Oxidative and Thermodynamic Study of Aliphatic Amino Acids by 1,3-dichloro-5,5-dimethylhydantoin in Aqueous Acetic Acid Medium

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Abstract: *The kinetics of reaction between aliphatic ℓ-amino acids and 1,3-dichloro-5,5-dimethylhydantoin have been studied in aqueous acetic acid medium yielding aliphatic aldehydes as the end-products by the ring cleavage oxidation. The catalytic effect of acid in the reaction rate reveal an interaction between oxidants species H_2O^+Cl and substrates. The observed order of reactivity ℓ-amino acids (ℓ-Glycine > ℓ-Alanine) was explained on the basis of conformational considerations. A plausible mechanism and rate law supported by thermodynamic parameters was discussed.*

Keywords: aliphatic aldehydes, demonstrates, reveals, plausible.

1. INTRODUCTION

The kinetics of the reactions involving the redox system[1] in chemistry of reactions of halo-compounds such form a separate branch, which is of great synthetic importance.[2-4] N-halo compounds have been extensively employed as oxidizing agents for the catalysed and uncatalyzed reactions.[5-12] DCDMH is of immense importance and has found limited applications. It is stable, commercially cheap and eco-friendly easily available market which has been rarely used as source of chlorine[13] or chlorination[14,15] and oxidation reactions[16,17]. Only few reports are available of its use in organic synthesis[18] and oxidation of chalcocones,[19] carbohydrates[20] etc, Although a lot of works on the oxidation of amino acids have been reported by different oxidants,[21-23] but no systematic study was made on oxidation of ℓ-alanine (CH_3CHNH_2COOH), ℓ-glycine (NH_2CH_2COOH) by 1,3-dichloro-5, 5-dimethylhydantoin, in aqueous acid medium.
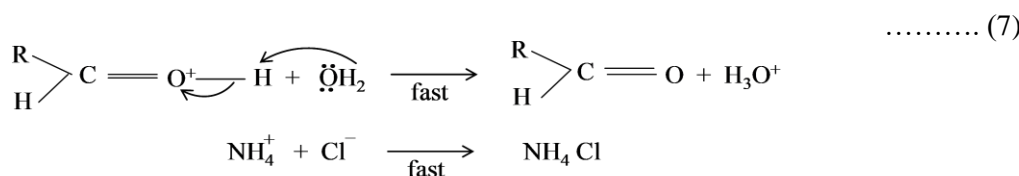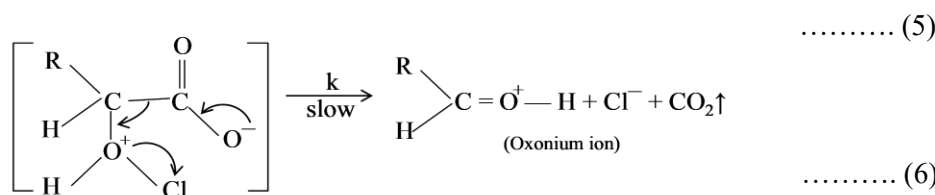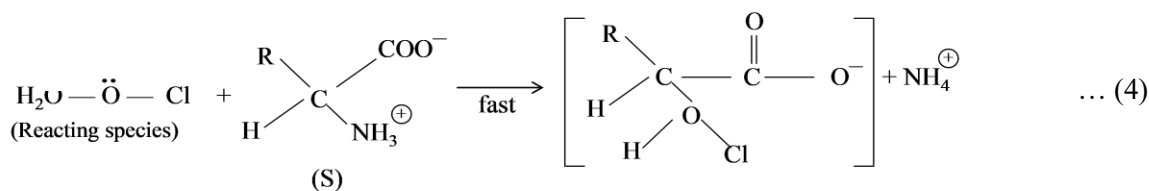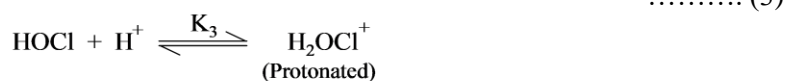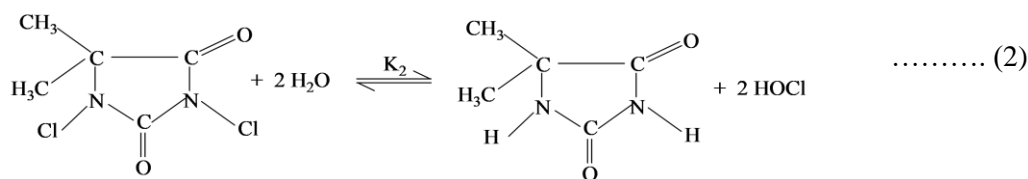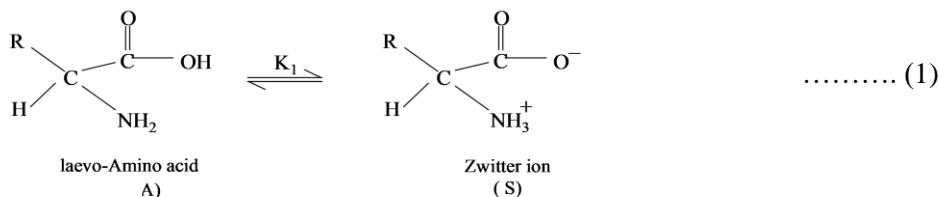
1. EXPERIMENTAL

