

OS (VIII) CATALYSED OXIDATION OF SCHIFF BASE BY CHLORAMINE – T IN AQUEOUS ACETIC ACID MEDIUM – KINETIC STUDY OF THE EFFECT OF OXIDANT , SUBSTRATE , SOLVENT AND CATALYST

¹ R.Kalpana Devi , ²G.Mathubala

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

ABSTRACT : The kinetic study of simple and substituted anils were studied under various conditions viz., solvent ,oxidants , electrolyte , catalysts and mixture of catalysts and temperature; simple and substituted anils , pyridinium Chloro Chromate(PCC) ,Pyridinium Dichromate (PDC) were prepared in the laboratory and kinetic study were carried out using **oxidant , substrate , solvent and catalyst** . The graphs were drawn at all relevant places and results were obtained in full satisfaction.

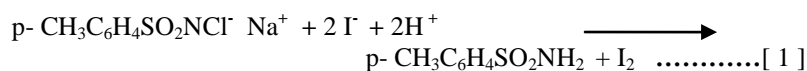
KEYWORDS: relevant, reagents , Chloramine –T , product analysis , pseudo – firstorder , parameters

1.INTRODUCTION

The diverse nature of chemistry of some n- halogeno and N- metallo 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 .[1] All compounds containing N – Cl bonds such as Chloramine – T (CAT) (p- CH₃C₆H₄SO₂NCINa.3H₂O) , dichloramine – T (CH₃C₆H₄SO₂NCl₂) and halazones (HOOC C₆H₄SO₂ HCl₂) are fairly stable and liberate iodine from acidified Potassium iodide solutions.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 . [2]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)^{3,4 (a) ,(b)} .[3] They are strong electrolytes and behave as strong oxidants in both acidic and alkaline media. 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.[4]



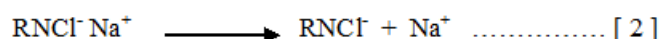
The reaction involves a two electron change and hence the equivalent weight is equal to its molecular weight / 2 .[5]

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

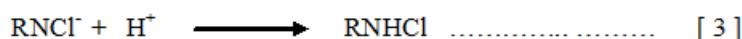
Vol. 4, Issue 5, May 2015

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 [RNC_lCl₂] .

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 [RNC_lCl₂] .

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. The reaction was found to be first orders each [H₂O₂] and [CAT], but inverse first order dependence on the concentration of RNH₂ .[6] 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)

3.1.A] Preparation of Pure p- tolenesulphonamide

The procedure used was that of Vogel.⁷ 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 a an evaporating dish on a water bath for 1 – 2 hrs. 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 . [7]The crude p- tolenesulphonylchloride was recrystallised from boiling water and dried at 100⁰ C . The pure product melted at 138⁰ C.

3.1.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 .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 .[8] 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.[9][10]

3.1.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 , strring the mixture gently after each addition until a clear solution was obtained. When the addition was completed , the hot solution was filtered and then allowed to cool spontaneously .[11] 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 – 179⁰ C.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 5, May 2015

IV.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 thrmostated at least for one hour before the run. The kinetics was carried out by mixing the substrate and oxidant in a appropriate solvent mixture.[12] The reaction was carried out under pseudo first order conditions , taking always the substrate in excess.

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.[13]

V.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 . [14]Benzaldehyde was confirmed by its semicarbazone (m.p.221⁰ c , lit. 222⁰ c) and 2,4 – DNP (m.p.236⁰ c , lit. 239⁰ c) derivatives.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 vibratin of N-O and band at 530 cm⁻¹ due to ring deformation and CNO bending vibration.[15]

VI.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

VILRESULTS AND DISCUSSINS

7.1.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 pseuo – first order rate constant k_{obs} . were calculated from those plots. [Table -4.1] [16]

Table – 4.1

$$\begin{aligned}
 [\text{Anil}] &= 1.0 \times 10^{-2} \text{ M} & \text{ACOH :H}_2\text{O} &= 60:40 \text{ (V/V)} \\
 [\text{OsO}_4] &= 1.0 \times 10^{-5} \text{ M} & \text{Temp.} &= 40^0 \text{ c} \\
 [\text{HClO}_4] &= 1.0 \times 10^{-2} \text{ M} & &
 \end{aligned}$$

[CAT] x 10 ³	$K_{obs} \cdot X 10^4 \text{ s}^{-1}$
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)

