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Os (Viii) Catalysed Oxidation Of Schiff Base By Chloramine – T In Aqueous Acetic Acid Medium – Kinetic Study

¹. G.Mathubala , ². R.Kalpana Devi

^{1.&2}Assistant Professor of Chemistry , Bharath university , Chennai, India

ABSTRACT : The effect of various meta and para -substituted anils on the reaction rate had been studied at four different temperatures viz., 35 , 40 , 45 and 50 ⁰ c and the thermodynamic parameters are also calculated. The analysis of rate constants of Ortho substituents reveals that the localized and delocalized effects are major components while Steric effect place only the minor role. In this paper we have studied OS (VIII) catalysed oxidation of SCHIFF base by Chloramine – T in aqueous acetic acid medium – kinetic study .

KEYWORDS : Steric effect , meta and para -substituted , Ortho substituents , minor role

1. .INTRODUCTION

Among oxo derivatives of variable valence metals , Chromium compound play the most important role , in oxidative reaction . A number of Chromium reagents are readily available . Almost every oxidisable functional group may undergo Chromium oxidation .Chromium (VI) containing reagents include Chromium acid , dichromate ion , Chromyl chloride , chromyl acetate , t – butyl Chromate , Chromylnitrate and Co – ordination complexes of Chromium trioxide .¹⁻²

Chromium (VI oxidations are usually performed under acidic condition . Co – solvents like (Jone’s reagent) benzene , methylenechloride (Two Phase system) are often added in order to deal with water insoluble organic complexes . The oxidation rate is generally high under acid catalysed conditions , however the low pH of the reaction medium and the presence of water favouring hydrolytic condition exclude the use of this class of reagents for the oxidation of molecules containing acid sensitive groups.[1][2]

Polymer supported Chromium (VI) reagents have also been developed. These reagents offer the advantage of reducing the work of procedure to more filtration . Recently some neutral or almost neutral Chromium (VI) reagents have been developed to effect oxidation under mild conditions. Pyridinium Chlorochromate (PCC) introduced by Corey et al³ is widely used in the oxidation of alcohols. Pyridinium flourochromate has a less pronounced acidity and is an effective agent for the oxidation of Plicyclic organic substitutes . [3]PFC was developed by Bhattacharjee and coworker .⁴

In 1986 , Narayanan and Balasuramaniam⁵ introduced Pyridinium bromochromate . This is an efficient oxidant for alcohols and a brominating agent as well . Firouzahadi and Coworkers used Zinc chromates. This is a very useful reagent for the oxidation of variety of organic compounds , including alcohols , oximes , olefins and aromatic hydrocarbons.[4]

They have also shown chromium peroxide complexes as versatile , mild and efficient oxidants in organic synthesis. Chlorotrimethyl Silone , Imidazolium dichromate , 2,2’ – Bipyridyl chlorochromate (BPCC) and the corresponding chromate (BPC) have been proposed as oxidants for the oxidation of the hydroxyl group to thr carbonyl group. 4 – (dimethyl amino) – pyridinium chlorochromate and chromyl nitrate have been shown to be efficient and mild oxidant in aprotic media.

Naphthyridium chlorochromate , Pyrazinium chlorochromate , tetrabutyl ammonium chlorochromate , dimethylpyrazole chromate , tetrabutyl ammonium dichromate ,

International Journal of Innovative Research in Science, Engineering and Technology

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Pyridine complex of oxodiperoxochromium and the dipyridine complex of chromium trioxide are some of the Chromium (VI) oxidants introduced in the last twenty years.

Quinolinium Chlorochromate was used by Bhavani et al to oxidize methyl phenyl sulphoxides.[5]

Quinolinium dichromate was introduced by Balasubramanian and Prathiba ⁶ as an effective oxidant under non – aqueous conditions.

Pyridium Chlorochromate (PCC) is irreplaceable in the generation of functional groups in highly unsaturated carbinols and pyrrols . yet mildly acidic character of Pyridinium chlorochromate precludes its use with acid sensitive substrates or products. Pyridium Chlorochromate oxidation has been investigated under various condition on different substrates .

