Kinetic Study Of Phosphotungustic Acid Catalyzed Oxidative Degradation Of Lactic Acid By N-Chloroisonicotinamide In Aqueous Acetic Acid Medium.

Sanjay K Singh[1], S S Parihar[2], Deepti Pandey[1*]
1.Department of Chemistry Govt.T.R.S. College Rewa
2. Department of Chemistry Govt. Girls Degree. College Rewa

ABSTRACT:
The PTA catalyzed oxidation of Lactic acid by a mild and selective oxidizing agent N-chloroisonicotinamide (NCIN) leads to the formation of corresponding aldehyde. The reaction found first order in NCIN. The reaction follows Arrhenius relationship with respect to Lactic acids. A retarding effect of acetic acid is observed. Various thermodynamic parameters have been computed.no evidence of Polymerization of acrylonitrile showed no effect of free radical on the rate of reaction. Stoichiometric study revealed 1:1 mole ratio. On the basis of thermodynamic parameters and stoichiometry a feasible mechanism has been proposed and rate law has been derived.
KEYWORDS: *AHA, Kinetics, Lactic acid, Mechanism, NCIN, Oxidation.*

I.   INTRODUCTION

Studies explore that phosphotungstic acid (PTA) is an environment-friendly catalysts amongst the list of catalyst and it is accepted as a green catalyst in kinetic field [1-7]. Aliphatic hydroxy acid (AHA) has an essential role in cosmetic, biological, and pharmaceutical industries. The kinetics of AHA with different oxidants have been reported [8-16].

Lactic acid (LA) $C_3H_6O_3$ is an aliphatic hydroxy acid with adjacent functional groups i.e., hydroxyl and carboxylic [17], also known as milk acid [18]. Many research scholars have reported the vital role of LA in industries [19-20], medicines [21-24], brain metabolism [25], pollution reduction [26], and biochemical industries [27-28].

N-chloroisonicotinamide (NCIN) is a new member of the N-halo family. NCIN, the derivative of Isonicotinamide is a mild, stable, efficient, and inexpensive oxidant for organic substates [29]. The elemental analysis and physical properties of NCIN affirm the presence of the N-X bond. For this reason, it is possible that the compound serving as an effective source of halonium ion. The study of benzyl ethers, benzaldehyde di-N-butyl acetal, and its derivatives [30-34] reveals the mildness and selectiveness of NCIN. The general review of the literature explored that no works have been reported about the oxidation of LA with NCIN in presence of PTA; so, this prompted for the present investigation and evaluate kinetic parameters as well as correlation analysis.

II.   MATERIALS AND METHODS

2.1 Chemicals
Chemicals employed in this study were of A.R. grade. Double distilled water used throughout the study. The solutions were prepared without any further purification of chemicals. The solution of NCIN prepared by reported method.

2.2 Kinetic experiment
The experiments was performed under pseudo-first-order conditions by keeping an excess of the substrate over NCIN. The experiments were carried out in a black-coated stopper glass vessel to avoid any photochemical effect. A thermo-stated water bath maintained the desired temperature within $\pm 0.1K$ (313K). Requisite volumes of all reagents, except NCIN, were introduced into a reaction vessel and equilibrated at 313K. A measured volume of NCIN, equilibrated separately at the same temperature, was rapidly poured into the reaction vessel. The progress of the reactions was monitored by examining aliquots of the reaction mixture for unconsumed NCIN iodometrically using starch as the indicator.

2.3 Product analysis

The end product from the oxidation of Lactic Acid was acetaldehyde and its presence confirm by existing conventional methods. The analysis of end product was carried out under kinetic conditions i.e., with the excess of LA was taken over NCIN. After completion of reaction the solution is treated with an excess (200ml) of saturated solution of 2,4- dinitrophenylhydrazine (DNPH) in 2 mol/dm^3 HCl and kept in refrigerator for 24 hours. The precipitate of 2,4- dinitrophenylhydrazone (DNP) filtered, dried and weighed respectively. recrystallize the crystal of DNP with ethanol and weighed again. The DNP was found identical (m.p. and mixed m.p.) with DNP of LA.

III. RESULT AND DISCUSSION

The oxidation of LA was carried out by NCIN in PTA at 313K under pseudo first order condition. The rate of LA and other experimental data were obtained. Oxidation of LA by NCIN in presence of PTA under the condition [NCIN] << [LA] [PTA] had the following kinetic feature.

