Apr 2026- Jun 2026 , Vol 9, No. 2, 1- 13 ISSN 2394-9449

Electronic Journal of Advanced Research

An International Peer review E-Journal of Advanced Research

Research Articles

ELUCIDATION OF THE KINETICS AND MECHANISM OF PROPANE-2-OL OXIDATION BY N-CHLOROPICOLINAMIDE.

Sanjay K Singh[1], Deepti Pandey[2*], Ritika yadav[3] , Aarti Tiwari[1]

1. Department of Chemistry Govt.T.R.S. College Rewa

2. Department of Chemistry, Govt PG College Rampur Naikin

3. Department of Chemistry, Govt Girls Degree College Rewa

** Corresponding author: pandeydeepti23@gmail.com*

Received: 12/06/2026 **Revised**: 15/06/2026 **Accepted**: 24/06/2026

ABSTRACT:

The oxidation of propane-2-ol by a mild and selective oxidizing agent N-chloropicolinamide (NCPA) leads to the formation of corresponding substituted prop-2-one. The reaction found first order in NCPA. The reaction follows Arrhenius relationship with respect to propan-2-ol. A retarding effect of acetic acid is observed. Various thermodynamic parameters have been computed. No evidence of Polymerization of acrylonitrile showed any 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: Kinetics, propane-2-ol, Mechanism, NCPA, Oxidation.

1. INTRODUCTION

N-halo oxidants have a broad history as an oxidant with different substrates.[1-11] N-chlorophthalimide (NCPA) is a new member of the N-halo family. The synthesis

and characterisation of N-chloropicolinamide for the quick oxidation of organic substrates are the topics of this research.[12-14] NCPA, the derivative of Phthalimide is a mild, stable, efficient, and inexpensive oxidant for organic substates. The elemental analysis and physical properties of NCPA 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 oxidation kinetics of secondary alcohol has been extensively studied. They have substaintially helped to our understanding of mechanistic pathway for reaction. Secondary alcohols are studied with various oxidants and follows first order kinetics [15-26].

The general review of the literature explored that no works have been reported about the oxidation of propan-2-ol with NCPA; so,this prompted for the present investigation and evaluate kinetic parameters as well as correlation analysis.

2. MATERIALS AND METHODS

2.1.1. 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 NCPA prepared by reported method.

2.1.2. Kinetic experiment

The experiments were performed under pseudo-first-order conditions by keeping an excess of the substrate over NCPA. 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 ± 0.1K (308K).Requisite volumes of all reagents, except NCPA, were introduced into a reaction vessel and equilibrated at 308K. A measured volume of NCPA, 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 NCPA iodometrically using starch as the indicator.

2.1.3. Product analysis

The end product from the oxidation of propan-2-ol was Prop-2-one 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 propan-2-ol was taken over NCPA. 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 propan-2-ol.

3. RESULT AND DISCUSSION

The oxidation of propan-2-ol was carried out by NCPA at 308K under pseudo first order condition. The rate of propan-2-ol and other experimental data were obtained. Oxidation of propan-2-ol by NCPA under the condition [NCPA] << [propan-2-ol] had the following kinetic feature.

3.1. Stoichiometric studies

The stoichiometric studies of oxidation of propan-2-ol by NCPA were carried out with excess of oxidant (NCPA) and maintaining other parameters constant (HOAc-H_2O = 30 % (v/v), Temperature = 308K).The stoichiometric results indicated 1 mole of substrate consumes 1 mole oxidant as represented by the following empirical equation:

$$CH_3\text{-}\underset{\underset{R}{|}}{C}HOH + C_5H_5NCONHCl \rightarrow CH_3\text{-}\underset{\underset{R}{|}}{C}{=}O + HCl + C_5H_5NCONH_2$$

Where R = CH_3 for propan-2-ol

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

3.2. Order with respect to [oxidant] [substrate]

When the substrate (SA1) is in large excess, the plots of log (a-x) vs time **(Figure 1)** are found to be linear, indicating first-order dependence on NCPA. The pseudo first-order rate constants in NCPA calculated at different initial concentrations of the reactants are found to be independent of the substrate concentration. The plot of k_1 *vs* [substrate] 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 substrate concentration.

