



Oxidation of Vicinal diols by Mn(VII) in Aqueous Medium, A Kinetic Study

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ABSTRACT

The kinetics of oxidation of two vicinal diols by potassium permanganate in aqueous solution was studied at λ_{\max} 525 nm. The vicinal diols yielded the carbonyl compounds due to the glycol bond cleavage. The reaction order with respect to KMnO_4 and diol was first order each and independent of the ionic strength of the reaction solution. Michaelis-Menten kinetics was observed with respect to diols. Addition of arylamide did not induce polymerization. Activation parameters were obtained from Arrhenius and Eyring's equations. The stoichiometry showed 1:1 consumption of one of KMnO_4 by diol. Activation parameters like E_a (kJ mol^{-1}), ΔH^\ddagger (kJ mol^{-1}), ΔS^\ddagger ($\text{kJ K}^{-1}\text{mol}^{-1}$), ΔG^\ddagger (kJ mol^{-1}) were 21.29, 18.60, -0.238 and 89.52 respectively for propane-1,2-diol and 25.73, 22.99, -0.22 and 88.55 respectively for Butane-1,2-diol. Same value of ΔG^\ddagger indicates same mechanism and negative values of ΔS^\ddagger indicates an associative mechanism and an orderly transition state. A mechanism involving the cleavage of glycol bond has been proposed based on the FTIR product analysis and spectroscopic data obtained.

Keywords: Butane-1,2-diol, kinetics, mechanism, potassium permanganate, propane-1,2- diol.

INTRODUCTION

Potassium permanganate is a versatile oxidant in many organic and inorganic reactions which has gained prominence in green chemistry [1]. It provides excellent results in both homogenous and heterogenous reactions [2-17]. Evaluation of the kinetic oxidation of volatile organic compounds by permanganate is an important in-situ chemical reaction for the remediation of hazardous volatile organic compounds found in ground water. It has been used for the treatment of liquid, slurry soils and sludges polluted with volatile organic compounds [18]. Several oxidizing agents have been employed for redox reactions of diols [19-27]. However, its redox reaction with permanganate has not been reported in the literature.

Consequently, kinetic parameter of the redox reaction between diols and potassium permanganate is worth exploring with the view to establishing the kinetic data and mechanism of the reaction.

EXPERIMENTAL

Materials and Methodology

Analytical grade potassium permanganate, diols (BDH, USA), potassium nitrate, ferrous ammonium sulphate and sulphuric acid (BDH, USA) were utilized without further purification by preparing their stock solutions in doubly distilled water. Potassium permanganate was standardized using ferrous ammonium sulphate in acidic medium. The kinetic study was undertaken using 1800 UV-Shimadzu Spectrophotometer (Japan) with a thermostated cell compartment and interfaced with a computer.

Kinetic Determination

In all the kinetic runs diol concentrations were kept in excess of potassium permanganate concentrations at 298K. Appropriate quantities of the reaction mixtures were measured into the cuvette and the reaction was started by adding requisite volume of KMnO_4 . All stock solutions were kept in a water bath for 30 minutes before the kinetic runs. The kinetic measurements were done by monitoring decrease in absorbance of KMnO_4 as a function of time at λ_{max} 525 nm. The pseudo-first order rate constant (k_{obs}) were obtained from a plot of $\ln A$ versus time.

RESULTS AND DISCUSSION

Stoichiometry and product study

Stoichiometric study was accomplished via spectroscopic titration at 525nm. The absorbances at infinite time of reaction mixtures containing different initial concentrations of diols in the range 2.66×10^{-3} - 1.07×10^{-2} M at fixed $[\text{KMnO}_4]$ and ionic strength at 3.97×10^{-5} and 6.67×10^{-3} M respectively were obtained. Consequently, the stoichiometry was determined from the plot of Absorbance at infinite time versus $[\text{Diol}]$. Hence, the result obtained showed that one mole of KMnO_4 consumed one mole of diol for the reaction.