Despite the introduction of numerous oxidants based on chromium (VI) not much work has been done to investigate the mechanism of oxidation in these cases.[6]

The diverse nature of chemistry of some n- halogeno and N- metalo reagents is consequence of their ability to act as a source of

1. Halogenonium cations
2. Hypohalite species
3. N- anions acting both as bases and nucleophiles and
4. Nitrenoids in limited cases .

The term chloramines is used to include all compounds , both organic and inorganic , containing one or more chlorine atoms attached to nitrogen. eg., Chloramines , Chloramines , Chloramides ,Chlorimides . All compounds containing N – Cl bonds such as Chloramine – T (CAT) (p- $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NCINa}\cdot 3\text{H}_2\text{O}$) , dichloramine – T ($\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NCl}_2$) and halozones ($\text{HOOC C}_6\text{H}_4\text{SO}_2 \text{HCl}_2$) are fairly stable and liberate iodine from acidified Potassium iodide solutions.[7]

Chloramine –T, the Sodium salt of N- Chloro – p - toluene – sulphonamide was first prepared by Chattaway ² by the treatment of sulphonamide with sodium hypochloramide . Chloramine – T can also be prepared from dichloramine –T which is obtained by passing chlorine into the solution of p –toluene sulphonamide in sodium hydroxide.

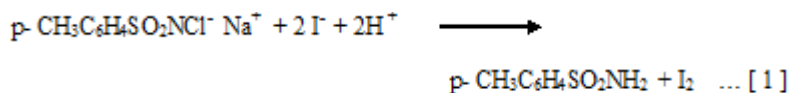
The structure of Chloramine – T is most commonly depicted as (fig.1) and occasionally as (fig.2)³ . They are strong electrolytes and behave as strong oxidants in both acidic and alkaline media. [8]

Chloramine –T has been used as a useful oxidant and it appears to be suitable for hypochlorides. Hypochlorous acid and monochloramides , all of which are very unstable . It does not liberate chlorine in acid solution and does not chlorinate many compounds which are easily attacked by chloride and Iodine from acidified Potassium iodide solution.

International Journal of Innovative Research in Science, Engineering and Technology

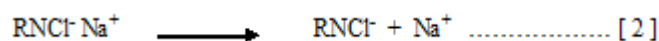
(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 6, June 2015



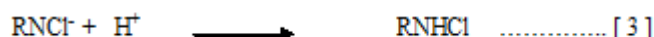
The reaction involves a two electron change and hence the equivalent weight is equal to its molecular weight / 2 .

Chloramine – T dissociates as



Where R = p- CH₃C₆H₄SO₂

The anion then picks up a proton to form the free acid and RNHCl



The free acid has not been isolated, but the evidence for its existence has been reported. The free acid then disproportionate giving to p – toluene sulphonamide [RNH₂] and dichloramine – T [RNCl₂].

II.KINETICS OF CHLORAMINOMETRIC OXIDATION

Coull and Co-workers⁶ were the first to investigate the kinetics and mechanism of decomposition of H₂O₂ by CAT in the presence of HCl. They determined the rate of the reaction using Read and Berkerson's logarithmic method.[9] The reaction was found to be first orders each [H₂O₂] and [CAT], but inverse first order dependence on the concentration of RNH₂. They suggested a mechanism involving the formation of molecular chlorine as a results of interaction between DCT and HCl.

