Oxidation of Uncatalyzed Cyclohexanone Oxime by Quinaldinium Fluorochromate [QNFC] in Aqueous Acetic Acid Medium

**A. Elavarasan[1], J. Dharmaraja[2]*, K.Maheswari[3],
V. Raj[4], J. Vijaya[1], S. Mohanapriya[1],**

Research Scholar[1], Assistant Professor[2], Graduate Teacher in Science[3], Professor & Head[4]
1. Department of Chemistry, Periyar University, Periyar Palkalai Nagar, Salem-636 011, Tamil Nadu, INDIA
2. Department of Chemistry, Arignar Anna Govt. Arts College, Vadachennimalai, Attur-636 121, Tamil Nadu, INDIA
3.Govt.Girls Higher Secondary school ,Devapandalam, Villupuram (Dt)- 606402, Tamil Nadu, INDIA
4. Department of Chemistry, Periyar University, Periyar Palkalai Nagar, Salem-636 011, Tamil Nadu, INDIA

ABSTRACT

Kinetics of oxidation of [cyclohexanone oxime] by [QNFC] in protic solvent system has been studied at 308 K. The product has been identified as corresponding ketonic group. A first order dependence of the reaction with respect to [QNFC], [cyclohexanone oxime] and [H+]] has been observed. The rate constant increased with increase in the concentration of perchloric acid. The reaction has been found to be catalyzed by H^+ ions. Increasing the percentage of the acetic acid medium increases the rate. Addition of sodium perchlorate increases the rate of reaction appreciably. No polymerization with acrylonitrile. The reaction has been conducted at four different temperature and the activation parameters were calculated. From the observed kinetic results a suitable mechanism was proposed.

Keywords – kinetics, oxidation, cyclohexanone oxime, QNFC,

1,INTRODUCTION

Oxidation reaction has been a subject of major importance to many chemists and elucidation of the mechanism is undoubtedly one of the most fascinating problems in the mind of chemists **[1-2].** Extensive studies on the mechanism of the oxidation of cyclohexanone oxime with several oxidants have been reported. Variety of new chromium (VI) oxidants together with special reaction conditions have been introduced for the regiospecific, chemospecific and stereospecific oxidative degeneration of functional groups in highly sensitive systems**[3-6].**

1.1 Quinaldinium fluorochromate (VI) as an oxidant:

The investigation of reaction kinetics in chemical reactions is the most important in deciding the reaction mechanisms. Chromium compounds have been proved to be versatile reagents for the oxidation of almost all the organic functional groups **[7-11].**Generally chromium(VI) oxidation reactions have been performed in aqueous acidic conditions, the source of chromium(VI) being chromium trioxide, sodium dichromate, potassium dichromate, chromyl chloride, chromyl acetate, t-butyl chromate (or) co-oxidation complexes of chromium trioxide. Chromium compounds have been widely used in aqueous and non-aqueous media for the oxidation of a variety of organic compounds **[12-14].**

Some of the other few examples of Cr(VI) oxidants reported in the literature are as follows:Polymer supported chromium (VI) reagents have also been developed.These reagents offer the advantage of simplifying the work procedure. Recently, some neutral chromium(VI) reagents like pyridinium fluorochromate (PFC), nicotinium dichromate (NDC) etc., have been developed to effect of oxidation under mild conditions. The oxidant quinaldinium fluorochromate (QNFC) **[15]** is used in the present work.

1.2 Oxidation of [cyclohexanone oxime]:

Oxidation reaction the most important role of kinetic reaction, like to the cyclohexanone oxime oxidations[**16**].

2. MATERIALS AND METHODS

2.1 Preparation of [cyclohexanone oxime]:

The corresponding cyclohexanone oxime was prepared as described by Vogal's *etal* [**17**].

2.2 Other chemicals:

[QNFC] was prepared by the method described in the literature[15]. All other chemicals were used as supplied without further purification used in this experiment are all of AR grade samples.