Induced polymerization of acrylamide

The oxidation of the vicinal diols by KMnO_4 , in nitrogen atmosphere did not induce polymerization of acrylamide.

Reaction orders

Generally, increase in pseudo-first order rate constant (k_{obs}) with increase in the concentration of $KMnO_4$ was observed and a first order dependence with respect to the concentration of $KMnO_4$ was obtained for each diol (Fig.1). An increase in pseudo-first-order rate constant (k_{obs}) with increase in diol concentration was observed (Table 1) and the slope of $\ln k_{obs}$ versus $\ln [Diol]$ gave 1 for both diols, indicating a first order dependence on the concentration of Diols.

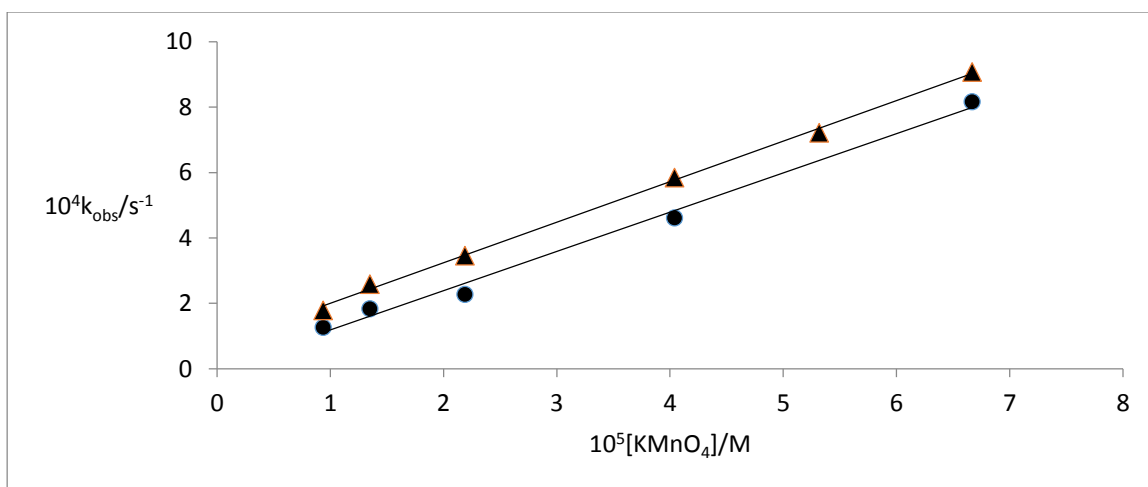


Fig. 1: Effect of $[KMnO_4]$ $[Diol]$ $4.00 \times 10^{-3} M$ $\mu = 6.67 \times 10^{-3} M$ $T = 298 K$
 (\blacktriangle Butane-1,2-diol \bullet Propane-1,2-diol)

Table 1: Effect of $[Diol]$

$10^3 [Diol] / M$	$10^4 k_{obs} / s^{-1}$	
	Propane-1,2-diol	Butane-1,2-diol
2.66	1.30	2.35
	2.34	3.52
4.00	2.87	4.92
5.34	3.67	5.67
6.67	4.08	6.02
8.00	4.66	7.50
9.34	5.12	8.95
10.70		

$[KMnO_4]$ $3.97 \times 10^{-5} M$ $\mu = 6.67 \times 10^{-3} M$ $T = 298 K$

Second order rate constants obtained from the slope of a plot of k_{obs} versus $[Diol]$ was $5.07 \times 10^{-2} M^{-1}s^{-1}$ and $8.25 \times 10^{-2} M^{-1}s^{-1}$ for propane-1,2-diol and Butane- 1,2-diol respectively. Variation of ionic strength of the reaction mixture using KNO_3 did not affect the pseudo-first order rate constant (k_{obs}), implying the participation of a neutral molecule in the reaction. There was a sharp increase in the pseudo-first order rate constant (k_{obs}) with increase in temperature (Fig.2) and activation parameters were obtained from Arrhenius and Eyring's equations and the obtained activation parameters are show in Table 2.