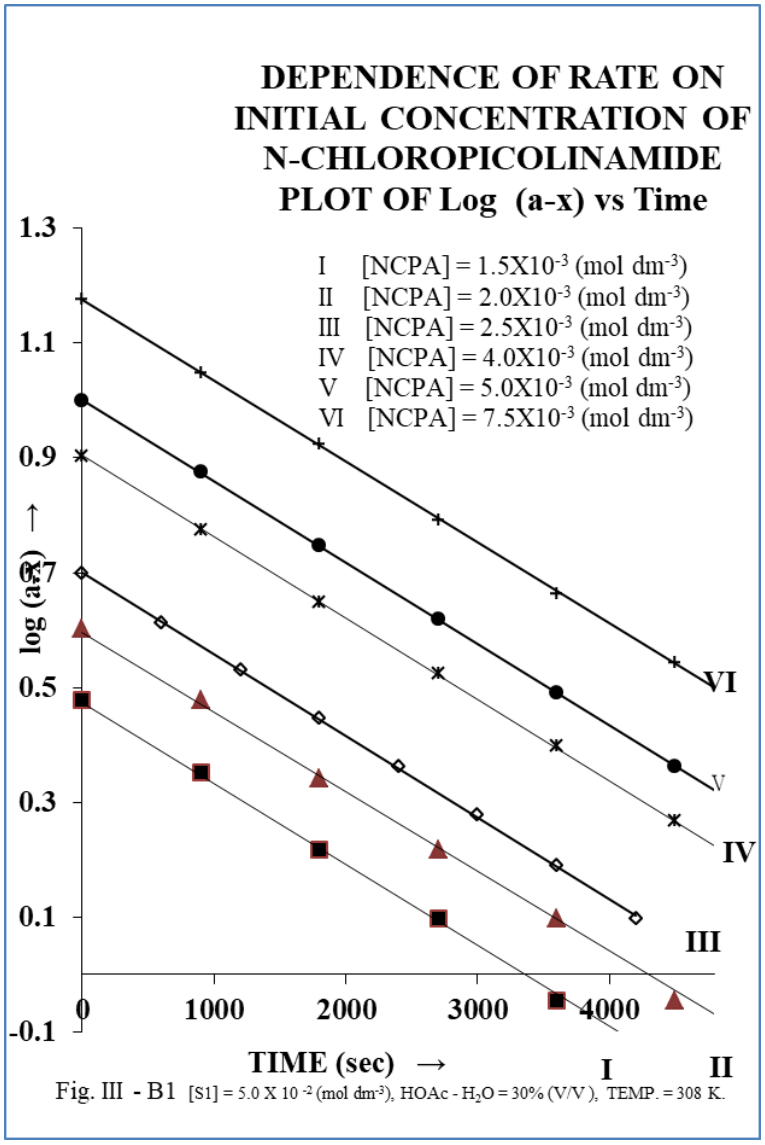


Figure 1: The plot of log (a-x) versus time. Conditions are given in Table 1.

Apr 2026- Jun 2026 , Vol 9, No. 2, 1- 13 ISSN 2394-9449
Electronic Journal of Advanced Research
An International Peer review E-Journal of Advanced Research