3.1 Stoichiometric studies

The stoichiometric studies of oxidation of LA by NCIN were carried out with excess of oxidant (NCIN) and maintaining other parameters constant (PTA 2.5 x 10^2 (mol dm^{-3}), HOAc-H$_2$O = 30 % (v/v), Temperature = 313K). The stoichiometric results indicated 1 mole of LA consumes 1 mole NCIN as represented by the following empirical equation:

$$C_3H_6O_3 + C_5H_5NCONHCl \quad CH_3CHO + CO_2 + HCl + C_5H_5NCONH_2$$

There is first order rate constant is unchanged with an increase in the NCIN.

3.2 Order with respect to [oxidant] [substrate]

When the LA are in large excess, the plots of log (a-x) vs time **(Figure 1)** are found to be linear, indicating first-order dependence on NCIN. The pseudo first-order rate constants in NCIN calculated at different initial concentrations of the reactants are found to be independent of the substrate concentration. The plot of k_1 *vs* [LA] is initially linear passing through origin and tends to obtain limiting value, bending towards horizontal axis **(Figure 2).** Hence the reaction follows fractional order behaviour with respect to the Lactic Acid concentration.
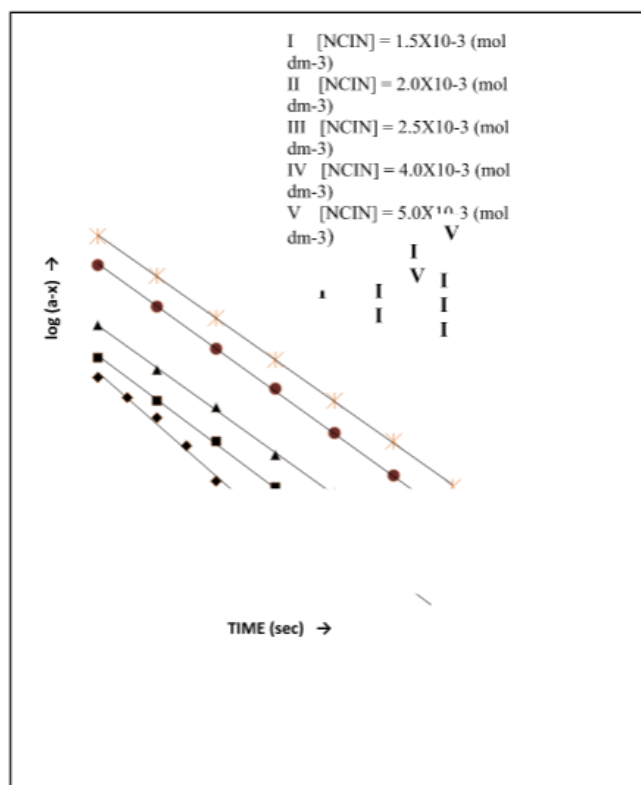

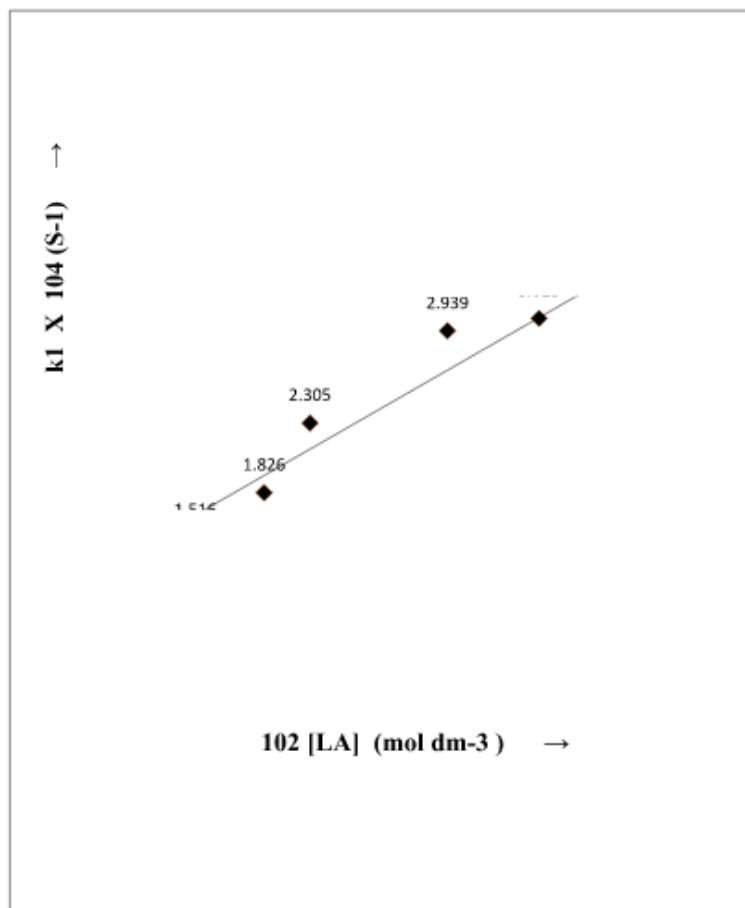**Figure 1:** The plot of log (a-x) versus time. Conditions are given in Table 1.

