaelis-Menten type of kinetic observed with respect to methionine. Activation parameters were calculated at different temperature. The product analysis and stoichiometric determination revealed that the oxidation of methionine resulted in the formation of the corresponding sulfoxide.

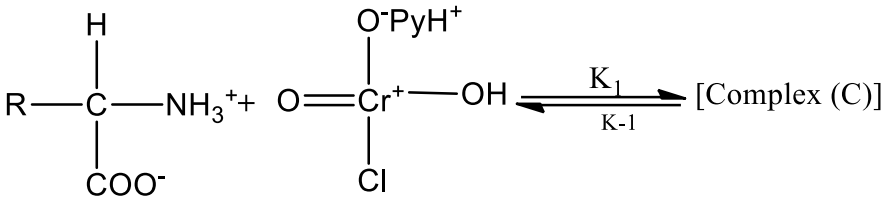
$$MT+BIDC \overset{K}{\rightleftharpoons} [\text{Complex}]$$

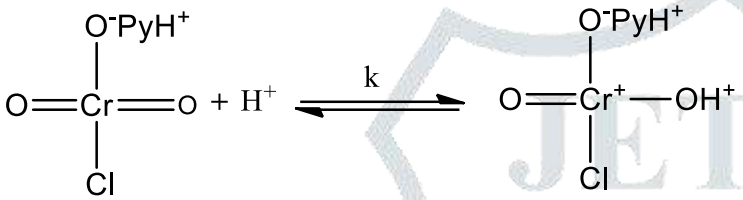
$$[\text{Complex}] \xrightarrow{K_2} \text{Products}$$

$$\text{Rate} = k_2K\ (MT)\ (BIDC)_t\ /1+K\ ([MT])$$

Where, $(BIDC)_t$ = [BIDC] + [Complex]

Pyridinium chlorochromate being one of the most available versatile oxidant agent[35]. A kinetic study of oxidation of phenyl alanine by pyridinium chorochromate in acidic DMF-water medium was reported by Hiran et al[36]. The reaction was investigated under pseudo first order conditions in the DMF–water solvent system at 313 K. They determined the stoichiometry of the reaction and found that three mole of amino acid consumed two mole of Cr (VI). The reaction was of first order each in pyridinium chorochromate, [$HClO_4$] and phenyl alanine concentrations.





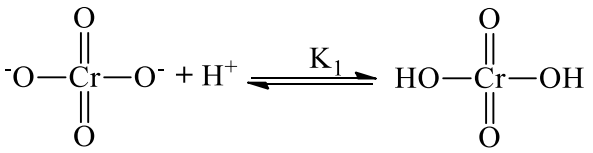
$$[\text{Complex(C)}] \xrightarrow[k']{\text{slow}} RCHO + NH_4^+ + CO_2 + Cr(IV)$$

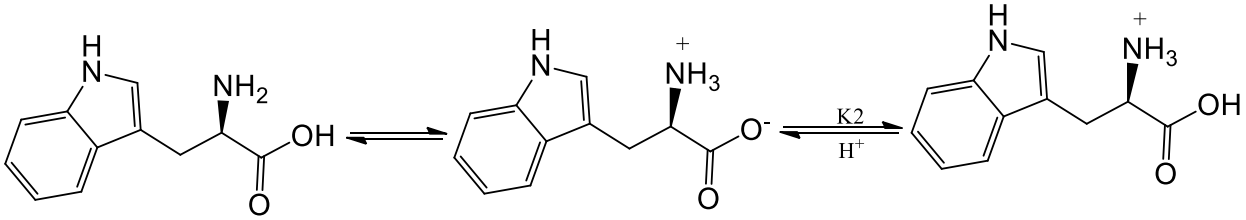
$$2Cr\,(V) + 2RCH(NH_2)COOH + 2H_2O \xrightarrow{\text{fast}} 2RCHO + 2CO_2 + 2NH_4^+ + 2Cr(III) + 2H^+$$