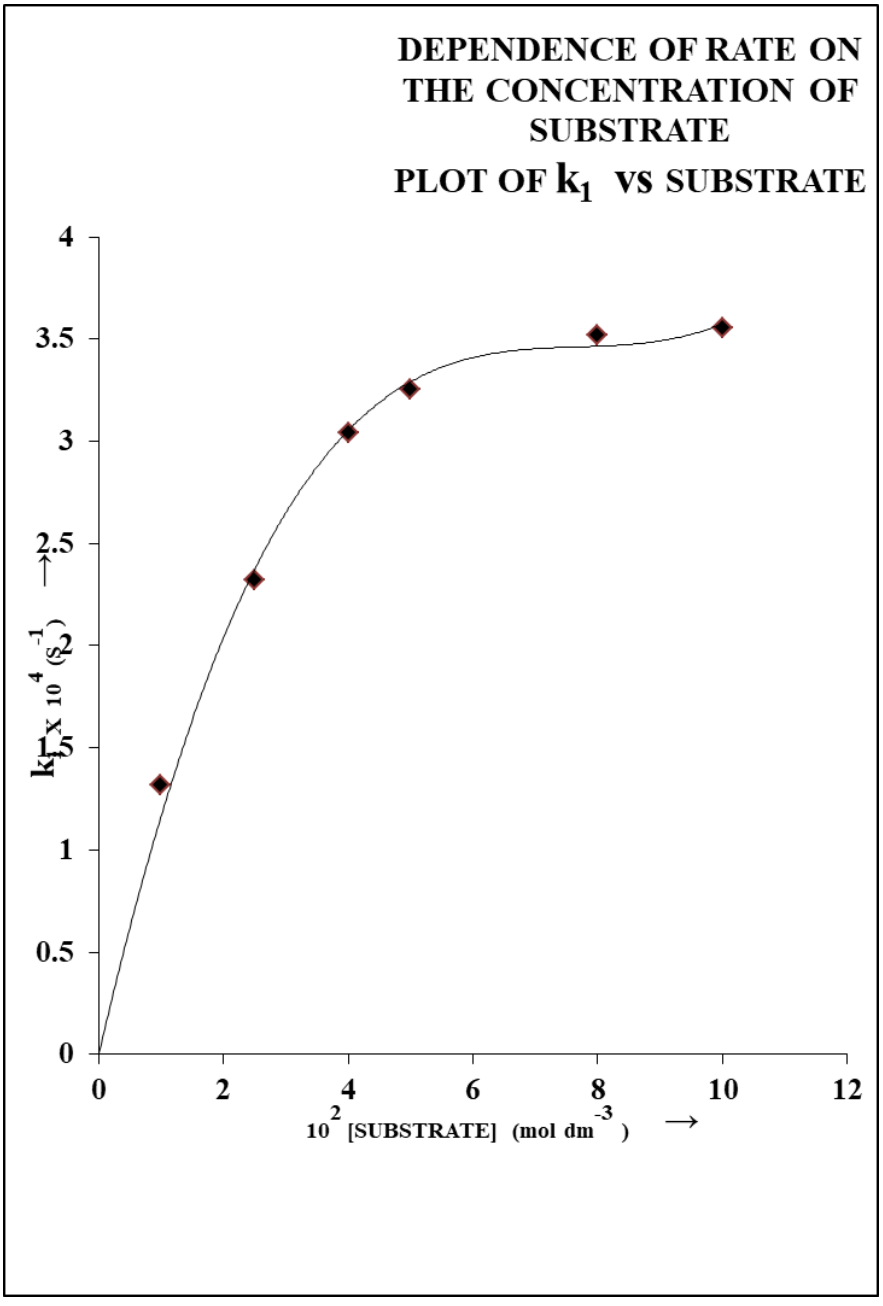


Figure 2: Dependence of k_1 on [Substrate]. Conditions are given in Table

Table 1: Effect of variation of reactants on pseudo-order rate constant k_1 at 308K

10^2 [Substrate] (mol dm^{-3})	10^3 [NCPA] (mol dm^{-3})	$[H^+]$ (mol dm^{-3})	% HOAc - H_2O	k_1x10^4 (s^{-1})
1.00	2.50	-	30	1.316
2.50	2.50	-	30	2.321
4.00	2.50	-	30	3.041
5.00	2.50	-	30	3.252
8.00	2.50	-	30	3.521
10.00	2.50	-	30	3.554
5.00	1.50	-	30	2.941
5.00	2.00	-	30	2.952
5.00	2.50		30	3.252
5.00	3.00	-	30	2.938
5.00	4.00	-	30	2.947
5.00	5.00	-	30	2.926
5.00	7.50	-	30	2.945
5.00	2.50	0.00	30	3.252
5.00	2.50	0.10	30	3.519
5.00	2.50	0.15	30	3.754
5.00	2.50	0.20	30	3.902
5.00	2.50	0.25	30	4.358
5.00	2.50	0.30	30	4.608
5.00	2.50	0.40	30	4.903
5.00	2.50	0.50	30	5.215
5.00	2.50	-	10	3.621
5.00	2.50	-	20	3.429
5.00	2.50	-	30	3.252
5.00	2.50	-	40	3.124
5.00	2.50	-	50	2.682

3.2.1. 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 3**) gave a straight line with positive intercept, suggesting that acid plays a complex role in the reaction system.