2.3 Product analysis and stoichiometry oxidation of [cyclohexanone oxime] by [QNFC]:

The required quantity of [cyclohexanone oxime] (0.1 mol), [QNFC] (0.1 mol) were mixed and   kept at room temperature under kinetic runs. The product was extracted with chloroform and then dried over anhydrous sodium sulfate. The chloroform layer was evaporated. The product obtained was cyclohexanone. The   product was confirmed   as

corresponding ketone   2,4-dinitrophenylhydrazine   derivative   test   (m.p. 197 °C; lit.200°C).

2.4 Purification of water:

All solutions were prepared from double distilled water. The following solutions of required concentrations were prepared and used for the kinetic studies: i) QNFC, perchloric acid, sodium perchlorate and manganous sulfate in water, ii) cyclohexanone oxime in acetic acid.

2.5 Kinetics and oxidation of [cyclohexanone oxime] by [QNFC]:

All the kinetic reactions were carried out under pseudo-first order conditions, keeping [substrate] >> [QNFC] in a solvent system of 50% (v/v) acetic acid-water medium at 308 K unless otherwise mentioned and the course of the reaction were followed by iodometrically.

3. RESULTS AND DISCUSSION

3.1. Effect of varying [QNFC]

The reactions were conducted with varying concentrations of QNFC and keeping all other reactant concentrations constant and the rate constants were calculated in **Table.1** .Further the plot of log titre *versus* time is linear, its evidenced for first order of the reaction.

Table 1. Effect of varying [QNFC] concentration

[cyclohexanone oxime] $= 12.50 \times 10^{-3}$ mol dm^{-3}

[HClO$_4$] $= 1.50 \times 10^{-3}$ mol dm^{-3}

Solvent $= 50\text{-}50$ (% v/v) AcOH-H$_2$O

Temperature $= 308$ K

10^3 [QNFC] (mol dm^{-3})	$10^4\, k_{obs}$ (s^{-1})
0.50	3.34
1.00	3.53
1.25	3.56
1.50	3.60
1.75	3.68
2.00	3.69

2.25	3.73

3.2. Effect of varying [cyclohexanone oxime]

The reactions were investigated with varying concentration of cyclohexanone oxime and keeping all other reactant concentrations constant and the observed rate constant values were given in **Table .2** Fig.1 A plot of log k_{obs} *versus* log [cyclohexanone oxime] is linear with a slope = 0.965, r = 0.987, sd = 0.037. These results show that first order dependence with respect to [cyclohexanone oxime] .

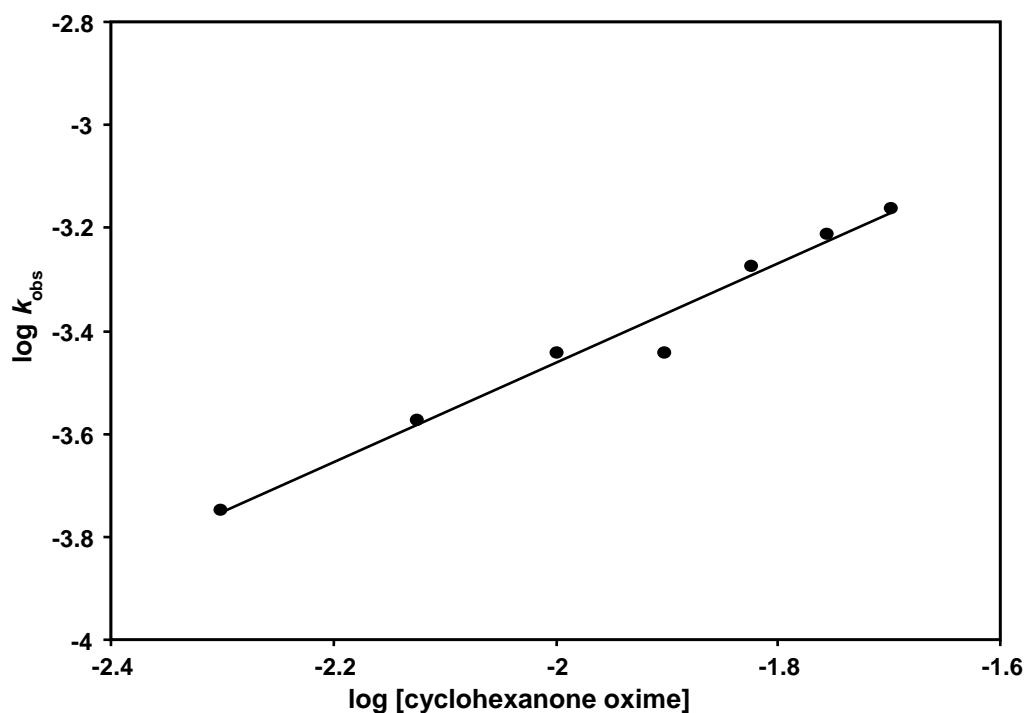**Table 2. Effect of varying [cyclohexanone oxime]**