III.EXPERIMENTAL

3.1.Preparation of Chloramine – T (CAT)

a) Preparation of Pure p- tolenesulphonamide

The procedure used was that of Vogel.⁷⁹ Ten grams of p- tolenesulphonylchloride and 20 g of ammonium carbonate were ground in a mortar to a fine powder. The mixture was heated in an evaporating dish on a water bath for 1 – 2 hrs. [10]and the mixture was stirred frequently with glass rod. After cooling the mixture was extracted with a little cold water to remove excess ammonium salts. The crude p- tolenesulphonylchloride was recrystallised from boiling water and dried at 100⁰ C. The pure product melted at 138⁰ C.

b) Preparation of Dichloramine – T (DCT)

This was prepared by the method of Kraus and Crede. p- tolenesulphonamide was dissolved in ten parts of 1 : 10 caustic soda and diluted with twenty parts of water. Chlorine gas was then passed into the solution until a voluminous white precipitate of dichloramine – T was formed.[11]This was collected on a Buckner funnel, thoroughly washed twice with 5 – 8 parts of water and finally with enough 10% alcohol to make a thin paste. The dilute alcohol washing was done very quickly and the substance was separated with air of a vacuum filter. It was then dried in a vacuum drier dichloramine –T was obtained, and its melting point is 82 - 83⁰ c.

C) Preparation of Chloramine – T (CAT)

Forty five ml of 10% sodium hydroxide solution was heated to a temperature of about 80⁰ and to which added 6 g of dichloramine – T in small quantities, stirring the mixture gently after each addition until a clear solution was

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 6, June 2015

obtained.[12] When the addition was completed, the hot solution was filtered and then allowed to cool spontaneously. The crystals were filtered with suction, washed with little brine solution, and dried in a desiccators over anhydrous calcium chloride. It was recrystallised from water; m.p. 175 – 179 °C.

3.2.Kinetic measurements

The reaction was carried out in 60 % aqueous acetic acid (V/V). Following solutions of desired concentrations were prepared.

1. Anil in Acetic acid
2. Chloramine – T in water
3. Sodium perchlorate in water
4. Sodium Chloride in water
5. Perchloric acid in water
6. Osmium tetroxide in dil – sodium hydroxide.

The solutions were thermostated at least for one hour before the run. The kinetics was carried out by mixing the substrate and oxidant in a appropriate solvent mixture. The reaction was carried out under pseudo first order conditions, taking always the substrate in excess.[13]

The progress of the reaction was monitored by withdrawing aliquots from the reaction mixture at regular intervals of time and estimating the unreacted CAT by iodometric method.

Product analysis

Under kinetic conditions, the reactants ratio anil : CAT (1 : 10) were mixed and allowed to react for about 2 days. The product was extracted with chloroform. The solvent was removed at reduced pressure after drying over anhydrous Na₂SO₄. The products were separated, after identifying by TLC, into individual components by Column Chromatography. Benzaldehyde was confirmed by its semicarbazone (m.p.221 °C, lit. 222 °C) and 2,4 – DNP (m.p.236 °C, lit. 239 °C) derivatives.[14]

Nitrobenzene was identified by recording IR spectrum and exhibits three bands at 1626, 1500, and 1019 cm⁻¹ attributed to stretching frequency of C-N. One sharp band at 1452 cm⁻¹ due to stretching vibration of N-O and band at 530 cm⁻¹ due to ring deformation and CNO bending vibration.

Stoichiometry

The stoichiometry of the reaction was determined by studying the reaction under the conditions of CAT >> anil and it was found to be 1:2

Stoichiometry

The stoichiometry of the reaction was determined by studying the reaction under the condition of CAT >> anil and it was found to be 1:1

IV.RESULTS AND DISCUSSIONS

4.1.Effects of varying concentrations of Oxidant

The oxidation of anil by CAT was investigated at several initial concentrations of the oxidant. The plot of logCAT Vs time, that is, the plot of log titre value Vs time was linear, indicating a first order dependence of rate on [CAT]. Values of the pseudo – first order rate constant k_{obs} were calculated from those plots. [Table -4.1]

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 6, June 2015

Table – 4.1

[Anil] = 1.0×10^{-2} M ACOH :H₂O = 60:40 (V/V)
[OsO₄] = 1.0×10^{-5} M Temp. = 40⁰ c
[HClO₄] = 1.0×10^{-2} M