Figure 2: Dependence of k_1 on [LA]. Conditions are given in Table 1.

3.1.2 Effect of variation of [PTA]

The concentration of PTA was varied while the concentration of *Lactic Acid* and, [NCIN] kept constant. Reaction is PTA catalysed with in a limit. The plot of $1/k_1$ vs. $1/[PTA]$ is obtained straight line with positive intercept, indicate complex formation (**Fig. 3, Table 1**).
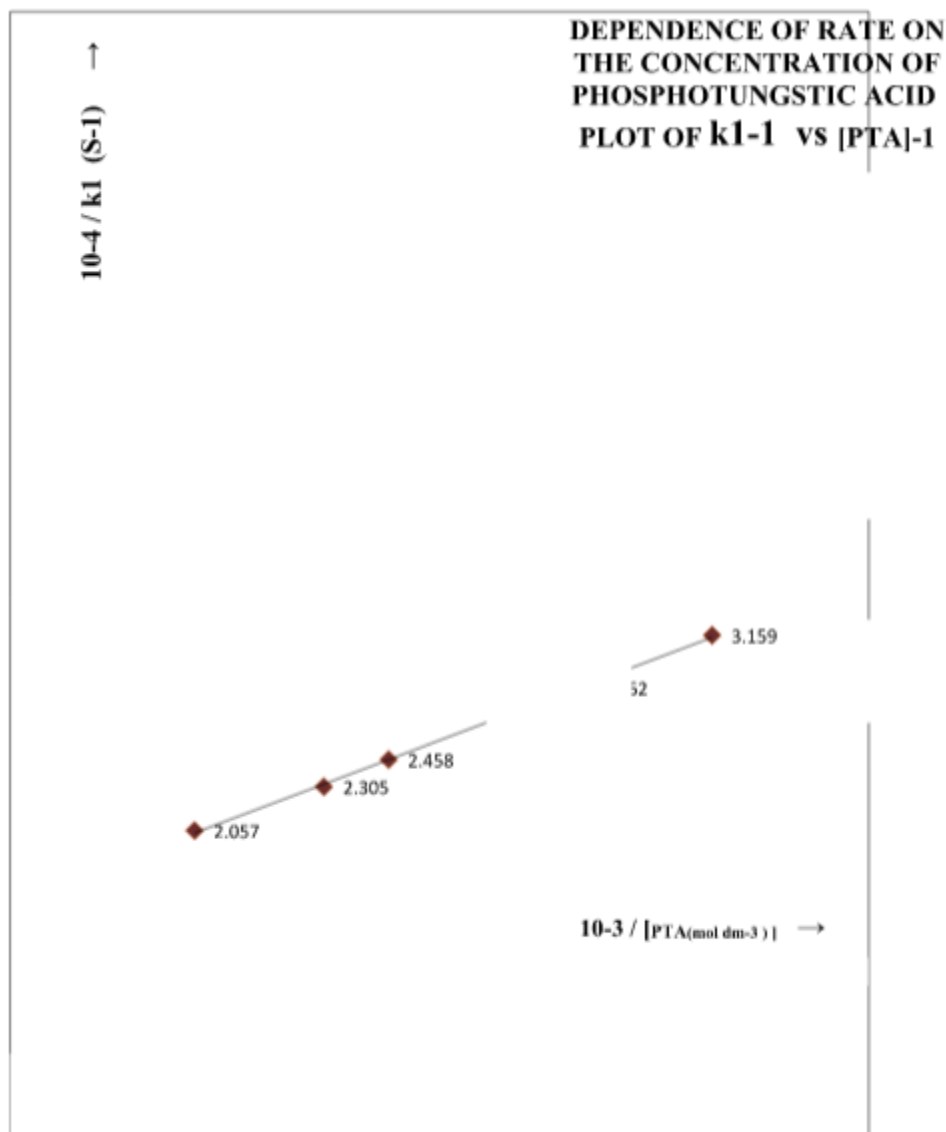
DEPENDENCE OF RATE ON THE CONCENTRATION OF PHOSPHOTUNGSTIC ACID PLOT OF k1-1 VS [PTA]-1