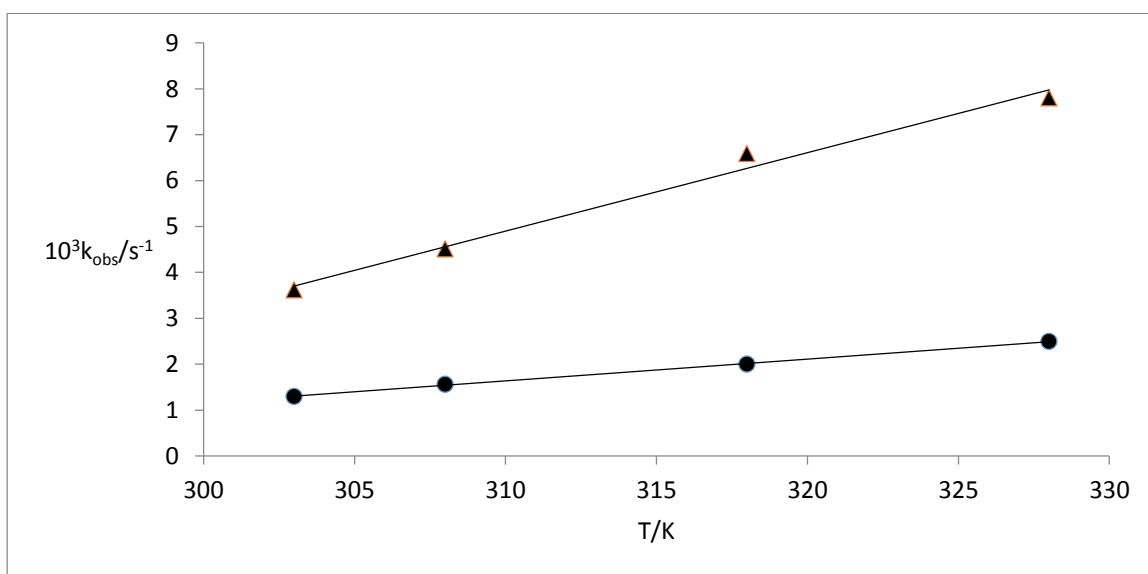


Fig. 2: Effect of Temperature

$[KMnO_4]$ $3.97 \times 10^{-5} M$ $[Diol]$ $4.00 \times 10^{-3} M$ $\mu = 6.67 \times 10^{-3} M$

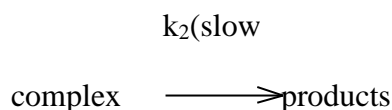
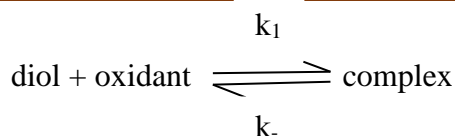
▲ Butane-1,2-diol ● Propane-1,2-diol)

Table 2: Activation parameters

Diol	E_a (kJ mol ⁻¹)	ΔH^\ddagger (kJ mol ⁻¹)	ΔS^\ddagger (kJ K ⁻¹ mol ⁻¹)	ΔG^\ddagger (kJ mol ⁻¹)
Propane-1,2-diol	21.29	18.60	-0.238	89.52
Butane-1,2-diol	25.73	22.99	-0.22	88.55

Rate law

Michaelis-Menten plot of $1/k_{obs}$ versus $1/[Diol]$ gave a straight line graph with an intercept, indicating the presence of an intermediate complex (Fig.3). The kinetic study showed first order dependence on both $[KMnO_4]$ and $[Diols]$. Therefore, a plausible mechanism is shown below:



Applying steady state approximation:

$$\text{Rate} = k[\text{diol}][\text{oxidant}]$$

$$\text{where, } k = \frac{k_2 k_1}{k_{-1} + k_2}$$

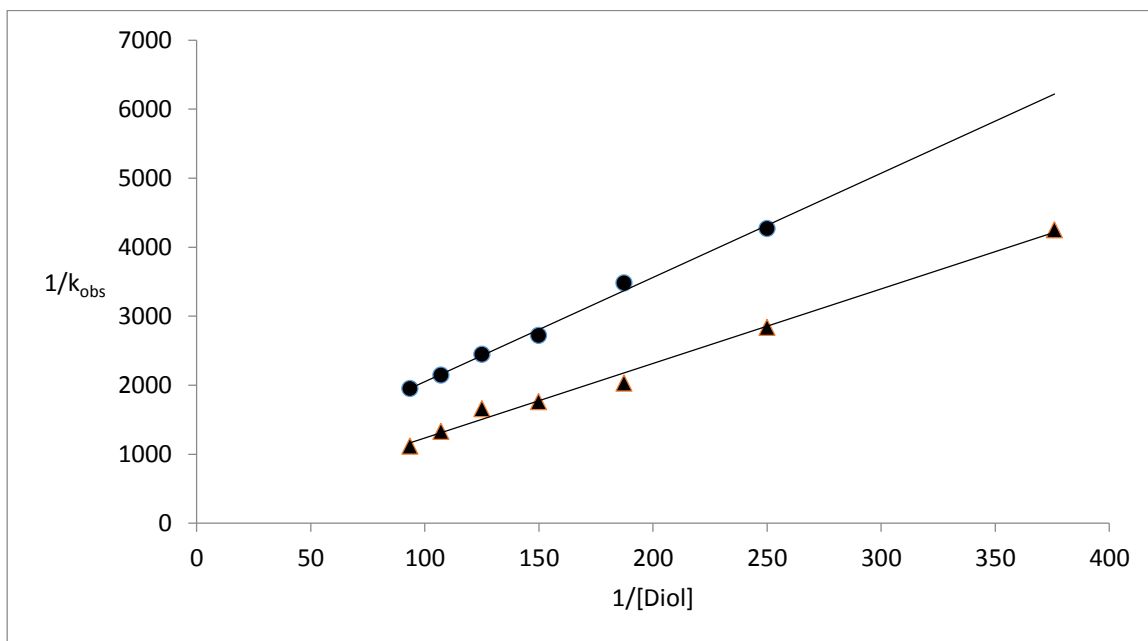


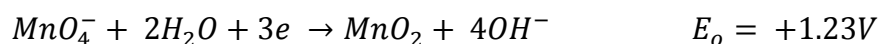
Fig. 3: Michaelis-Menten plot (▲ Butane-1,2-diol ● Propane-1,2-diol)

Mechanism involving glycol-bond fission has been proposed for the oxidation of vicinal diols. However, this assertion seems not to be a general affirmative statement as the oxidation of some vicinal diols in some oxidants does not involve the glycol C-C bond cleavage. Vicinal diols are oxidized to α -hydroxy-carboxylates in the presence of gold nano colloids [28], while quinolinium dichromate oxidizes both vicinal and non-vicinal diols to α -hydroxy carbonyl compounds [29]. Furthermore, α -hydroxyl ketones were the major

products when hydrogen peroxide was used to oxidize vicinal diols [30] and oxidation of vicinal diols by KBrO_3 and KHSO_4 also gave α -hydroxyl ketones in good yield [31]. *o*-iodoxybenzoic acid oxidizes vicinal diols without the cleavage of glycol C-C bond resulting to the formation of α -ketol or α -diketone[32]. However, vicinal diols suffers oxidative cleavage of the carbon-carbon bond in the presence of strong oxidants like sodium periodate (NaIO_4) or lead tetraacetate($\text{Pb}(\text{OAc})_4$) resulting in the formation of two carbonyl groups via glycol cleavage [33].