All the reagents and solvents used were of analytical grade (B.D.H. C.D.H. and Acros). The solution of DCDMH is standardized iodometrically.[24] The solution of sodium thiosulphate was prepared by taking a B.D.H. grade simple in a doubly distilled water and was standardized against copper sulphate solution using KI and starch as an indicator iodometrically. The standard solution of HCl was determined by titrating it against standard NaOH solution using phenolphthalein as an indicator. Other solutions of NaCl, KCl, DMH were prepared by dissolving their requisite amount of AnalaR sample in distilled water. The reaction kinetics was studied by using thermostat maintained at constant temperature. The rate constant was determined by integration method.

2. RESULTS AND DISCUSSION

The probe of reactions occur at measurable rate within a temperature range 303 and 308 K respectively. The kinetic data have been collected for under the experimental condition [substrate] > [oxidant] [DCDMH] ($1.25 - 5.0 \times 10^{-3}$ mol dm^{-3}) and at fixed concentration of other reactants at constant temperatures. The unit slope of plot of log [DCDMH] vs. time was found to be linear indicating first-order dependency of rate. The first-order kinetic rate was obtained with in concentrations of ℓ-amino acids ($0.50 - 5.00 \times 10^{-2}$ mol dm^{-3}) The reaction rate constants was measured various [H^+] ($0.20 - 1.25$ mol dm^{-3}) (Table:1) which was found catalyzed in reactions. The plot of log k vs. log [H^+] (Fig. 1) is obtained linear with approximately unit slope showing the rate of reaction is proportional to the first power of [HCl]. The rate was enhanced by increasing the percentage composition of solvent polarity. Insignificant affection rate was observed by successive addition of primary salts. The Dimethyl hydantoin found to retard the reaction rate. The activation and thermodynamic parameters were evaluated for the reactions understudy (Table:2). The Arrhenius plots of log k vs. 1/T (Figs. 2 & 3). Suggested the more reactive Amine has lowest energy of activation substrate. Similar mechanism prevail in both the substrate over all the reactions are enthalpy controlled. The Arrhenius plot of log k_{obs} vs. 1/T were plotted which were found to be liner. It is obvious from the thermodynamic parameter that $\Delta H^{\#}$ and $\Delta S^{\#}$ which play important role in controlling the rates of reactions.
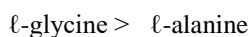
MECHANISM

1,3-dichloro-5,5-dimethylhydantoin (DCDMH) on hydrolysis yields finally dimethyl- hydantoin (DMH) in aqueous solution. The following equilibrium exists.

………. (1)

………. (2)

………. (3)

$$HOCl + H^+ \underset{K_3}{\rightleftharpoons} H_2OCl^+ \text{ (Protonated)}$$

… (4)

………. (5)

………. (6)

………. (7)

$$NH_4^+ + Cl^- \xrightarrow{fast} NH_4Cl$$

The final rate law derived based on mechanism using steady state approximation is represented by equation (8).

$$\frac{-d}{dt}[DCDMH] = \frac{k\,K_1\,K_2\,K_3\,[S]\,[H^+]}{[DMH] + K_2} \qquad ………. (8)$$

The observed order of reactivity was found in sequence

$$\ell\text{-glycine} > \ell\text{-alanine}$$

The similar mechanism has also been earlier reported by authors[25,26] for the study of ℓ-AA- DCDMH system. The reaction yielded acetaldehyde and formaldehyde as the end-products which is characterized by the spot test and other modern physical methods.