Figure 3: Double reciprocal plot depicting the dependence of the reaction rate on the concentration of PTA. Conditions are given in Table 1.

Table 1: Effect of variation of reactants on pseudo-order rate constant k_1 at 313K

10^2 [Substrate] (mol dm^{-3})	10^3 [NCIN] (mol dm^{-3})	[H$^+$] (mol dm^{-3})	[PTA] (mol dm^{-3})	% HOAc - H$_2$O	k_1x10^4 (s^1)
2.50	2.50	-	2.50	30	1.516
4.00	2.50	-	2.50	30	1.826
5.00	2.50	-	2.50	30	2.305
8.00	2.50	-	2.50	30	2.939
10.00	2.50	-	2.50	30	3.025
12.50	2.50	-	2.50	30	3.311
5.00	1.00	-	2.50	30	2.323
5.00	2.00	-	2.50	30	2.310
5.00	2.50	-	2.50	30	2.305
5.00	4.00	-	2.50	30	2.289
5.00	5.00	-	2.50	30	2.312
5.00	2.50	0.10	2.50	30	2.305
5.00	2.50	0.15	2.50	30	2.206
5.00	2.50	0.20	2.50	30	2.023
5.00	2.50	0.25	2.50	30	1.916
5.00	2.50	0.30	2.50	30	1.751
5.00	2.50	0.40	2.50	30	1.451
5.00	2.50	0.50	2.50	30	1.242
5.00	2.50	-	1.00	30	2.057

5.00	2.50	-	2.00	30	2.305
5.00	2.50	-	2.50	30	2.458
5.00	2.50	-	4.00	30	2.862
5.00	2.50	-	5.00	30	3.159
5.00	2.50	-	2.50	10	3.106
5.00	2.50	-	2.50	20	2.769
5.00	2.50	-	2.50	30	2.305
5.00	2.50	-	2.50	40	2.109
5.00	2.50	-	2.50	50	1.742

3.1.3   Effect of variation of [H⁺]:

The catalysed kinetics was observed by the addition of perchloric acid. On varying perchloric acid concentration there is an increase in reaction rate (**Table 1**). The plot of log k_1 versus [H⁺] (**Figure 4**) gave a straight line with positive intercept, suggesting that acid plays a complex role in the reaction system.
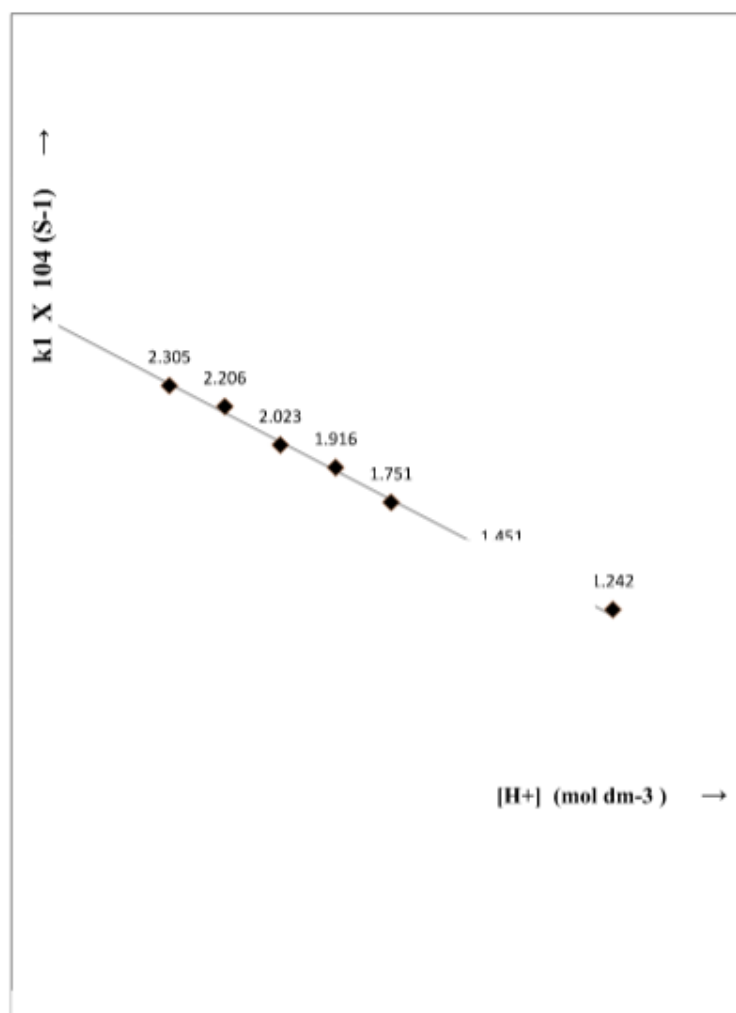