The permanganate ion is ambiphilic in nature, because the empty d-orbitals on the central metal are electrophiles and the electron pairs on the oxygen atoms are nucleophilic in character [34]. Potassium permanganate ion has a tetrahedral geometry with π -bonding. It is reported to be stable in neutral or slightly alkaline medium [35].

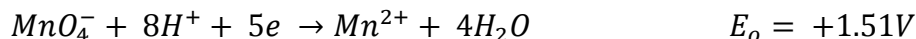
In aqueous solution, permanganate functions as a powerful oxidizing agent.



However, in strong base, manganate ion is produced



While in acid solution, permanganate is reduced to Mn^{2+}



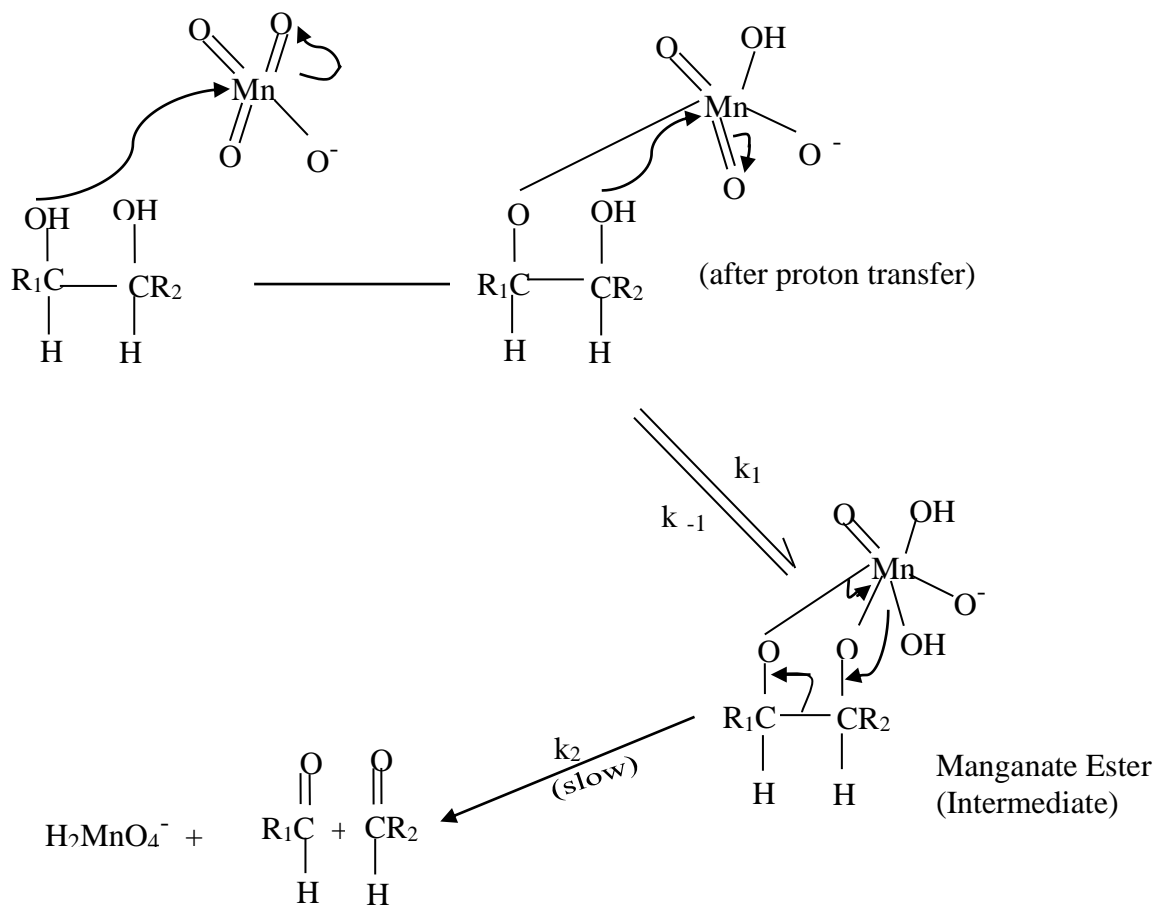
The oxidation of diols by KMnO_4 can be likened to that by NaIO_4 . The kinetic and spectroscopic results of product analysis show the presence of two carbonyl (ketone) compounds which must have resulted from the glycol C-C bond cleavage of the diol via the production of a manganate ester. Like NaIO_4 , KMnO_4 changes from +7 \rightarrow +5 in the process of cleaving the C-C bond to form two C=O π bonds.