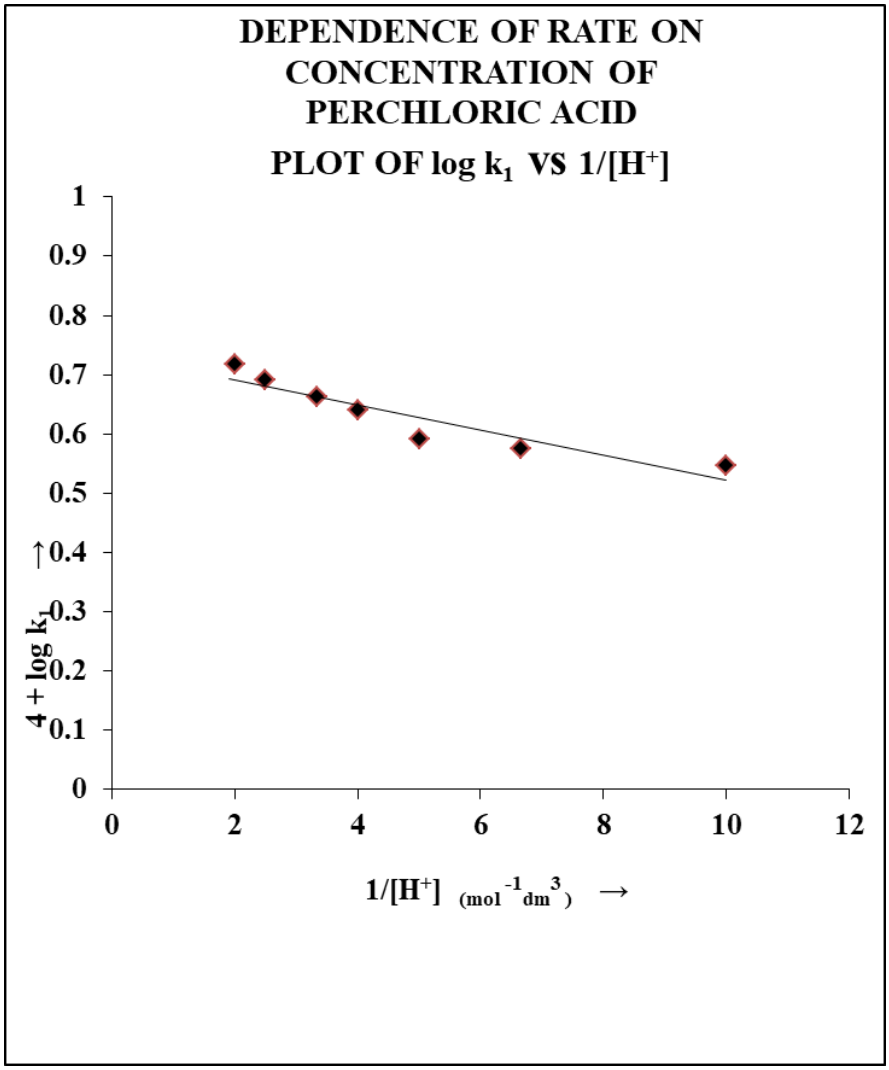


Figure 3: Dependence of k_1 on $[H^+]$. Conditions are given in Table 1.

3.2.2. 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.

3.2.3. Effect of ionic strength and Picolinamide:

The reaction rate was not influenced by the addition of chemically neutral salt. Hence the ionic behavior on slow step in the reaction mechanism is ruled out. Addition of picolinamide (one of the reaction products), at constant NCPA and substrate concentration, decreases the rate of reaction. The retardation of reaction rate on the addition of picolinamide suggests a pre-equilibrium step that involves a process in which picolinamide is one of the products. If this equilibrium is involved in the oxidation process the retardation should be an inverse function of picolinamide concentration.

3.2.4. 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.