$$[QNFC] \quad = \quad 1.50 \times 10^{-3} \text{ mol dm}^{-3}$$

$$[HClO_4] \quad = \quad 1.50 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\text{Solvent} \quad = \quad 50\text{-}50 \text{ (\% v/v) AcOH-H}_2\text{O}$$

$$\text{Temperature} \quad = \quad 308 \text{ K}$$

10^3 [cyclohexanone oxime] (mol dm^{-3})	$10^4 \, k_{obs}$ (s^{-1})
05.00	02.32
07.50	02.61
10.00	03.00
12.50	03.60
15.00	05.94
17.50	07.11
20.00	09.08

Uncatalyst (r = 0.987; sd = 0.037)

Fig.1.log k_{obs} versus log [cyclohexanone oxime]

3.3. Effect of varying [HClO₄]

The reaction of perchloric acid and keeping all other reactant concentrations constant. The rate constants increased with increase in the concentration of perchloric acid **Table.3** The plot of log k_{obs} *versus* log [H$^+$] Fig.2 shows that first order dependence is observed (slope = 1.02; r = 0.990; sd = 0.033) in the case of reaction.

Table . 3. Effect of varying [HClO₄] concentration
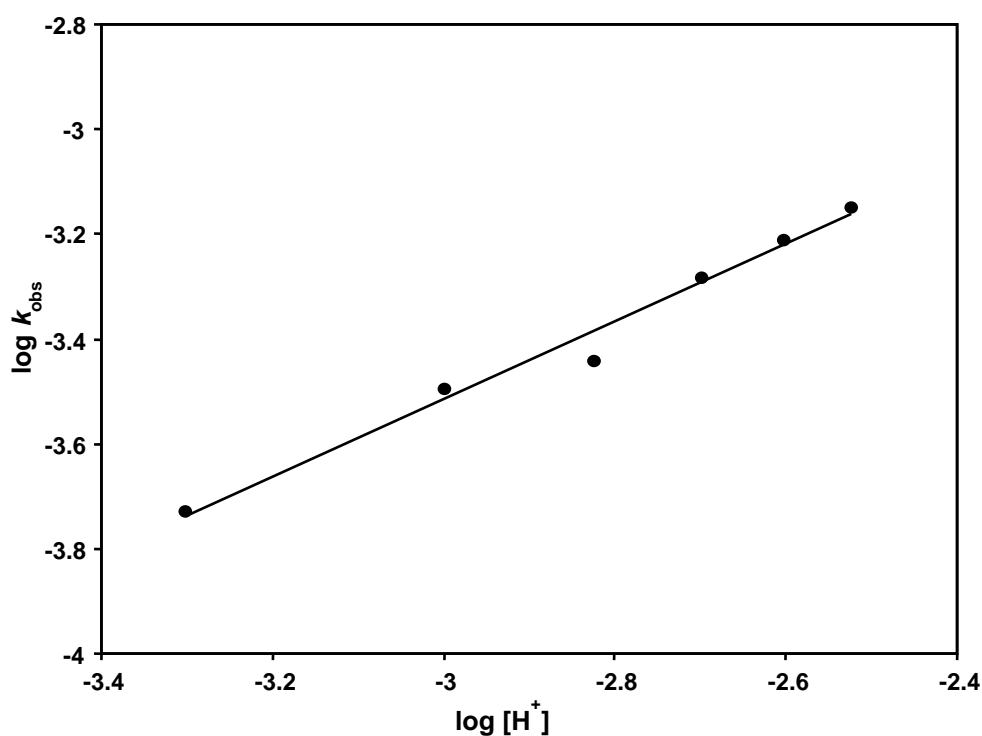
cyclohexanone oxime]   = 12.50 × 10^{-3} mol dm^{-3}