4. CONCLUSION

1,3-dichloro-5,5-dimethylhydantoin (DCDMH) has been found as moderate oxidant for the oxidation of ℓ–alanine and ℓ–glycine.

The thermodynamic and activation parameters determined are well in accordance with the reactions involving Zwitter ions which supported the rate determining step in the mechanism.

Table 1 : *Effect of concentration of Acid on rate of reaction*
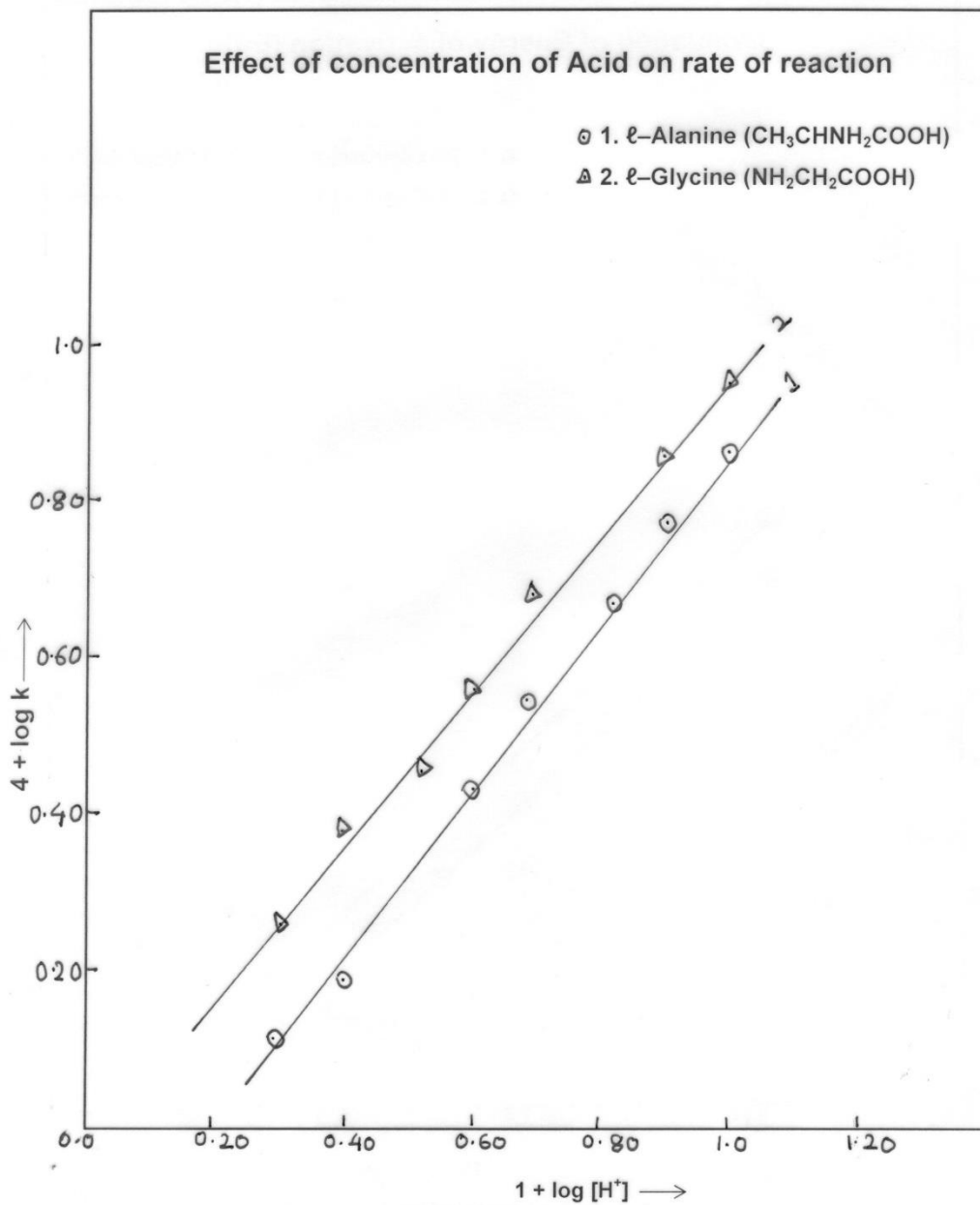
$10^3 \times$ [DCDMH] (mol dm^{-3}) = 2.50 (1, 2) ;
$10^2 \times$ [Substrate] (mol dm^{-3}) = 2.00 (1), 1.25 (2) ;
CH$_3$COOH- H$_2$O % (v/v) = 30 (1), 20 (2) ;
Temp. K = 303 (1), 308 (2)