3.2.5. Effect of temperature:

The effect of temperature on the reactions of propan-2-ol with NCPA in 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 Propan-2-ol-NCPA system

Substrate	Ea ($kJ\ mol^{-1}$)	A (s^{-1})	ΔH* ($kJ\ mol^{-1}$)	ΔG* ($kJ\ mol^{-1}$)	-ΔS* ($JK^{-1}\ mol^{-1}$)
Propan-2-ol	**72.548**	**$0.99x10^{8}$**	**68.126**	**90.136**	**69.531**

4. MECHANISM

The concentration of NCPA was found to be constant over a period of time. So, it was found that there was no appreciable reaction between acid and NCPA.

Retarding effect of picolinamide & solvent and positive effect of H+ clearly ruled out the NCPA, CH3COOCl, CH3COO+HOCl 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.

$$NCPA + H_2O \quad HOCl + Picolinamide$$

Apr 2026- Jun 2026 , Vol 9, No. 2, 1- 13 ISSN 2394-9449
Electronic Journal of Advanced Research
An International Peer review E-Journal of Advanced Research

$$NCPA + H^+ \rightleftharpoons NCPAH^+$$

$$NCPA + H^+ \rightleftharpoons Picolinamide + Cl^+$$

$$NCPA + H_2O \rightleftharpoons HOCl + Picolinamide$$

$$HOCl + H^+ \rightleftharpoons H_2O^+Cl$$

$$NCPAH^+ + H_2O \rightleftharpoons H_2O^+Cl + Picolinamide$$

$$NCPA + CH_3COOH \rightleftharpoons Picolinamide + CH_3COOCl$$

$$CH_3COOCl + H^+ \rightleftharpoons CH_3COO^+HCl$$

$$NCPA + H_2O \overset{K_1}{\rightleftharpoons} HOCl + Picolinamide\ (PA) \quad (1)$$

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

$$NCPA + H^+ \rightleftharpoons NCPAH^+ \quad (3)$$

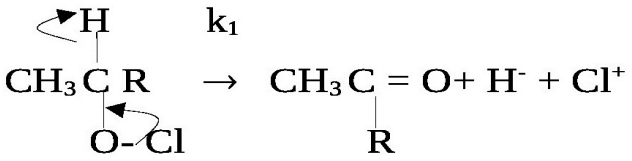
$$NCPAH^+ + H_2O \rightleftharpoons H_2O^+Cl + Picolinamide\ (PA) \quad (4)$$

$$CH_3\underset{OH}{CH}R + HOCl \overset{K_3}{\rightleftharpoons} CH_3\underset{O\text{-}Cl}{CH}R + H_2O \quad (5)$$

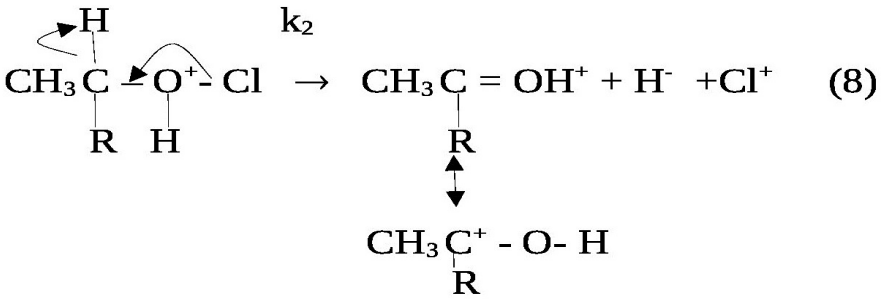
$X_1^{\#}$

$$CH_3\underset{OH}{CH}R + H_2O^+Cl \overset{K_4}{\rightleftharpoons} CH_3\underset{O^+HCl}{CH}R + H_2O \quad (6)$$

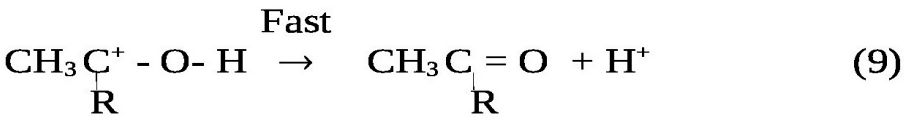
$X_2^{\#}$



(7)



(8)



(9)

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;

$$k_{obs} = \frac{[SA]\ (k_1K_3 + k_2K_4\,K_2\,[H^+])\,K_1}{[PA] + K_1 + K_3\,[SA]\,K_1 + K_2\,K_1\,[H^+]\,(1+K_4\,[SA])}$$

This proposed rate law explained all experimental facts.