[QNFC]   = 1.50 × 10^{-3} mol dm^{-3}

Solvent   = 50-50 (% v/v) AcOH-H$_2$O

Temperature = 308 K

10^3 [HClO₄] (mol dm^{-3})	10^4 k_{obs} (s^{-1})
0.50	2.47
1.00	3.53

1.50	3.60
2.00	5.17
2.50	7.61
3.00	9.41

Uncatalyst (r = 0.990; sd = 0.033)

Fig.2. Plot of log k_{obs} versus log $[H^+]$

3.4. Effect of varying solvent composition

The reactions were conducted with different solvent composition of acetic acid-water mixture and keeping all other reactant concentrations constant and the corresponding rate constants were given in **Table .4** . This suggests that an ion-dipole interaction may be involved in the mechanistic pathway. A plot of log k_{obs} *versus* 1/D is linear with a positive slope in the reactions.

Table .4. Effect of varying solvent composition

[cyclohexanone oxime] $= 12.50 \times 10^{-3}$ mol dm^{-3}

[QNFC] $= 1.50 \times 10^{-3}$ mol dm^{-3}

[HClO$_4$ $= 1.50 \times 10^{-3}$ mol dm^{-3}

Temperature $= 308$ K

AcOH-H$_2$O (% v/v)	$10^4 k_{ob}$ (s^{-1})
30-70	2.25
35-65	2.61
40-60	3.34
45-55	3.53
50-50	3.60
55-45	5.05
60-40	6.42
65-35	7.02
70-30	8.55

3.5. Effect of added [NaClO$_4$], [acrylonitrile] and [MnSO$_4$]

The rate data was measured with different concentration of NaClO$_4$ and keeping all other reactant concentrations constant. The rate constants slightly decrease with increase in the concentration of NaClO$_4$ suggest that the reaction may be between an ion and a neutral molecule. Added acrylonitrile rules out the possibility of radical pathway mechanism. Added Mn^{2+} showing uncatalytic effect on the reaction rate in **Table .5**.

Table 5. Effect of varying [NaClO$_4$], [acrylonitrile] and [MnSO$_4$]

[cyclohexanone oxime] $= 12.50 \times 10^{-3}$ mol dm^{-3}

[QNFC] $= 1.50 \times 10^{-3}$ mol dm^{-3},

[HClO$_4$] $= 1.50 \times 10^{-3}$ mol dm^{-3},

Temperature $= 308$ K,

10^4 [NaClO$_4$] (mol dm^{-3})	10^4 k_{obs} (s^{-1})	10^4 [Acrylonitrile] (mol dm^{-3})	10^4 k_{obs} (s^{-1})	10^4 [MnSO$_4$] (mol dm^{-3})	10^4 k_{obs} (s^{-1})
0.00	3.60	0.00	3.60	0.00	3.60
0.50	3.55	0.50	3.62	0.50	3.71
0.75	3.52	0.75	3.63	0.75	3.83
1.00	3.50	1.00	3,71	1.00	3.96

3.6. Rate dependence on different oxidants

The reactions were carried out in the presence of different oxidizing agents *viz.,* QNFC, PFC and NDC and keeping all other reactant concentrations constant, the measured rate constant values were given in **Table 6**. The observed results show that QNFC show higher oxidizing efficiency.