[CAT] x 10 ³	K _{obs} .X 10 ⁴ s ⁻¹
0.5	1.340
1.0	1.073
1.25	1.061
1.5	1.155

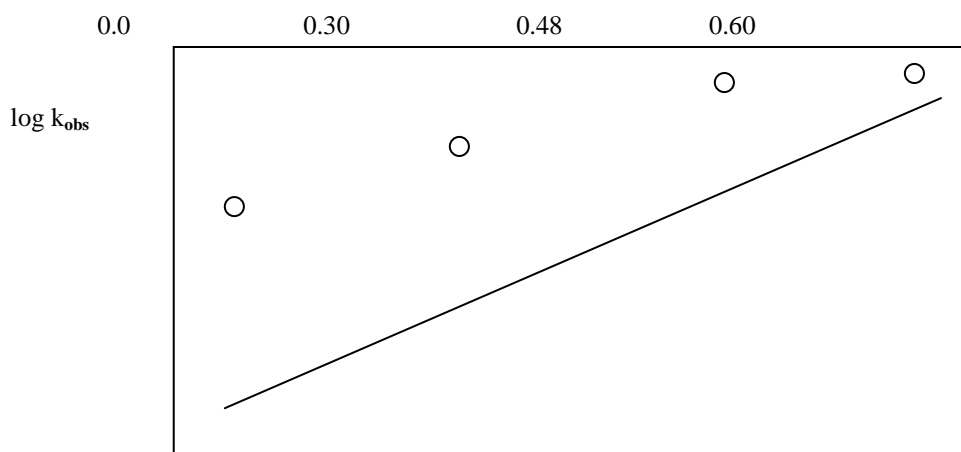
4.2.Effect of varying concentration of Substrate

The reaction was carried out with varying concentration of anil , always in excess , with the constant concentrations of other reactants . The rate constant increased linearly with substrate concentration (Table – 4.2).[15] The plot of log [Sub.] Vs log k_{obs}. Gave a straight line with slope of 2.0 (fig .3). Hence the order with respect to substrate was found to be 2

Table – 4.2

[CAT] = 1.0×10^{-3} M ACOH :H₂O = 60:40 (V/V)
[OsO₄] = 1.0×10^{-5} M Temp. = 40⁰ c
[HClO₄] = 1.0×10^{-2} M

[Anil] x 10 ³	K _{obs} .X 10 ⁴ s ⁻¹
0.5	1.340
1.0	1.073
1.25	1.061
1.5	1.155



International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 6, June 2015

4.3. Effect of solvent composition

The reaction was carried out at three different compositions acetic acid – water mixture . The rate constants were found to decrease as the percentage of acetic acid increases. [Table 4.3]

Table – 4.3

[CAT] = 1.0×10^{-3} M [Anil] = 1.0×10^{-2} M
[OsO₄] = 1.0×10^{-5} M Temp. = 40⁰ c
[HClO₄] = 1.0×10^{-2} M