S. No.	[H$^+$] (mol dm^{-3})	$\longleftarrow$ 10^4 k$_{obs}$ (s^{-1}) $\longrightarrow$	
		ℓ-alanine (CH$_3$CHNH$_2$ COOH)	ℓ-glycine (NH$_2$CH$_2$COOH)
		(1)	(2)
1.	0.20	1.33	1.82
2.	0.25	1.55	2.42
3.	0.33	2.29	2.89
4.	0.40	2.71	3.63
5.	0.50	3.47	4.75
6.	0.66	4.65	-
7.	0.80	5.98	7.23
8.	1.00	7.24	8.87

1. ℓ-alanine   2. ℓ-glycine

Fig. 1 10^3[DCDMH] (mol dm^{-3}) =2.50 (1, 2) ;
10^2[Substrate] (mol dm^{-3}) =2.00 (1), 1.25 (2), ;
HOAc–H$_2$O % (v/v) = 30(1), 1.25 (2) ;
Temp. K = 303 (1), 308 (2)
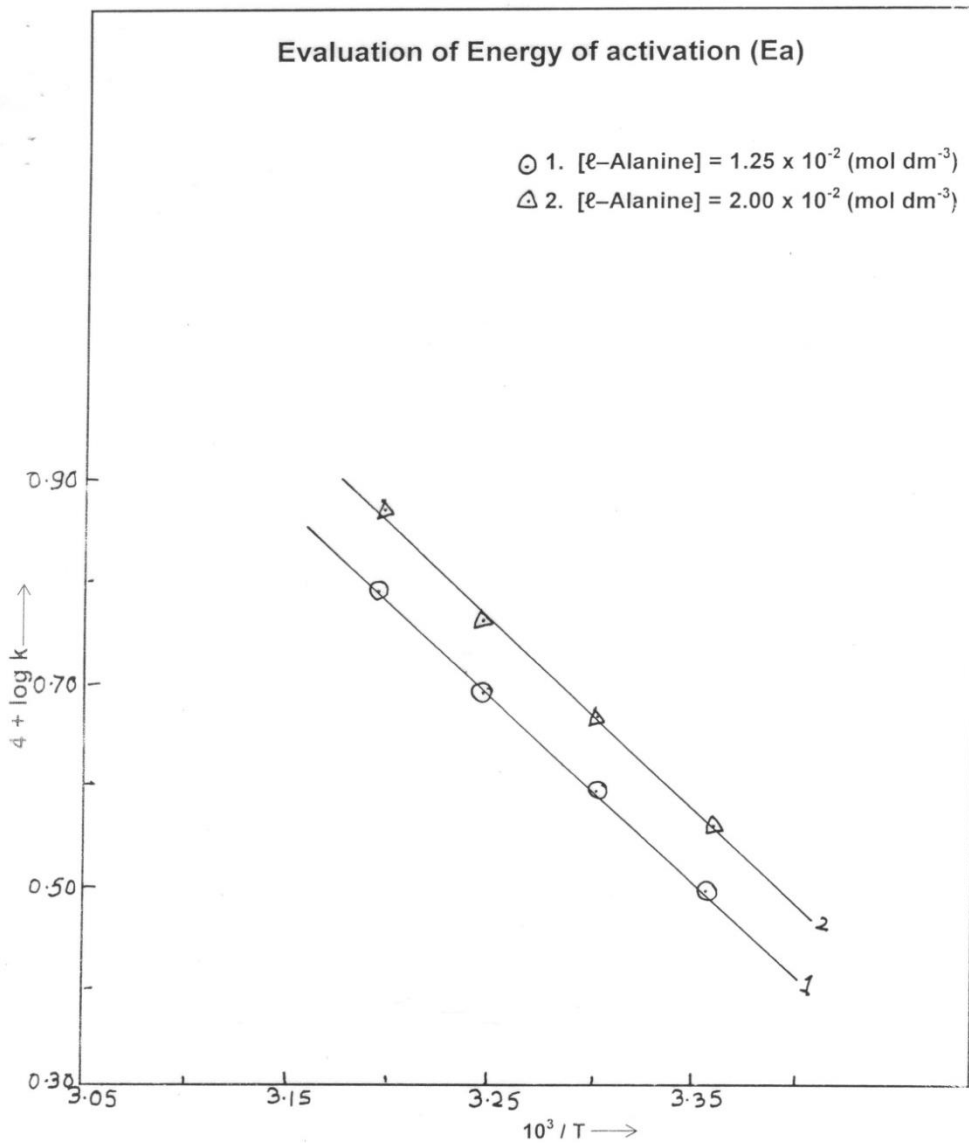
Fig. 2