Table 6. Rate constants for the oxidation of cyclohexanone oxime with various chromium(VI) reagents

$$[\text{cyclohexanone oxime}] = 12.50 \times 10^{-3} \text{ mol dm}^{-3},$$

$$[\text{HClO}_4] = 1.50 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\text{Solvent} = 50\text{-}50(\% \text{v/v})\text{AcOH-H}_2\text{O},$$

$$\text{Temperature} = 308 \text{ K},$$

Oxidant	10^3 [Oxidant] (mol dm^{-3})	uncatalyzed reaction 10^4 k_{obs} (s^{-1})
QNFC	1.50	3.60
PFC	1.50	3.55
NDC	1.50	2.91

3.7. Effect of temperature

The reactions were carried out at four different temperatures *viz.,* 303, 308, 313 and 318 K and keeping all other reactant concentrations constant and the rate constants were calculated in **Table 7.** The thermodynamic parameters were calculated form the Eyring's plot of ln k_{obs}/T *versus* 1/T Fig.3 The oxidation reaction has been conducted at four different temperatures and the activation parameters were calculated. $S\Delta H^{\#}$ =39.00 kJ mol^{-1} and $\Delta S^{\#}$ = -173.45 J K^{-1} mol^{-1}.

Table 7. Effect of temperature on reaction rates

[cyclohexanone oxime] = 12.50×10^{-3} mol dm^{-3},

[QNFC] = 1.50×10^{-3} mol dm^{-3}

[HClO$_4$] = 1.50×10^{-3} mol dm^{-3},

Solvent = 50-50(%v/v)AcOH-H$_2$O,

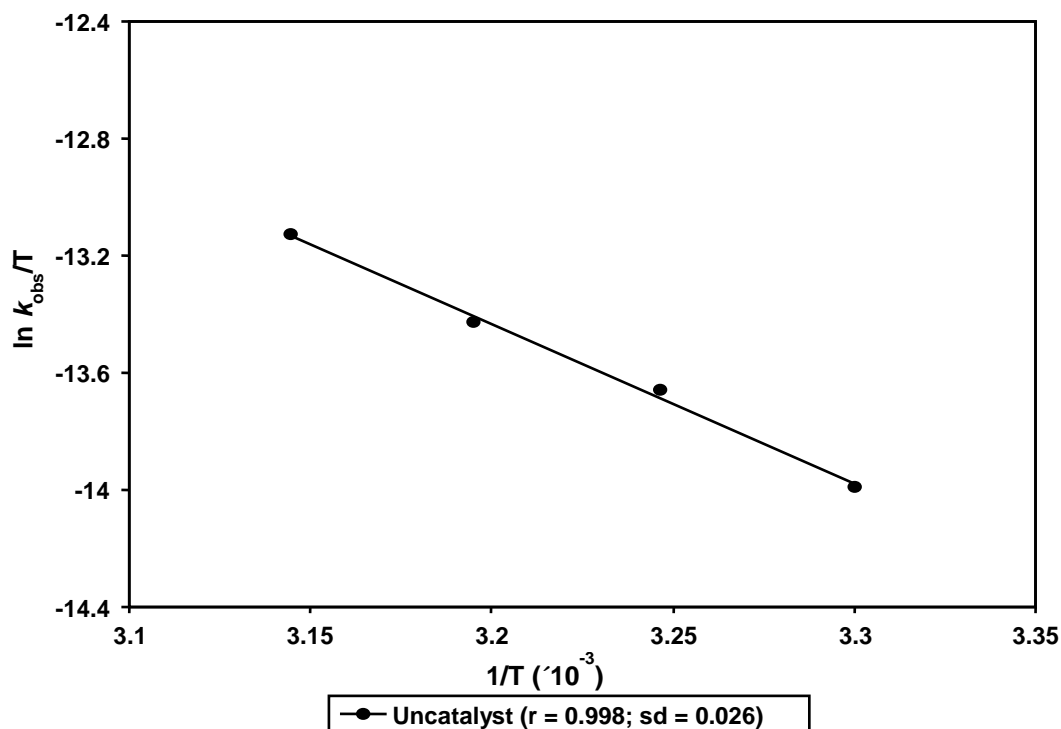| Temperature (K)	$10^4\,k_{obs}$ (s^{-1})
303	2.22
308	3.60
313	4.86
318	6.09