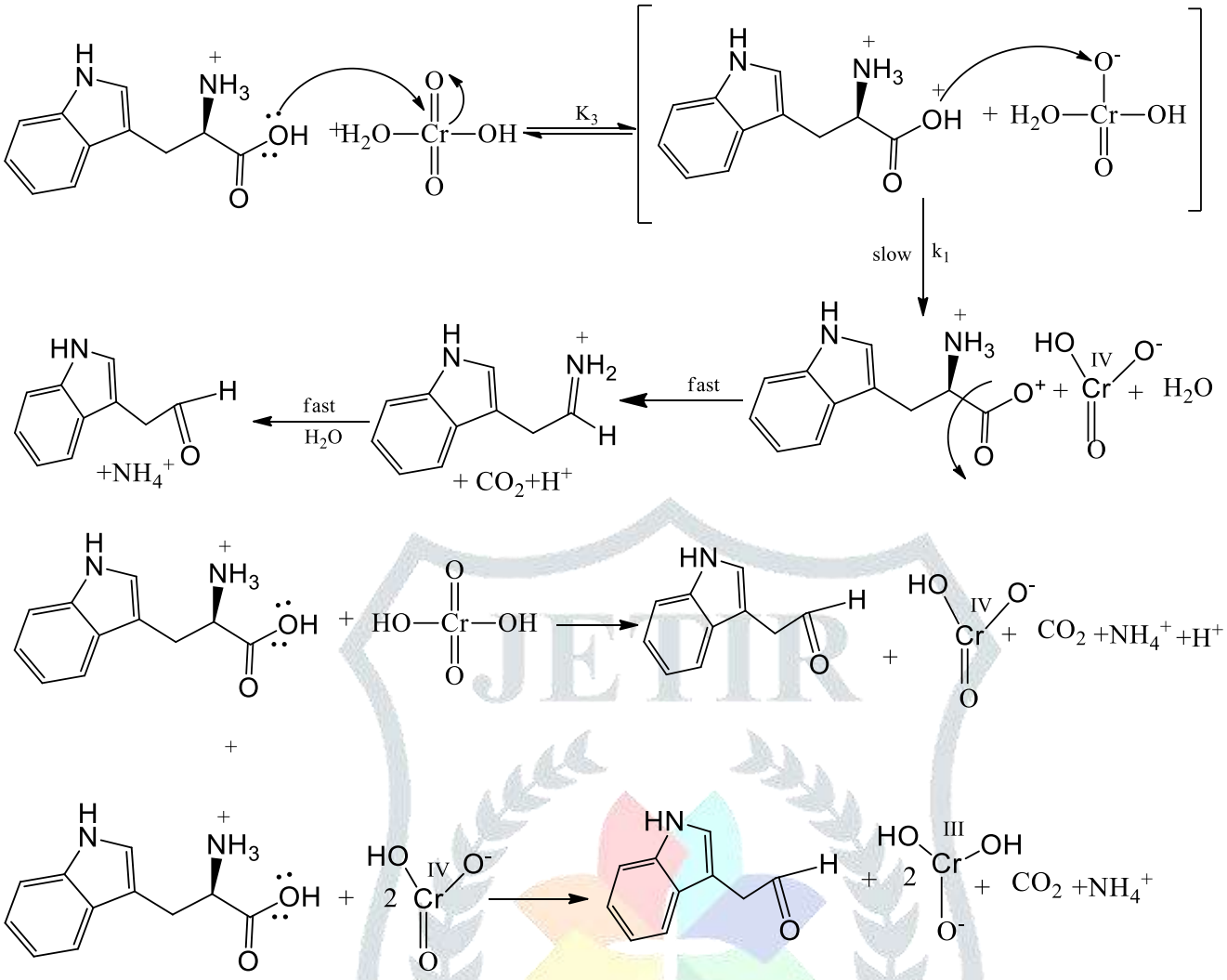
[PCC]

On the basis of above proposed mechanism they suggested that in the reaction of oxidation of phenyl alanine by PCC in DMF-water media in pecrchloric acid the neutral amino acid takes part in the reaction, protonated amino acid was not involved in the reaction.

The kinetics and mechanistic study of oxidation of L-tryptophane by chromic acid in sulphuric acid medium at constant ionic strength have been investigated by spectrophotometrically[37]. The reaction was found to be first order with respect to [chromic acid], fractional order with respect to [tryptophane] and fractional-second order with respect to [acid]. The final product of the oxidation reaction were identified as corresponding aldehyde (indol-3-acetyaldehyde), CO_2 and ammonium ion. The stoichiometry of the reaction showed that three moles of tryptophane consumes two moles of chromic acid. The mechanism of the reaction has been proposed and thermodynamic parameters were evaluated.







A comparative study of oxidation of dl-alanine by different Cr (VI) oxidants has been studied in partial non-aqueous medium in the presence of perchloric acid spectrophotometrically by Rathor and Dangarh[38] . The oxidation rate order was found with respect to different oxidants are: QDC > PDC > PCC.

Conclusion

Oxidation is an essential operation in organic synthesis and several reagents have been developed for a wide variety of transformation. Oxidations of various amino acids by chromium (VI) oxidants have been reported in this paper. The compounds of chromium (VI) have played an important role in oxidation reaction in organic chemistry. Amino acids are an important class of organic substrates which play a important role in biochemical processes. This review will hopefully stimulate further application of chromium (VI) reagents as oxidants.