Fig. III-15 [DCDMH] = 2.50×10^{-3} (mol dm^{-3}) ; [H^{+}] = 0.66 (mol dm^{-3}) ;
HOAc-H$_2$O = 30 % (v/v)
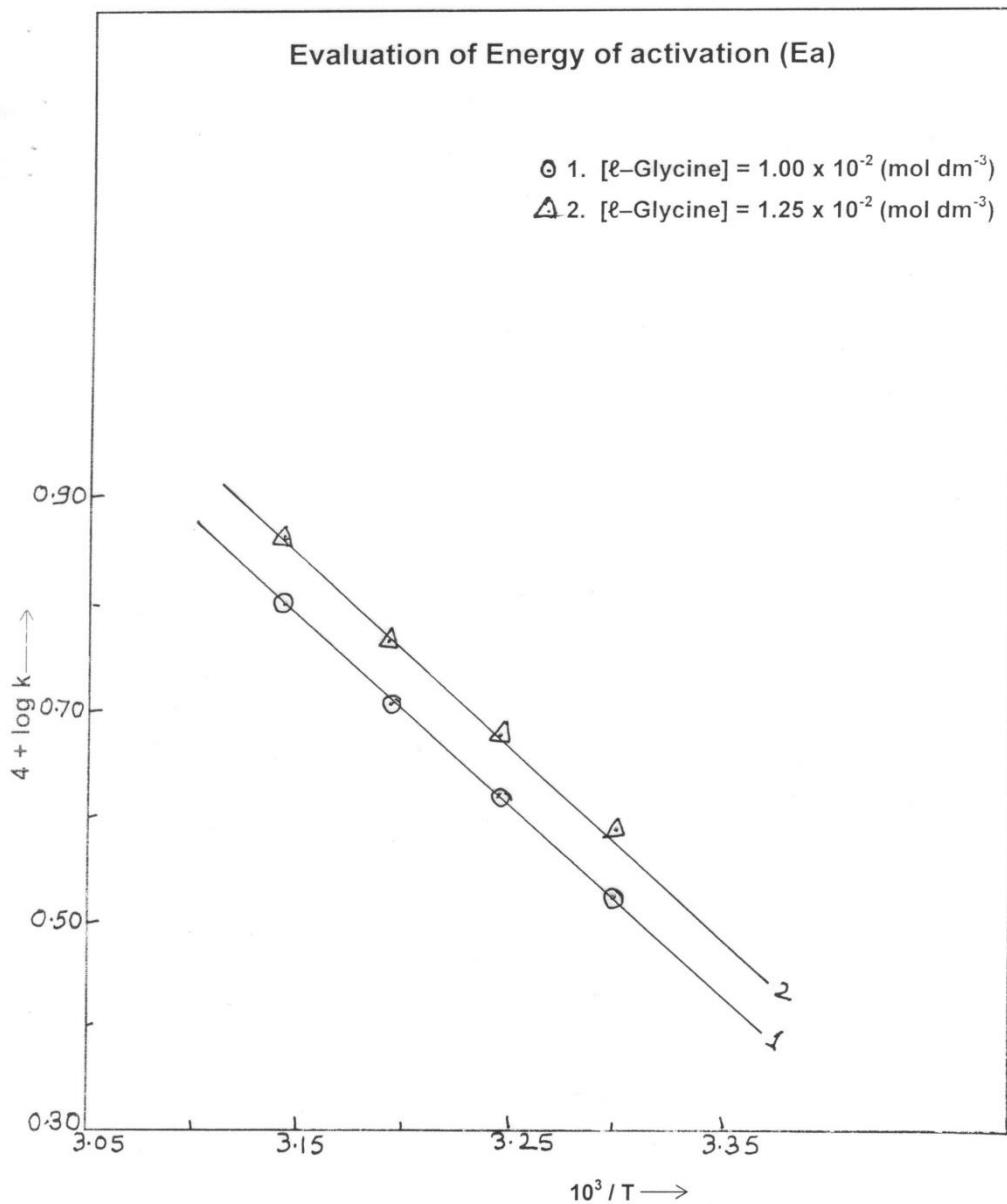
Fig. 3   Fig. III-16   [DCDMH] = 2.50 x 10^{-3} (mol dm^{-3}) ; [H$^+$] = 0.50 (mol dm^{-3}) ;
HOAc-H$_2$O = 20 % (v/v)