% of Acetic Acid	K _{obs} × 10 ⁴ s ⁻¹
50	3.152
60	1.073
70	0.865

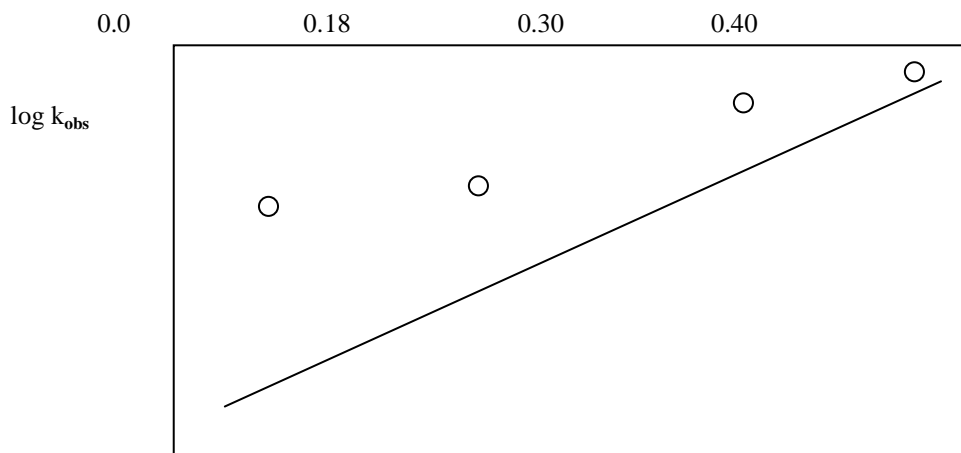
4.4. Effect of Catalyst

At constant concentration and temperature of substrate , oxidant and Perchloric acid , the reaction was carried out at four different concentrations of Os O4. The plot of log [OsO₄] Vs log k_{obs} , gave a straight with slope 0.6 [Table 4.4 ; Fig. 4]

Table – 4.4

[CAT] = 1.0×10^{-3} M [Anil] = 1.0×10^{-2} M
[HClO₄] = 1.0×10^{-2} M AcOH : H₂O = 60 : 40 (V/V)
Temp. = 40⁰ c

[OsO ₄] × 10 ⁵ M	K _{obs} × 10 ⁴ s ⁻¹
1.0	1.073
1.5	1.265
2.0	1.561
2.5	1.868



4.5. Effect of Perchloric Acid

The reaction was followed with varying concentration of Perchloric acid and by keeping other [reactants] constant. It was found that as the concentration of Perchloric acid increased , the rate constant decreased . The plot of log [HClO₄] against logK_{obs} . gave a straight line of slope of 0.28 (Table 4.5 ; Fig. 5)

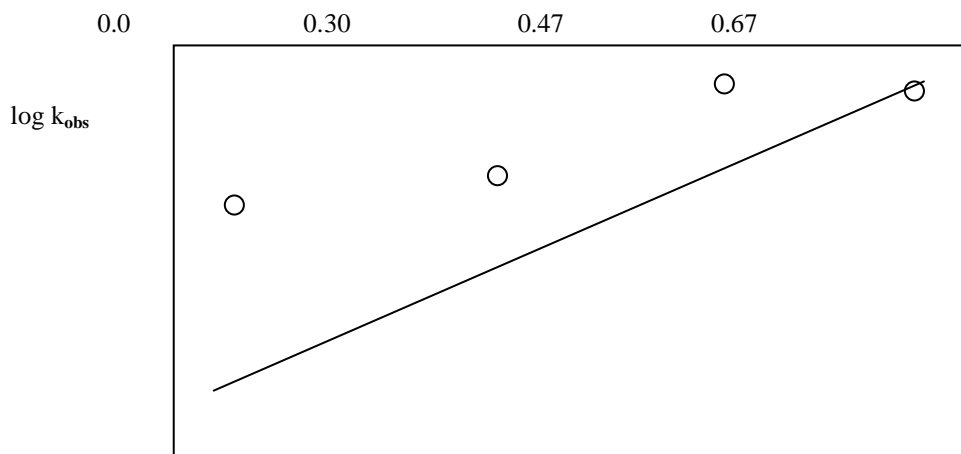
International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 6, June 2015

Table – 4.5
 [CAT] = 1.0×10^{-3} M [Anil] = 1.0×10^{-2} M
 [OsO₄] = 1.0×10^{-5} M AcOH : H₂O = 60 : 40 (V/V)
 Temp. = 40⁰ c

[HClO ₄] x 10 ⁵ M	K _{obs.} X 10 ⁴ s ⁻¹
1.0	10.73
2.0	9.216
3.0	8.323
4.0	7.153



4.6.Effect of Sodium Perchlorate

The rate of the reaction was found to increase with increase in the concentration of added Sodium Perchlorate. [Table 4.6]

Table – 4.6
 [CAT] = 1.0×10^{-3} M [Anil] = 1.0×10^{-2} M
 [OsO₄] = 1.0×10^{-5} M AcOH : H₂O = 60 : 40 (V/V)
 [HClO₄] X 10² M Temp. = 40⁰ c