References

1. Yathirajan, H.S., Raju, C.R., Mohana, K.N, Sheena, S. and Padmarajaiah, N. 2003. Kinetics and mechanism of oxidation of L-isoleucine and L-ornithine hydrochloride by sodium N-bromobenzenesulphonamide in perchloric acid medium. Truk. J. Chem. 27: 571-580.
2. Nadh, R.V. and Sireesha, M. 2015. Kinetics and mechanism of Ru (III) catalysed and uncatalysed oxidation of DL-alanine by N-bromosuccinimide. Bul. Chem. Comm. 47:13-21.
3. Goel, A. and Sharma, S. 2010. Mechanistic study of the oxidation of L-phenyl alanine by hexacynoferrate (III) catalyzed by iridium (III) in aqueous alkaline medium. Trans. Met. Chem. 35: 549-554.

4. Penghui, D., Wen, L. Hongbon, C. Zhao, H. and Ching, H.H. 2018. Oxidation of amino acids by peracetic acid: Reaction kinetics pathways and theoretical calculations. Water Res X. 1.
5. Fawzy, A. Guesmi, N. E.I., Ali, H.M. and Abdallah, M. 2018. Oxidation of tryptophan by permanganate ion in acid, Neutral and alkaline media: A comparative kinetic and mechanistic study. J. Mater. Environ. Sci., 9(6): 1645-1665.
6. Vaijayanthi, S.P. and Mathiyalagan, N. 2013. Kinetics of oxidation of amino acids by a newly synthesized oxidant, N-chloropyrazinamide in aqueous acetic medium. Int. Lett. Chem., Phys and Astro.16:1-8.
7. Jose, T.P., Nandibewoor S.T. and Tuwar, S.M. 2006. Kinetics and mechanism of the oxidation of vanillin by hexacynoferrate (III) in aqueous alkaline medium. J. Sol. Chem., 35(1): 51-62.
8. Goel, A. and Sharma, A. 2012. A kinetic and mechanistic study on the oxidation of arginine and lysine by hexacynoferrate (III) catalysed by iridium (III) in aqueous alkaline medium. J. Chem. Eng. Mate. Sci. 3(1):1-6.
9. Iloukhani, H. and Bahrami, H. 1998. Kinetic studies and mechanism on the permanganic oxidation of L-Glutamine in strong medium in the presence and absence of sliver (I). J. Chem. Kinet. 31: 95-102.
10. Mansoor, S.S. and Shafi S.S. 2015. Oxidation of methionine by Tetra Ethyl Ammonium Chlorochromate in Non-aqueous media- A kinetic and mechanistic study. Arabian J. Chem. 8(4): 480-486.
11. Dipti, Tomar, A. and Kumar, A. 2012. Kinetics and mechanistic studies of the oxidation of crotonaldehyde by tetraethylammonium chlorochromate in aqueous acetic acid medium. Oxid. Commun. 35(3): 569-576.
12. Krishnamoorthy, G.S. and Periyasamy, S.K. 2012. Oxidation of α,β-unsaturated alcohols by Quanladinium Florochromate. Int. Lett. Chem. Phys. Astron. 5: 8-19.
13. Bhupendra, A.M.B. and Hiran, B.L. 2012. Kinetics and mechanism of oxidation of benzaldehyde and 4-nitrobenzaldehyde by pyridinium dichloromate in aquo-acetic acid medium. 35(3): 560-568.
14. Costa, M. 1997. Toxicity and Carcinogenicity of Cr (VI) in animal models and humans, Crit. Rev. Toxicol. 27: 431:442.
15. Corey, E.J. Barette, M. and Magriotis, P.A. 1985. A new Cr (VI) reagent for the catalytic oxidation of secondary alcohols to ketones. Tetrahedron Lett. 26:5855-5858.
16. Reddy, P.S., Yadagiri, P., Lumin, S., Shin, D.S. and Falck, J.R. 1988. Modified pyridinium chlorochromate oxidation of aldehydes to carbonyl azides/acyl azides or carboxylic acids. Synthetic Communications, 18(5):545-551.
17. Irona, N. and Mahanti, M.K. 1994. Kinetics and mechanism of the oxidative cleavage of unsaturated acids by quilonium dichromate. Bull. Chem. Soc. Japan, 67(8):2320-2322.
18. Bhattacharjee, M.N. Chaudhuri M.K. Dasgupta, H.S. Roy, N. and Khathing, D.T. 1982. Pyridinium florochromate: a new and efficient oxidant for organic substrates. Synthesis (Stuttg), 7:588-590.
19. Swami, P., Yajurvedi, D., Mishra, P. and Sharma, P.K. 2009. Oxidation of some α-hydroxy acids by tetraethylamonium chlorochromate: a kinetic and mechanistic study. Int. J. Chem. Kinet., 00:1-6.
20. Malani, N., Pohani, S., Baghmar, M. and Sharma, P.K. 2008. Kinetics and mechanism of oxidation of some thioacids by morpholinium chlorochromate. Ind. J. Chem., 47A: 1373-1376.
21. Patel, S., Kuanar M., Nayak, B.B., Banichul, H. and Mishra, B.K. 2005. Cetyltrimethylammonium dichromate: a phase transferring oxidant, Synth. Commun., 35: 1033.
22. Srinivasan, R., Ramesh, C.V., Madhulatha, W. and Balasunbramanian, K. 1996. Oxidation of alcohols by quinolinium chlorochromate. Ind. J. Chem., Sec. B, 35B: 480.
23. Muregesan, V. and Pandurangan, A. 1992. Quinolinium fluorochromate: a new reagent for the oxidation of organic compounds. Ind. J. Chem. Sec. B., 31B: 377.
24. Collins, J.C., Hess, W.W. and Frank, F.J. 1968. Dipyridinium chromium (VI) oxide oxidation of alcohols in dichloromethane. Tetrahedron Lett., 9(30): 3363.
25. Guziec, F.S. and Luzzio, F.A. 1980. The oxidation of alcohols using 2,2'-Bipyridinium chlorochromate. Synthesis, 9: 691.
26. Hosseinzahed, R., Tabakhsh, M. and Yazdani-Niaki, M. 2002. Dicarboxylpyridinium chlorochromate: a mild, efficient and selective reagent for oxidative deprotection of oximes to carbonyl compounds, Tetrahydron Lett., 43: 9413-9416.