Negative entropy of activation shows that there is immobilization of a large number of solvent molecules due to high solvation of the charged ends. Furthermore negative entropy of activation points to the presence of a rigid transition state in the oxidation reaction. Hence, the involvement of both hydroxyl groups in the rate-determining step is indicated [36].

The observed Michaelis-Menten kinetics with respect to diol concentration suggests an intermediate complex formation by the interaction between the non-bonded pairs of electrons of the hydroxyl oxygen and permanganate ion in a rapid pre-equilibrium. FTIR spectrum of

the product showed 2 weak bands of C-H stretching at 2750-2850 cm^{-1} and C=O stretching at 1725 cm^{-1} , indicative of the presence of aldehyde.

Thus on the basis of the above experimental facts, the following scheme of reaction has been proposed (scheme I)



The scheme shows two distinct paths of reaction, involving the bimolecular collision of the permanganate ion and neutral diol molecule and the formation of an intermediate complex (Manganate ester) which disproportionate in slow step via a cyclic concerted symmetrical transition state to product formation. The rate controlling step is considered to be the step involving glycol C-C bond cleavage [37]. High positive values of ΔG^\ddagger indicate highly solvated transition state while same value of ΔG^\ddagger indicates same mechanism for the two vicinal diols investigated [38, 39].

REFERENCES

1. Shaabani, A., Mirzaei, P., Naderi, S. & Lee, D.G. (2004). Green oxidation. The use of Potassium permanganate supported manganese dioxide. *Tetrahedron*, 60, 11415-11420.
2. Deraniyagala, S.P. & Premasiri, T.N.T. (1999). Kinetics and mechanism of oxidation of ethyl acetate by potassium permanganate in acidic medium. *Vidyodaya J. of Sci*, 8, 149-159.
3. Basheer, K.M., Joseph, J. & Nair, T.D.R. (2013). Kinetics of the oxidation of Benzhdrols with permanganate under phase Transfer catalysis in organic solvents. *Modern Research Catalysis*, 2, 35-38.
4. Fawzy, A., Zaafarany, I.A, Khairou, K.S., Almazroai, L.S., Bawazeer, T.M., Al-Jahdali, B.A. (2016). Oxidation of caffeine by permanganate ion in perchloric and sulfuric acid solutions. A comparative kinetic study. *Science Journal of chemistry*, 4(2), 19-28.
5. Fayad, P.B, Zamyadi, A., Broseus, R., Prevost, M. & Sauve, S. (2013). Degradation of progestagens by oxidation with potassium permanganate in waste water effluents, *Chemistry Central Journal*, 7, 84-90.
6. Ariga, G.G, Nandibewoor, S.T. & Chimatader, S.A. (2016). Free –radical-induced oxidation degradation of antibacterial drug, methyl parabeen by permanganate in alkaline medium. A kinetic and mechanistic approach. *Cogent Chemistry*, 2 (1), 45-52.
7. Fawzy, A., Ahmed, S.A, Althagafi, I.I., Morad, M.H. & Khairou, K.S.(2016). Kinetics and mechanistic study of permanganate oxidation of Fluorenone Hydrazone in Alkaline medium. *Advances in Physical Chemistry*, 1-10.
8. Rajendran, P., Bashpa, P. & Bijudas, K. (2017). Kinetic and mechanistic studies of the oxidation of naphthalene by potassium permanganate in aqueous acetic medium. *Journal of Chemical and Pharmaceutical Sciences*, 10 (1), 198-202.
9. Gour, R., Dhobal, B.S, Hussain, S. & Farooqui, M. (2011). Oxidation of chemical compounds. Kinetics and mechanistic approach. *J. Chem.. Pharm. Res.*, 3(5), 750-761.
10. Panari, R.G, Chougali, R.B. & Nandibewoor, S.T. (1998). Oxidation of mandelic acid by alkaline potassium permanganate. A kinetic study. *J. Physical Org. Chemistry*, 11 (7), 448-454.
11. Girgis, M.M, El-Shatoury, S.A., Khalil, Z.H. (1985). Kinetics and mechanism of oxidation of lactic acid by KMnO_4 in H_2SO_4 medium. *Can. J. Chem*, 63, 3317-3321.