[NaClO ₄] x 10 ⁵ M	K _{obs.} X 10 ⁴ s ⁻¹
0.0	1.073
5.0	1.487
10.0	1.691
15.0	1.860

4.7.Effect of added Sodium Chloride

It was found that there was no influence on the rate of oxidation by the added Chloride [Table 4.7]

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 6, June 2015

Table – 4.7

$[CAT] = 1.0 \times 10^{-3} \text{ M}$ $[OsO_4] = 1.0 \times 10^{-5} \text{ M}$ $[HClO_4] \times 10^2 \text{ M}$	$[Anil] = 1.0 \times 10^{-2} \text{ M}$ $AcOH : H_2O = 60 : 40 \text{ (V/V)}$ $Temp. = 40^0 \text{ c}$
$[NaCl] \times 10^3 \text{ M}$	$K_{obs} \cdot X 10^4 \text{ s}^{-1}$
0.0	1.073
5.0	1.052
10.0	1.056
15.0	1.024

4.8.Effect of PTSA

It was observed that no change in the rate of oxidation while adding p – toluenesulphonamide by keeping other [reactans] constant.

4.9.Test with Acrylonitrile

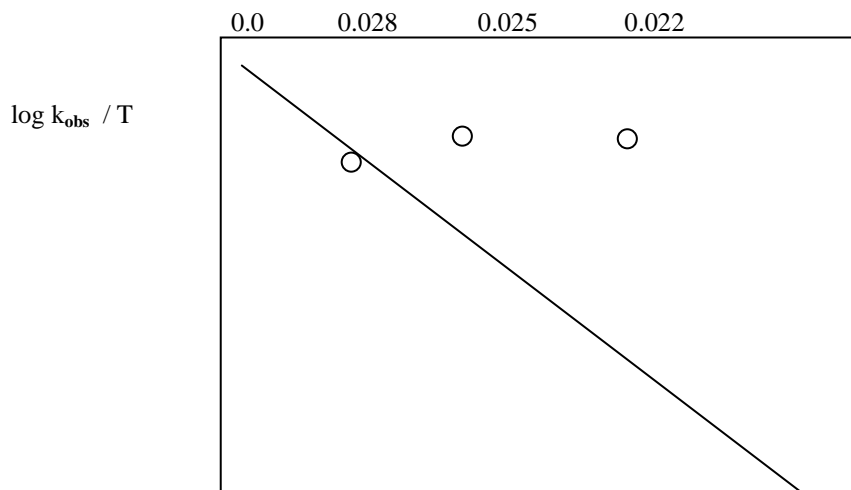
It was found that no turbidity observed while a drop of acrylonitrile in the reaction mixture . hence it indicate the absence of free radicals

4.10.Effect of Temperature

The reaction was studied in the temperature range 35^0 c to 45^0 c . The rate increased with increase in Temperature as shown by the table 4.8 .[Table 4.8 ; Fig.6]

Table – 4.8

$[CAT] = 1.0 \times 10^{-3} \text{ M}$ $[OsO_4] = 1.0 \times 10^{-5} \text{ M}$ $[HClO_4] \times 10^2 \text{ M}$	$[Anil] = 1.0 \times 10^{-2} \text{ M}$ $AcOH : H_2O = 60 : 40 \text{ (V/V)}$ $Temp. = 40^0 \text{ c}$
Temp. $^0 \text{ c}$	$K_{obs} \cdot X 10^5 \text{ s}^{-1}$
35	2.65
40	10.73
45	24.04