27. Kassaee, M.K., Mahjoub, A.R. and Ghammami, S. 2003. Tetramethylammonium fluorochromate (VI): a new and efficient oxidant for organic substrates. Tetrahedron Lett., 44: 4555-4557.
28. Eimanieh, H., Ghammami, S. and Mahammadi, M.K. 2007. Cetyltrimethylammonium bromochromate: a new and efficient oxidant for organic substrates. Synth. Commun., 37:601-605.
29. Mansoor, S.S. and Shafi, S.S. 2014. Oxidation of aliphatic alcohols by triethylammonium chlorochromate in non-aqueous medium- a kinetic and mechanistic study. Arabian J. Chem., 7(3): 312-318.
30. Ghamami, S., Golzani, M. and Lashagri, A. 2016. Three new tetraphenylphosponium halochromate (VI), $[(C_6H_5)_4P]$ $[CrO_3X]$, (X= F, Cl, Br): Efficient and mild reagents for oxidation of organic substrates. Asian J. Res. Chem., 9(5): 193-196.
31. Vivekanandan, K. and Narayanan, R.L. 2015. Oxidative decarboxylation and deamination of essential amino acids by nicotinium dichromate- a kinetic study. Int. Lett. Chem. Phys. Astro., 6: 66-72.
32. Mathur, S., Yadav, M.B. and Devra, V. 2015. Oxidation of lysine by chromium (VI) in acid perchlorate medium: a kinetic study. Int. J. Chem. Sci., 13(2): 641-649.
33. Kharche, A.P., Khandave, P. and Shastri, I.M. 2018. Kinetics and mechanism of the oxidation of DL-methionine by imidazolium dichromate. Int. J. Res. Anal. Rev. 5(1): 269-275.
34. Pandey, D. and Khotari, S. 2009. Kinetics and mechanism of the oxidation of DL-methionine by benzimidazolium dichromate. Prog. Reac. Kinet. Mech. 34: 199-209.
35. Meena, M.L. 2021. Oxidation of Leucine by Pyridinium Chlorochromate in Acidic DMF–Water Medium: Kinetic Mechanistic Studies. Der. Pharmacia. Lett., 13(3):37-41.
36. Hiran, B.L., Meena, M.L., Khuntwal, J. and Lal, K. 2016. Oxidation of phenyl alanine by pyridinium chlorochromate in acidic DMF-water medium: a kinetic study. Arabian J. Chem., 9(2): S1801-S1806.
37. Fawzy, A., Ashour, S.S., Musleh, M.A., Hassan R.M. and Asghar, B.H. 2016. Kinetics and mechanistic approach to the chromic acid oxidation of L-tryptophan with a spectral detection of chromium(III) product. J. Saudi Chem. Soc., 20(4): 450-458.
38. Rathor, S. and Dangarh, B.K. 2017. Comparative study of oxidation of dl-alanine by different Cr (chromium) (VI) oxidants in partial non-aqueous medium. Int. J. Sci. Res., 6(8): 388-389.