12. Shaabani, A., Tavasoli-Rod, F. & Lee, D.G. (2011). Potassium permanganate oxidation of organic compounds. *Synthetic Communications*, 35(4), 571-580.
13. Sayyed, H.S., Mazhar, F.N., Gaikwad, O.O. (2010). Kinetic and mechanistic study of oxidation of Esters by KMnO₄, *International Journal of ChemTech Research*, 2 (1), 242-249.
14. Sen Gupta, K.K, Adhikari, M., Sen Gupta, S. (1989). Kinetics of oxidation of ethanol by potassium permanganate in perchloric acid medium, *Reaction Kinetics and Catalysis Letters* 38 (2), 313-318.
15. Sheeba, P.S., Nair, T.D.R. (2001). Kinetic studies on permanganate oxidation of acetophenones under phase transfer catalysis. *Indian J. Chem.*, 40A, 610-612.
16. Fawzy, A., El-Guesmi, N., Ali, H.M., Abdallah, M. (2018). Oxidation of Tryptophan by permanganate ion in acid, Neutral and Alkaline Media. A comparative kinetic and mechanistic study. *Journal of Materials and Environmental Sciences*, 9 (6), 1645-1655.
17. Sankhe, S., Shah, S., Bhavsar, B. (2017). Kinetic study of oxidation of certain Amino-Acids by KMnO₄ in moderately concentrated Acidic Media. A review. *Int. J. Res. In Applied Science and Engineering*, 5 (IX), 368-370.
18. Mahmoodlu, M.G., Hasanizadeh, S.M. & Hartog, N. (2014). Evaluation of the kinetic oxidation of aqueous volatile organic compounds by permanganate. *Science of the Total Environment*, 485-486:755-763
19. Anelli, P.L., Banfi, S., Montanari, F. & Quici, S. (1989). Oxidation of diols with alkali hypochlorites catalysed by oxammonium salts under two-phase conditions. *J. Org. Chem*, 54, 12, 2970-2972.
20. Myata, A., Furukawa, M., Irie, R. & Katsuki, T. (2002). Catalytic aerobic oxidation of diols under photo-irradiation . *Tetrahedron Letters*, 43 (19), 3481-3484.
21. Sheikh, T.M., Hong, F. (2013). Efficient method for the oxidation of aldehydes and diols with tert-butylhydroperoxide under transition metal-free conditions. *Tetrahedron*, 69 (42), 8929-8935.
22. Jhulki, S., Seth, S., Mondal, M., Moorthy, J.N. (2014). Facile organocatalytic domino oxidation of diols to lactones by in situ-generated TetMe-IBX. *Tetrahedron* 70 (13), 2286-2293.