Fig.3 plot of ln k_{obs}/T *versus* 1/T

3.8. Mechanism and rate law:

Uncatalyzed oxidation of cyclohexanone oxime by QNFC

The $HCrO_2^-$ first protonates to give H_2CrO_4 in an equilibrium step. $HCrO_4^-$ reacts with to cyclohexanone oxime give a complex (C_1) in the slow step. Then this complex (C_1) dissociates to give products as follows:
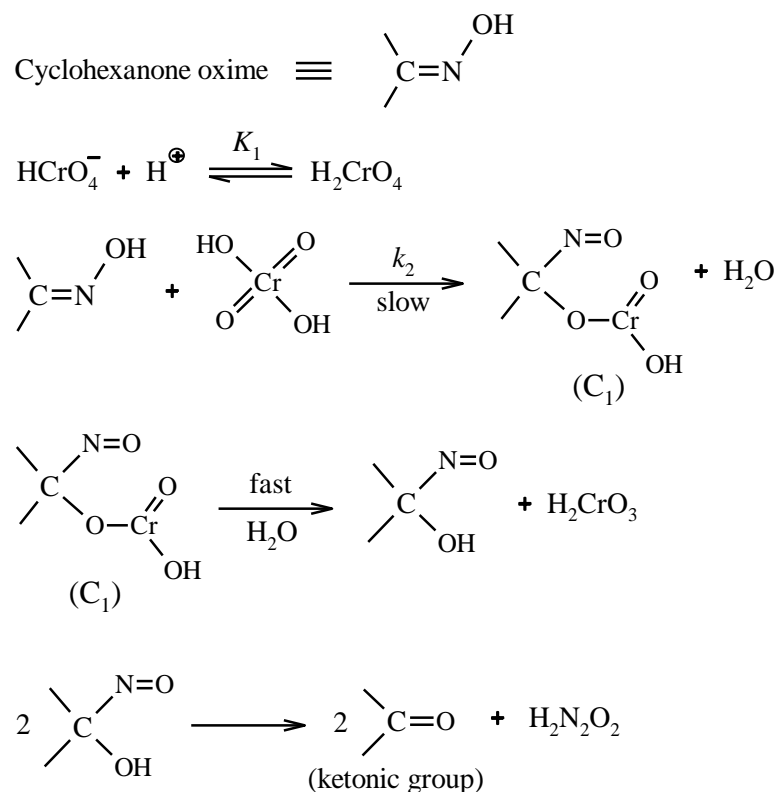
The proposed mechanism has been characterized with the following rate law:

$$\text{Rate law} = \frac{-d[Cr(VI)]}{dt} = K_1 k_2 [\text{cyclohexanoneoxime}][Cr(VI)][H^+]$$

The proposed mechanism explains the first order dependence on [cyclohexanone oxime], [QNFC] and [H$^+$]

APPLICATION

Oxidation reaction has been a subject of major most importance to many chemists and elucidation of the mechanism is undoubtedly one of the most fascinating problems in the mind of chemists.

CONCLUSION

The reaction is carried out in aqueous acetic acid medium at **308 K** and the following results were obtained. First order dependence with respect to [QNFC], [cyclohexanone oxime] and [H+] has been observed. Increase in the percentage of acetic acid increases the rate of the reaction. Added acrylonitrile has no effect on the reaction rate, ruling out the possibility of free radical pathway mechanism. The oxidation reaction has been conducted

at four different temperatures and the activation parameters were calculated. For uncatalyzed reaction $\Delta H^{\#} = 39.00$ kJ mol^{-1} and $\Delta S^{\#} = -173.45$ J K^{-1} mol^{-1} The reaction is characterized by low enthalpy of activation and negative entropy of activation.

REFERENCES

[1] S. Sundaram, N. Venkatasubramaniyan, N.V. Anantakrishnan.(1976).Oxidations with Cr (VI), *J. Sci. Indust.Res.,*35,

[2] J. Muzart, (1992).Chromium-catalyzed oxidations in organic synthesis, *Chem. Rev.,* 92, 113-140.