Table 2 : *Activation and Thermodynamic parameters for ℓ-amino acids- 1,3-dichloro-5,5-dimethylhydantoin system*

S. No.	Substrate	Ea (kJ mol^{-1})	A (s^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})	$-\Delta S^{\#}$ (JK^{-1} mol^{-1})
1.	ℓ-Alaine (CH$_3$CHNH$_2$COOH)	35.34	2.75×10^2	32.80	84.18	168.23
2.	ℓ-Glycine (NH$_2$CH$_2$COOH)	33.91	1.83×10^2	30.82	84.30	175.86

REFERENCES

[1]   Hudlicky, M. : Oxidation of organic chemistry, American Chemical Society, Washington, D.C., 1990.

[2]   Patrocino, F.A. : J. Organomet Chem., 2000, **220(b)**, 603.

[3]   Dhurn, P.S., Mohe, N.U., and Salunkhe, M.M. : Synth. Commun. 2001, **31**, 3653.

[4]   Bondgar, B.P., Uppalla, L.S. and Sadavarte, V.S. : Syn. Lett. 2001, **11**, 1715.

[5]   Thenraja, D., Subramanian, P., and Srinivasan, C. ; J. Chem. Soc., Perkin Trans., 2002, 2.

[6]   Mukaiyama, T., Mastsuo, J.I.,, Lida, D. and Kitagawa, H. : Chem. Lett. 2001, **8**, 846.

[7]   Mukherjee, J. and Banerji, K.K. : J. Org. Chem. 1981, **46**, 2323.

[8]   Singh, A.K., Singh, V., Rahmani, S., Singh, A.K., and Singh, B. : J. Mol. Catal. A.: 2003, **197**, 91.

[9]   Filler, R. : Chem. Rev., 1963, **63**, 21.

[10]   Balasubramaniyan, P.V., and Mathigalagan, N. ; J. Chem. Pharm. Res., 2011, **3**, 522.

[11]   Shrinivasan, N.S., and Venkatasubramanian, N. : Tetrahedron Lett. 1970, **11**, 2039.

[12]   Vivekanandan, K., and Nambi, K.; J. Indian Chem. Soc., 1999, **76**, 198.

[13]   Kolvari, E., Ghorbani-Choghamarani, A., Salehi, P., Shbiini, F., and Zolfigol, M.A. : J. Iran. Chem. Soc., 2007, **4**, 126.

[14]   Xu,Z., Zhang, D., and Zou, Z. : Synth. Commun. 2006, **36**, 255.

[15]   Skibinska, M., Zahn, F.A., Czarnacka, A., and Lewenstein, W. : Acta. Pol. Pharm. 1969, **6**, 25.

[16]   Khazaei, A, Amini-Manesh, A. : J. Chin. Chem. Soc., 2005, **52**, 1017.

[17]   Khazaei, A, Amini-Manesh, A. : Synthesis, 2005, 1929.

[18]   Nicolet, B.N., and Shinn, L.A. : J. Am. Chem. Soc., 1929, **51**, 1615-1622.

[19]   Tamil selvi, P., and Karunakaran, K. : Asian J. Chem., 2015, **27(5)**, 17254-1728.

[20]   Mergrregor, W.H., and Carpenter, F.H. : J. Bio Chemistgry, 1962, **1**, 53-62.

[21]   Wright, N.C. : J. Bio Chem., 1936, **30**, 1661-1676.

[22]   Kumar, M.N., Mantelingu, K., Bhardregowda, D.G. and Rangappa, K.S. : J. Mol. Catal. A.: Chem., 2009, **309**, 172-177.

[23]   Lingegbowda, N.S., Kumara, M.N., Channegowda, D. Rangappa, K.S. and Made-gowda, N.M. : J. Mol. Catal. A : Chem., 2007, **269**, 225-233.

[24]   Rao, Shan, and Dhannure, K. : Ph. D. .Thesis, Nagarjuna University, India, 2003.

[25]   Neeraj, Shweta, Parihar, S.S. and Dwivedi, A.P. : Int. J. Adv. Research in Chemical Science (IJARCS) 2018, **4**, 9-14.

[26]   Neeraj, Shweta, Parihar, S.S. and Dwivedi, A.P. : Int. J. Adv. Research in Chemical Science (IJARCS) 2018, **5**, 25-30.