23. Miller, S.A., Bobbitt, J.M. & Leadbeater, N.E. (2017). Oxidation of terminal diols using an oxommonium salt. *Organic and Biomelecular Chemistry*, 13, 34-42.
24. Osamu, O., Hitomi, A., Yoshihiro, M. & Yousuke, B. (2007). Asymmetric oxidation of 1,2-diols using N-bromosuccinimide in the presence of chiral copper catalyst. *Tetrahedron Letters*, 48(49), 8668-8672.
25. Satoshi, S., Daisuke, K. & Yasutaka, I. (1997). Oxidation of Diols and Ethers by NaBrO₃/NaHSO₃ Reagent. *Bulletin of the Chemical Society of Japan*, 70 (10), 20-25.
26. Vyas, S., Sharma, P.K. (2004). Kinetics and mechanism of oxidation of some vicinal and non-vicinal diols by quinolinium bromochromate. *Indian Journal of Chemistry*, 43A, 1219-1223.
27. McAuley, A., Oswald, T. & Haines, R.I. (1983). Kinetics and mechanism of the oxidation of ascorbic acid and benzene diols by nichel(III) tetraazamacrocycles in aqueous perchlorate acid. *Can. J. Chem.* 61, 1120.
28. Mertens, P.G.N., Bulut, M., Gevers, L.E.M., Vankelecom, I.F.J., Jacobs, P.A. & Devos D.E. (2005). Catalytic oxidation of 1,2-diols to a α -hydroxy-carboxylates with stabilized gold nanocolloids combined with a membrane-based catalyst separation. *Catalysis Letters*, 102 (1-2), 57-61.
29. Kuotsu, B., Tiewsoh, E., Debroy, A. & Mahanti, M.K. (1996). Quinolinium Dichromate oxidation of Diols: A kinetic study. *J. Org. Chem.*, 61(25), 8875-8877.
30. Mecozzi, F., Dong, J.J., Saisaha, P. & Browne, W.R. (2017). Oxidation of vicinal diols to α -hydroxy ketones with H₂O₂ and a simple Manganese catalyst. *J. Org. Chem.*, (46), 6919-6925.
31. Wiliam, J.M., Kuriyama, M., Onomura, O. (2014). Simple method of selective oxidation of 1,2-diols in water with KBrO₃/KHSO₄. *Tetrahedron Letters*, 55 (48), 6589-6592.
32. Frigerio, M. & Santagostino, M. (1994). A mild oxidizing agent for alcohols and 1,2-diols: o-iodoxybenzoic acid (IBX) in DMSO, *Tetrahedron Letters*, 35 (43), 8019-8022.
33. Sklarz, B. (1967). Organic chemistry of periodates. *Q. Rev. Chem. Soc.*, 21, 3.
34. Dash, S., Patel, S., Mishra, B.K. (2009). Oxidation by permanganate: Synthetic and mechanistic aspect. *Tetrahedron*, 65, 707-739.
35. Cotton, F.A. & Wilkinson, G. (1980). Advanced inorganic chemistry, John Wiley and Sons, New-york, NY, 747.

36. Goswami, G., Kothari, S. & Banerji, K. (2001). Kinetics and mechanism of the oxidation of some diols by benzyltrimethyl ammonium tri bromide. *Chem..Sci*, 113, 43-54.
37. Sankhla, P.S. & Mehrotra, R.N. (1973). Kinetics of oxidation of propane-1,3- and butane-1,4- diols by Cerium(IV) in sulphuric acid. *J. Inorg. Nucl. Chem.*, 35(3), 891-899.
38. Kumar, A. (2013). Comparative study of kinetics of catalysed oxidation of D(+) galactose and lactose by Ruthenium(III) in Alkaline medium. *Oriental Journal of Chemistry*, 29(2), 815-821.
39. Surendra, T. (2014). Oxidation of Benzyl alcohol by hypervalent iodine. A kinetic and mechanistic study. *World Journal of Pharmacy and Pharmaceutical Sciences*, 3 (3), 1844-1851.