International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 6, June 2015

REFERENCES

- 1.M.M.Campell and G.Johnson , Chem. Rev., 1978 , 78 , 65
- 2.Lydia Caroline M., Vasudevan S., "Growth and characterization of pure and doped bis thiourea zinc acetate: Semiorganic nonlinear optical single crystals", Current Applied Physics, ISSN : 1567-1739, 9(5) (2009) pp. 1054-1061.
- 3.F.D.Chattaway , J.Chem. Soc. , 1905 , 1 , 145
- 4.Lydia Caroline, M., Kandasamy, A., Mohan, R., Vasudevan, S., "Growth and characterization of dichlorobis 1-proline Zn(II): A semiorganic nonlinear optical single crystal", Journal of Crystal Growth, ISSN : 0022-0248, 311(4) (2009) pp. 1161-1165.
- 5.G.Mann and W.J.Pope , J.Chem.Soc. 1922 , 1052 ; 1924 , 911
6. Nagarajan, C., Madheswaran, M., "Experimental study and steady state stability analysis of CLL-T series parallel resonant converter with fuzzy controller using state space analysis", Iranian Journal of Electrical and Electronic Engineering, ISSN : 1735-2827, 8(3) (2012) pp.259-267.
7. M.M.natarajan and V.Thiagarajan , J.Chem.Soc. Perkin Trans II , 1975 , 1590
8. Parthasarathy R., Ilavarasan R., Karrunakaran C.M., "Antidiabetic activity of Thespesia Populnea bark and leaf extract against streptozotocin induced diabetic rats", International Journal of PharmTech Research, ISSN : 0974-4290, 1(4) (2009) pp. 1069-1072.
- 9.P.S.Radhakrishnamurthi and B.Sahu , Indian J.Chem. 1978 , 16A , 259
10. Poongothai S., Ilavarasan R., Karrunakaran C.M., "Simultaneous and accurate determination of vitamins B1, B6, B12 and alpha-lipoic acid in multivitamin capsule by reverse-phase high performance liquid chromatographic method", International Journal of Pharmacy and Pharmaceutical Sciences, ISSN : 0975 - 1491, 2(S4) (2010) pp. 133-139.
- 11.Vivekanandan ,K.Venkata Rao , M.Sakappa and Sp.Shanmuganathan , Indian J.Chem., 1978 , 16 A , 519
- 12.k.Ganapathy and P.Jeyaganthi , J.Indian Chem.Soc., 1984 , 61 , 393
- 13.M.S.Ramachandran and T.S. Vivekanandan , Bul. Chem. Soc.Japan , 1987 , 60 , 3397
- 14.C.K.Mythily , K.S.Rangappa and D.S.Mahadevappa , Indian J.Chem . 1990 , 29A , 676
- 15.V.Balasubramanian and V.thiagarajan , Int. J.Chem. kinet., 1975 , 7 , 605
16. J. Pavithra,A Study on Distribution Channels in Cement Industry , International Journal of Innovative Research in Science, Engineering and Technology,ISSN: 2319-8753,pp 192-199,Vol. 1, Issue 2, December 2012.
17. J.Arul Hency Sheela, QUALITATIVE ANALYSIS OF SECONDARY METABOLITES OF THE PLANT CLEMATIS GOURIANA , International Journal of Innovative Research in Science, Engineering and Technology , ISSN: 2319-8753 , pp 2831-2834,Vol. 2, Issue 7, July 2013.
18. J. Pavithra, A Study on the Role of Foreign Direct Investment in Retail industry in India , International Journal of Innovative Research in Science, Engineering and Technology , ISSN: 2319-8753, pp 71-81,Vol. 1, Issue 1, Nov 2012.
19. J.Arul Hency Sheela, Qualitative Analysis of Primary Metabolites of the Plant Clematis Gouriana , International Journal of Innovative Research in Science, Engineering and Technology , ISSN: 2319-8753, pp 9011-9013 ,Vol. 3, Issue 2, February 2014.
20. J. Pavithra, Advertising Ethics in India , International Journal of Innovative Research in Science, Engineering and Technology , ISSN: 2319-8753 , pp 225-229,Vol. 1, Issue 2, December 2012.
21. J.Arul Hency Sheela, Phytochemical Constituents of the Plant Clematis Gouriana , International Journal of Innovative Research in Science, Engineering and Technology ,ISSN: 2319-8753 , pp 9965-9968 ,Vol. 3, Issue 3, March 2014.