# Os (VIII) Catalysed Oxidation of Schiff Base by Chloramine – T in Aqueous Acetic acid medium – Kinetic study of the effect of Substrate

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**ABSTRACT :** *The kinetic study of simple and substituted anils ware 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 , pseuo – firstorder ,parameters*

## 1.INTRODUCTION

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- $CH_3C_6H_4SO_2NClNa.3H2O$ ) , dichloramine – T ( $CH_3C_6H_4SO_2NCl_2$) and halazones ( HOOC $C_6H_4SO_2$ $HCl_2$ ) 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 hypochlonamide . 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)] . 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.

$$p\text{-} CH_3C_6H_4SO_2NCl^- \ Na^+ + 2\ I^- + 2H^+ \longrightarrow$$

$$p\text{-} CH_3C_6H_4SO_2NH_2 + I_2 \ \dots\dots\dots[\ 1\ ]$$
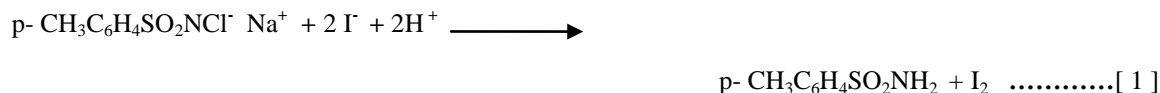
The reaction involves a two electron change and hence the equivalent weight is equal to its molecular weight **/** 2 .

Chloramine – T dissociates as

$$RNCl^- \ Na^+ \longrightarrow RNCl^- + Na^+ \ \dots\dots\dots\dots\dots\dots \ [\ 2\ ]$$
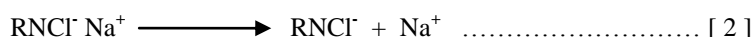
Where R = p- $CH_3C_6H_4SO_2$

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

$$RNCl^- + H^+ \longrightarrow RNHCl \ \dots\dots\dots \ \dots\dots\dots\dots\dots. \ [\ 3\ ]$$

The free acidhas 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].

## 2.KINETICS OF CHLORAMINOMETRIC OXIDATION

Coull and Co –workers[6] 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 . They suggested a mechanism involving the formation of molecular chlorine as a results of interaction between DCT and HCl.

## 3.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 . The crude p- tolenesulphonylchloride was recrystallised from boiling water and dried at $100^0$ C . The pure product melted at $138^0$ C.

3.1.B] Preparation of Dichloramine – T ( DCT )

This was prepared by the method of Krausand 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 . 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 - $83^0$ c.

3.1.C]) Preparation of Chloramine – T (CAT)

Forty five ml of 10% sodium hydroxide solution was heated to a temperature of about $80^0$ 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 . 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 – $179^0$ C.

## 4.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. 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.

## 5.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.$221^0$ c , lit. $222^0$ c ) and 2,4 – DNP (m.p.$236^0$ c , lit. $239^0$ 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.

## 6.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

## 7.RESULTS AND DISCUSSIONS

### 7.1.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 ]. 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] $= 1.0 \times 10^{-3}$ M  ACOH :H2O $= 60:40$ (V/V)

[OsO$_4$] $= 1.0 \times 10^{-5}$ M  Temp. $= 40^{0}$ c

[HClO$_4$] $= 1.0 \times 10^{-2}$ M

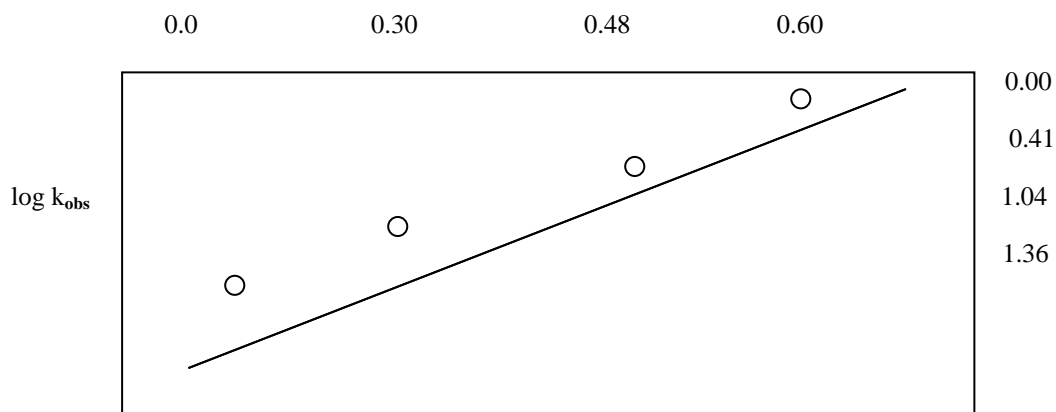| [Anil ] x $10^3$ | K$_{obs}$.X $10^4$ s$^{-1}$ |
|---|---|
| 0.5 | 1.340 |
| 1.0 | 1.073 |
| 1.25 | 1.061 |
| 1.5 | 1.155 |



Fig. 3

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