Figure 4: Dependence of k_1 on [H⁺]. Conditions are given in Table 1.

3.1.4   Effect of solvent on reaction velocity:

The rate was studied at different concentrations of the solvent. It is observed that the rate decreases with increasing concentration of acetic acid.

3.1.5   Effect of ionic strength and isonicotinamide:

The reaction rate was not influenced by the addition of chemically neutral salt. Hence the ionic behaviour on slow step in the reaction mechanism is ruled out. Addition of isonicotinamide (one of the reaction products), at constant NCIN, PTA and LA concentration, decreases the rate of reaction.The retardation of reaction rate on the addition of isonicotinamide suggests a pre-equilibrium step that involves a process in which isonicotinamide is

one of the products. If this equilibrium is involved in the oxidation process the retardation should be an inverse function of isonicotinamide concentration.

3.1.6   Effect of Product and Free Radical Inhibitor:
  The reaction under study failed to induce polymerization of added acrylonitrile discarding the presence of free radicals and free radical path.

3.1.7   Effect of temperature:
The effect of temperature on the reactions of Lactic Acid with NCIN in presence of PTA was also studied. The value of energy of activation, ΔS, ΔH & ΔG were computed. These values are summarized in **Table 2** along with the other parameters.
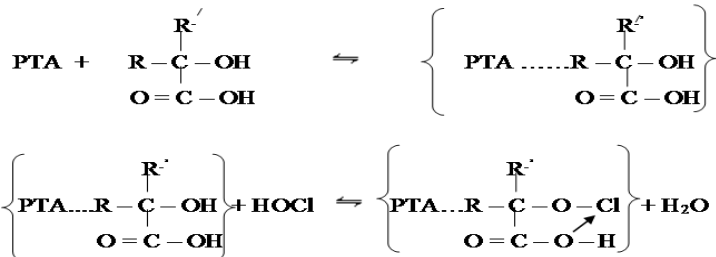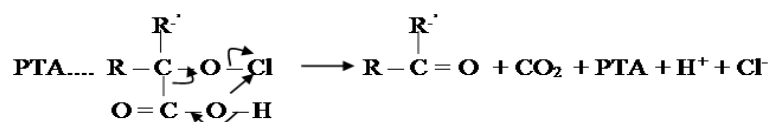
Table 2: Thermodynamic parameters of LA-NCIN system

Substrate	Ea (kJ mol^{-1})	A (s^{-1})	H* (kJ mol^{-1})	G* (kJ mol^{-1})	-S* (JK^{-1} mol^{-1})
LA	69.03	4.271×10^8	66.26	91.029	82.21

IV.   MECHANISM
The concentration of NCIN in the presence of PTA was found to be constant over a period of time. So, it was found that there was no appreciable reaction between phosphotungstic acid and NCIN. Hence it was likely that PTA is forming a complex with LA. The mechanism for the catalysed reaction was likely to proceed through the formation of complex between PTA and LA in a fast step which is being attacked by active species of NCIN and forming an activated complex, which is decomposed in a slow rate determining step. Based on the above experimental facts, the following mechanism for the PTA catalysed oxidative degradation of LA by NCIN is proposed.