[3] S.B. Patuari, S.V. Khansole, and Y.B. Vibhute.(2009). *J. Iran. Chem. Soc.,*6: 399. 518-538.

[4] P. Dinesh and K. Seema *Prog. Rean. (2009) Kinetics andMechanism,*34: 199.

[5] A. Yoganath and S.S. Mansoor,(2015) *Oriental J. Chem.* 31,17-23.

[6] A. Rao, T. Purohit, P. Swami, P. Purohit and P.K. Sharma, (2016) *Eur. Chem. Bull.* 5,189-192.

[7] K. Ilayaraja and A. Ambica.(2015). *Nat. Environ. Poll. Technol.* 14, 771-776.

[8] K.P. Thooyamani, V. Khanaa, R. Udayakumar. (2014) *Middle East J. Sci. Res.* 20.2456-2459.

[9] Q. Jin, Z. Hu, Z. Jin, L. Qiu, W. Zhong and Z. Pan.(2012) *Bioresourse Technol.* 117,148-154.

[10] K.P. Thooyamani, V. Khanaa and R. Udayakumar. (2013)*Middle East J. Sci. Res.* 18,1768-1774.

[11] C. Lopez, A. Gonzalex, F.D. Cossio and C. Palomo.(1985). *Synthetic Commun.,*15, 1197.

[12] S. Gopinath, M. Sundararaj, S. Elangovan and E. Rathakrishnan.(2015). *Int. J. Turbo Jet Eng.* 32,73-83.

[13] V. Murugesan and A. Pandurangan.(1992)*Indian J. Chem. B,*31, 377.

[14] K. Lingeswaran, S.S. Prasad Karamcheti, M. Gopikrishnan and G. Ramu.(2014)*Middle East J. Sci. Res.* 20, 812-814.

[15] Melek Canbult, Ozdemir and Ozgun. (2014).*Turkish journal of chemistry,*38,63-69.

[16] S.Senthilkumar and A.N.Palaniappan.(2011). *Rasayan journal of chemistry.vol.4,* 802-805.

[17] Vogal's (1978).Text Book of practical organic chemistry,4th Edn.,ELBS,P.909,[RJC-856/2011].

[18] Jain, Anjali, et al. "Kinetics of Bioethanol Production Using Saccharomyces cerevisiae Strain Y-35." International Journal of Applied and Natural Sciences (IJANS) 5.5 (2016) 87-96

[19] Sharma, N., B. H. A. S. K. A. R. Vemu, and VINOD KUMAR Dumka. "Pharmacokinetics of lincomycin following single intramuscular administration in goats." *International Journal of Agricultural Science and Research (IJASR)* 7.2 (2017): 555-560.

[20] MAJUMDER, ARGHYA, BITAN KUMAR SARKAR, and MAHARSHI GHOSH DASTIDAR. "STUDY ON REDUCTION KINETICS OF IRON ORE SINTER USING COKE DUST." International Journal of Metallurgical & Materials Science and Engineering (IJMMSE) 8.1 (2018) 19-26

[21] SHASTRY, VIDYAVATI, H. RAMYASHREE, and KS RAVINDRA. "KINETICS AND MECHANISM OF OXIDATION OF OMEPRAZOLE BY POTASSIUM FERRATE." International Journal of Medicince and Pharmaceutical Science (IJMPS) 9.6 (2019) 9-18

[22] Bakker, Charitha Thambiliyagodage1& Martin G. "HETEROATOM RICH MESOPOROUS CARBON SUPPORTED GOLD NANOPARTICLES–AN EFFICIENT CATALYST FOR BENZYL ALCOHOL OXIDATION." IMPACT: International Journal of Research in Applied, Natural and Social Sciences (IMPACT: IJRANSS) 7.2 (2019) 13-28

[23] HALLEM, ALIH, and ISRAA NAYYEF KADHIM. "Improving Oxidation Behavior of (Alpha-Beta)(Cu-Zn40) Brass by Aluminum Addition." International Journal of Mechanical and Production Engineering Research and Development (IJMPERD) 9.1 (2019) 329-340