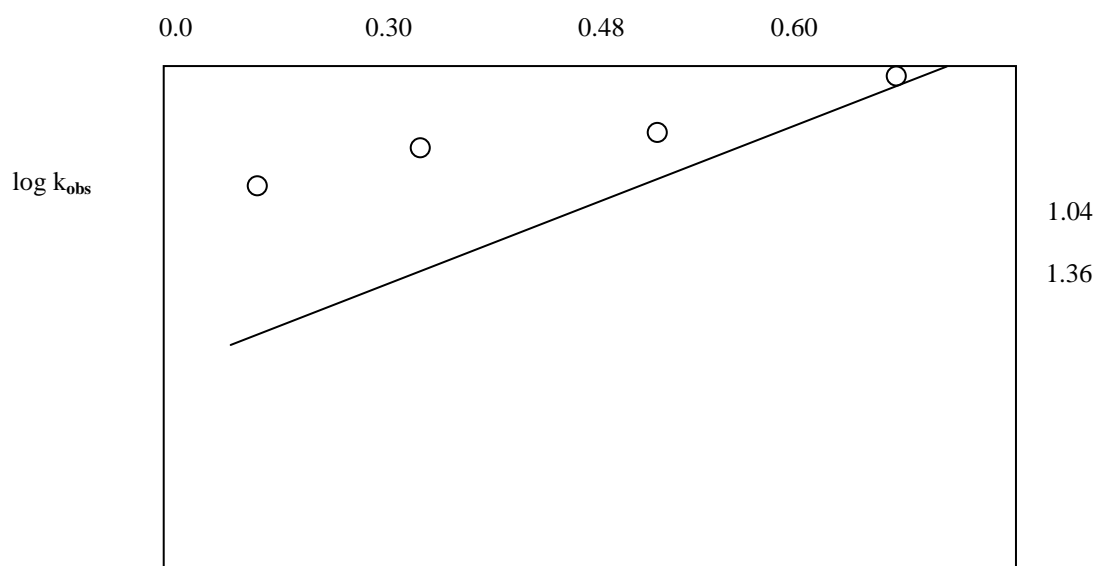
Vol. 4, Issue 5, May 2015

7.2. 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. [17] The rate constant increased linearly with substrate concentration (Table – 4.2). The plot of $\log [\text{Sub.}]$ Vs $\log k_{\text{obs}}$. 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
 $[\text{CAT}] = 1.0 \times 10^{-3} \text{ M}$ $\text{ACOH} : \text{H}_2\text{O} = 60:40 \text{ (V/V)}$
 $[\text{OsO}_4] = 1.0 \times 10^{-5} \text{ M}$ $\text{Temp.} = 40^\circ \text{ c}$
 $[\text{HClO}_4] = 1.0 \times 10^{-2} \text{ M}$

$[\text{Anil}] \times 10^3$	$K_{\text{obs}} \times 10^4 \text{ s}^{-1}$
0.5	1.340
1.0	1.073
1.25	1.061
1.5	1.155



7.3. 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]

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 5, May 2015

Table – 4.3

$$\begin{aligned}
 [\text{CAT}] &= 1.0 \times 10^{-3} \text{ M} & [\text{Anil}] &= 1.0 \times 10^{-2} \text{ M} \\
 [\text{OsO}_4] &= 1.0 \times 10^{-5} \text{ M} & \text{Temp.} &= 40^\circ \text{ c} \\
 [\text{HClO}_4] &= 1.0 \times 10^{-2} \text{ M} & &
 \end{aligned}$$

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

7.4.Effect of Catalyst

At constant concentration and temperature of substrate, oxidant and Perchloric acid, the reaction was carried out at four different concentrations of OsO₄. [18] The plot of log [OsO₄] Vs log k_{obs}, gave a straight line with slope 0.6 [Table 4.4 ; Fig. 4]

Table – 4.4

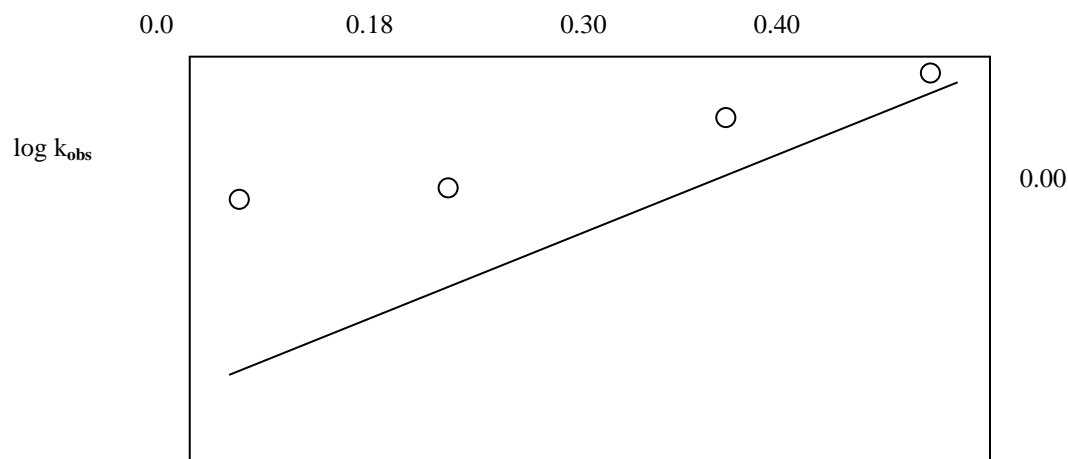
$$\begin{aligned}
 [\text{CAT}] &= 1.0 \times 10^{-3} \text{ M} & [\text{Anil}] &= 1.0 \times 10^{-2} \text{ M} \\
 [\text{HClO}_4] &= 1.0 \times 10^{-2} \text{ M} & \text{AcOH : H}_2\text{O} &= 60 : 40 \text{ (V/V)} \\
 & & \text{Temp.} &= 40^\circ \text{ c}
 \end{aligned}$$