Retarding effect of INA & solvent and positive effect of H+ clearly ruled out the NCIN, CH3COOCl, CH3COO+HCl are not prime reactive species from the list of possible reactive species. Thus, the only choice and possibility that is left as a remote prime active species more probable is for HOCl. Our kinetic finding also suggests to us to assume that HOCl is to be considered as the most predominant, fertile reacting species. This leads to the postulation of the following overall mechanism and rate law.

$$NCIN + H_2O \underset{}{\overset{K_1}{\rightleftharpoons}} HOCl + \text{Isonicotinamide (INA)} \quad \dots\dots (1)$$

$$HOCl + H \overset{K_2}{\rightleftharpoons} H_2O^+Cl \quad \dots\dots\dots (2)$$

$$NCIN + H^+ \rightleftharpoons NCINH^+ \quad \dots\dots\dots (3)$$

$$NCINH^+ + H_2O \rightleftharpoons H_2O^+Cl + \text{Isonicotinamide} \dots\dots\dots (4)$$

$$HA + PTA \overset{K_3}{\rightleftharpoons} C_1 \quad \dots\dots\dots(5)$$

$$C_1 + HOCl \overset{K_4}{\rightleftharpoons} (X_1{}^{\#}) + H_2O \quad \dots\dots\dots (6)$$

$$(X_1{}^{\#}) \overset{k_1}{\rightarrow} RCHO + HCl + 2CO_2 + PTA \quad \dots\dots\dots(7)$$
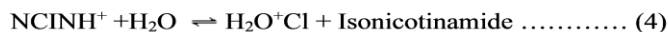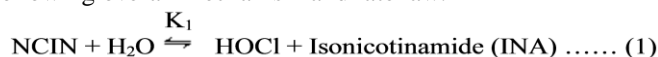
Where R= CH_3 for lactic acid and R'= H for lactic acid

On the basis of the aforementioned steps involved in the proposed mechanism and at steady state approximation condition, the final rate law is derived as;

$$k_{obs}^{-1} = \frac{1}{[HA]}\left\{\frac{[INA] + K_1 + K_1 K_2 [H^+]}{k_1 K_1 K_3 K_4}\right\}\frac{1}{[PTA]} + \frac{1}{k_1}$$

This proposed rate law explained all experimental facts.

V.   CONCLUSION

Lactic acid is an aliphatic hydroxy acid. At first substrate formed a complex with PTA which is attacked by HOCl, an active species of NCIN. Just like the oxidation of aliphatic hydroxy acid with NCSA [35-36] and NBIN [37], NCIN also exhibits similar kinetics with aliphatic hydroxy acid. An intermediate complex formed which is decomposes in a slow rate determining step and give the product. The reaction obeys Arrhenius relationship. The proposed mechanism is in good accordance with experimental findings.