5. CONCLUSION

Prop-2-ol is a secondary alcohol. At first substrate formed a complex which is attacked by HOCl, an active species of NCPA. Just like the oxidation of some other compounds with N-halo oxidants [27-28], NCPA also exhibits similar kinetics with different substrates. 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.

6. REFERENCES

1. Mathiyalagan M., J. Indian Chem.Soc, 2011,88, 865.
2. Priya V, Balasubramaniyan M., Mathiyalagan M., J. Chem. Pharm. Res., 2011, 3, 522.
3. Ramakrishnan P. S., Asian J. Chem., 2000,12, 1096.
4. Goyal S., Kothari, J. Chem. Res., 2002, (S)2, 1259.
5. Tomer A.,Kumar A., J. Indian Chem. Soc., 2006,83, 1153.
6. Pusphalatha J., Vivekanandan K, J. Indian Chem. Soc., 2009, 86, 895.
7. Kavitha S., Alphonse I. , Indian J. Chem., 2005, 44A, 715.
8. Mathiyalagan M., Priya V., John Basco J., J. Indian Chem. Soc., 2006, 86, 453.
9. Farook N. A. M, J. Solution chem, 2007,36, 345.
10. Mathiyalagan N., Shenbagam K., Kavitha M., Asian J. Chem., 2010, 22, 265.
11. Singh R. A, Singh K., Singh S. K., J. Chem Pharm. Res., 2010, 2, 684.
12. Ramkuma B., Asian J. Chem., 2001,13, 777.
13. Subalakshmi M., Priya V., Rasayan J. Chem., 2019, 12, 3,|1493.
14. Senbagam K. and Mathiyalagan N., Orient J. Chem., 2013, 29, 747.
15. Prakash O.M., Sharma P.K., Oxid. Commun. 2003, 26, 4, 517.
16. Baumstark A.L., Vasquez P.C., Cunningham M.,Leggett R., Pamela M., Heterocyclic Commun., 2010, 16, 4-6, 217.
17. Meenakshisundaram S., Socklingam R., Collect. Czech. Chem. Commun. 2001, 66, 877.
18. Kumar R., Panday D., Kothari S., Progress in Reaction Kinetics and Mechanism, 2011, 36, 1, 1.
19. Puttaswamy, Ramchandrappa R., Madegowda N. M.,Synthesis and Reactivity in

Inorganic and Metal-Organic chemistry, 2002,32,7,1263.

20. *Sharma D., Pancharia P., Vyas S., Kotai L., Sharma P. K.,* Int. J. Chem., 2011, 1, 1, 29.
21. Purohit V., Mishra P., Eur. Chem. Bull., 2016, 5, 8, 324.
22. Sayyed-Alangi, S. Z., Sajjadi-Ghotbabadi, H., Baei, M. T., Naderi, S., E-J. Chem., 2011, 8, 2, 815.
23. Vyas N., Goswami G., Choudhary A., Prasadrao, P. T. S. R. K.,Sharma V., Int. J. Chem., 2015, 4, 3, 215.
24. Rao A., Panwar S., Prakash O., Vyas S., Sharma P. K., J. Chem. Bio, Phy.Sci., Sec. A, 2016, 6, 3, 876
25. Alhaji N. M. I., Mamani R., Kaiyalvizhi K., Chem. Sci. Trans., 2016, 5, 1, 258.
26. Rao A., Purohit T., Swami P., Purohit P., Sharma P. K., Eur. Chem. Bull., 2016, 5, 5, 189.
27. Priya, V., Balasubramaniyan, M., Mathiyalagan, N., J. Chem. Pharm. Res., 2011, 3, 1, 522.
28. Patwari, S.B., Khansole, S.V., Vibhute, Y.B., J. Iran. Chem. Soc., 2009, 6, 2, 399.