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

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 5, May 2015



REFERENCES

- 1.M.M.Campell and G.Johnson , Chem. Rev., 1978 , 78 , 65
- 2.Kumarave A., Udayakumar R., "Web portal visits patterns predicted by intuitionistic fuzzy approach", Indian Journal of Science and Technology, ISSN : 0974-6846, 6(S6) (2013) pp. 4549-4553.
- 3.F.D.Chattaway , J.Chem. Soc. , 1905 , 1 , 145
- 4.G.Mann and W.J.Pope , J.Chem.Soc. 1922 , 1052 ; 1924 , 911
- 5.Kumaravel, A., Meetei, O.N., "An application of non-uniform cellular automata for efficient cryptography", Indian Journal of Science and Technology, ISSN : 0974-6846, 6(S5) (2013) pp.4560-4566.
6. J.Holloway , J.Kenyon and H.Phillips , J.Chem. Soc., 1928 , 3000
- 7.S.G.Clarke , J.Kenyon and H.Phillips , J.Chem. Soc., 1927 , 188 ; 1930 1225
- 8.Kumaravel, A., Pradeepa, R., "Efficient molecule reduction for drug design by intelligent search methods", International Journal of Pharma and Bio Sciences, ISSN : 0975-6299, 4(2) (2013) pp.B1023-B1029.
- 9.P.S.Radhakrishnamurthi and B.Sahu , Indian J.Chem. 1978 , 16A , 259
10. J.Coull , J.B.Hope and B.Genguell , J.Am.Chem.Soc., 1935 , 57 , 1489
- 11.Kumaravel, A., Pradeepa, R., "Layered approach for predicting protein subcellular localization in yeast microarray data", Indian Journal of Science and Technology, ISSN : 0974-6846, 6(S5) (2013) pp.4567-4571.
- 12.Vivekanandan ,K.Venkata Rao , M.Sakappa and SP.Shanmuganathan , Indian J.Chem., 1978 , 16 A , 519
- 13.K.Ganapathy and P.Jeyaganthi , J.Indian Chem.Soc., 1984 , 61 , 393
- 14.M.S.Ramachandran and T.S. Vivekanandan , Bul. Chem. Soc.Japan , 1987 , 60 , 3397
- 15.C.K.Mythily , K.S.Rangappa and D.S.Mahadevappa , Indian J.Chem . 1990 , 29A , 676
- 16.V.Balasubramanian and V.thiagarajan , Int. J.Chem. kinet., 1975 , 7 , 605
17. Kumaravel, A., Udhayakumarapandian, D., "Construction of meta classifiers for apple scab infections", International Journal of Pharma and Bio Sciences, ISSN : 0975-6299, 4(4) (2013) pp.B1207-B1213.
18. M.M.Natarajan and V.Thiagarajan , J.Chem.Soc. Perkin Trans II , 1975 , 1590
19. G.Mathubala , Dr.T.Jayadoss, Evaluation of Non-Conventional Fertilizers On The Growth Response of Zinnia Seedlings ,International Journal of Innovative Research in Science, Engineering and Technology, ISSN: 2319-8753, pp 8360-8376 , Vol. 3, Issue 1, January 2014.
20. G.Mathubala , S.Rosy Christy , Hazardous Materials - Restriction, International Journal of Innovative Research in Science, Engineering and Technology, ISSN: 2319-8753 , pp 4398-4400 , Vol. 2, Issue 9, September 2013.
21. G.Mathubala, Dr.V.Krishnasamy , KINETICS OF OXIDATION OF SCHIFF BASE BY CHLORAMINE –T CATALYSED BY MIXTURE OF Os (VIII) AND Ru (III) – EFFECT OF OSMIUM TETRAOXIDE AND RUTHENIUM CHLORIDE , International Journal of Innovative Research in Science, Engineering and Technology , ISSN: 2319-8753 , pp 2756-2762, Vol. 2, Issue 7, July 2013 .
22. G.Mathubala, Dr.V.Krishnasamy , KINETICS OF OS(VIII) CATALYSED OXIDATION OF BENZALDEHYDE ANILS BY PDC – STUDY OF THE EFFECTS OF SUBSTRATE , International Journal of Innovative Research in Science, Engineering and Technology , ISSN: 2319-8753 , pp 2467-2472 , Vol. 2, Issue 5, May 2013.
23. H.S.RUPA, Role of Human Resource Manager in Managing Stress of Employees in Manufacturing Concerns , International Journal of Innovative Research in Science, Engineering and Technology , ISSN: 2319-8753, pp 10234-10237,Vol. 3, Issue 3, March 2014.
24. G.Ayyapan,Chemo Informatics QSAR Analysis of Nitroaromatic Compounds Toxicity,International Journal of Innovative Research in Science, Engineering and Technology, ISSN: 2319-8753, pp 372-375, Vol. 2, Issue 2, February 2013.