REFERENCES

[1].   Cindric M., Veksli Z., Kamenara B., *Croat. Chem. Acta.*, 82 (2), 345, **2009**.
[2].   Skrzpek J., Witczak T., Grzesik M., Witczak M., *Int. J. Chem. Kinet*., 41, 12, **2009**.
[3].   Supale A. R., Gokavi G. S., *React.Kinet.Catal.Lett.,* 96 (1) 83, **2009**.
[4].   Bogdanovic D. B., Anyunovic I. H., Todorovic M., Mioc U. B., Zakrzewska J., J. Serb.Chem. Soc., 73 (2), 197, **2008**.
[5].   SatpathyP. K., Das G. C., Mohanty P., *Indian J. Chem.,* 47A, 1199, **2008**.
[6].   Rajmane D. S., Kapshikar K. V., Gokavi G. S., *Indian J. Chem.,* 45A, 1626, **2006.**
[7].   Bharad Jagdish V., Madje Balaji R., Ubale Milind B., Archives of Applied Science Research, 2 (3):143-152, **2010**.
[8].   Purohit, V., Mishra, P., International Journal of Innovative research & Review, 6(1), 27-37. **2018**.
[9].   Chadrasekaran, S., Subramani, Dr. K., Int. Journal, for Scientific Research & Development, 3(11), **2016**.
[10].   Khan, N., Dwivedi Arvind P., Khan K, Dwivedi, H.P., Int. Journal of Advanced Rearch in Chemical Science, 5(6),15-19, **2018**.
[11].   Chandsekaran S and Subramani K., International *Journal of Science and Research Development* 3 (11) -114-118, (**2016**).
[12].   Subash A, Malik VS, Shafi SS and Mansoor SS., *Der Pharmacia Lettre, Scholars Research Library* 7(11) 100-106. (**2015**).
[13].   Kumar R, Solanki J, Hedau I, Purohit P. and Sharma V., JCBPS; Section A; 8(4), 619-630, **2018**.
[14].   Alhaji NMI, Mamani R and Kayalvizhi K., Chemical Science Transactions 5(1) 232-238, (2016).
[15].   Hedau I, Solanki J, Sharma R, Songara U and Sharma V., *Journal of Applied Chemistry* 6 (5) 846-854, (**2017**).
[16].   Pushpalatha L., *International Letters of Chemistry, Physics and Astronomy* 52 111-119, (**2015**).
[17].   Ahmed SZ, Shafi SS and Mansoor SS., *Pelagia Research Library* 3 (1) 123-129, **2012**.
[18].   Y. Zilberter, T. Zilberter, P.Bregestovski, Trends Pharmacol. Sci. 2010, 31 (9), 394.
[19].   J.A. Aas, A.L. Griffen, S.R. Dardis, A.M. Lee, I. Olsen, F.E. Dewhirst, E.J. Leys, B.J. Paster, Journal of clinical microbiology, 2008, 46 (4), 1407.
[20].   P.W.Caufield, Y. Li, A. Dasanayake, D. Saxena, Caries Res. 2007, 41 (1), 2.
[21].   Y. Zilberter, T. Zilberter, P.Bregestovski, Trends Pharmacol. Sci. 2010, 31 (9), 394.
[22].   M.T.Wyss, R. Jolivet, A.Buck, P.J. Magistretti, B. Weber, J. Neurosci. 2011, 31 (20), 7477.
[23].   L.B. Gladden, J. Physiol. (Lond.), 2004, 558, 5.
[24].   L. Pellerin, A.K. Bouzier-Sore, A. Aubert, et al. Glia, 2007, 55 (12), 1251.
[25].   Baghmar, D. Purohit, P., Sharma I. K., Baghmar M., And Vinita Sharma, Int. J. Chem. Sci.: 9(3), 1247-1260, **2011**.
[26].   H. Y. Wang, F. Li, S. P. Liang, and X. H.chen , Chemistry & Bioengineering, 22(12), 29−31, **2005**.
[27].   JinhuanShan, FangWang, Changying Song, and Heye Wang., Research Letters in Inorganic Chemistry, doi:10.1155/2008/314045, **2008**.
[28].   Qian Yin, Lichen Yin, Hua Wang, and Jianjun Cheng*, Accounts of Chemical Research, vol., 48, 1777−1787, **2015**.
[29].   Priya V., Mathiyalangan N., Asian journal of Chemistry,23(4), 1871-1872, **2011.**
[30].   Priya V.,Reena Mary A.,Zaijeyanthi P.,Mathiyalangan N., International journal of research and development in pharmacy and life sciences,3(6),1304-1309, **2014.**
[31].   Priya V., Subalakshmi M., International Journal of Scientific Research, 9(6(D)), 27441-27443, **2018.**
[32].   Priya V., Subalakshmi M., International Journal for Research in Applied Science & Engineering Technology (IJRASET), 6(1)2099-2103,**2018.**
[33].   Priya V., Subalakshmi M., Research Journal of Chemical and Environmental Sciences, 5(4),14-17,**2017.**
[34].   Priya V., Subalakshmi M., International Journal of ChemTech Research, 10(10),658-665,**2017.**
[35].   Khan M.U., Sharma V.K. Sharma K. Dwivedi H.P., Oxid Commun., 14(1), 62-65, **1991**.
[36].   Khan M.U., Verma J.K. Singh V.R., Dwivedi H.P., Oxid Commun., 16(3), 235-239, **1993**.
[37].   Prajapati A., Dwivedi A.P., Parihar S.S., International Jou. Of chem. Sc. Vol. 3 (4). 09-11 **(2019)**