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KINETIC STUDY OF THE EFFECT OF PERCHLORIC ACID , SODIUM PERCHLORATE SODIUM CHLORIDE , P - TOLUENESULPHANAMIDE AND TEMPERATURE ON THE OS(VIII) CATALYSED OXIDATION OF SCHIFF BASE BY CHLORAMINE-TIN AQUEOUS ACETIC ACID MEDIUM

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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 perchloric acid , sodium perchlorate , sodium chloride , p – toluenesulphonamide and at temperatures . The graphs were drawn at all relevant places and results were obtained in full satisfaction.

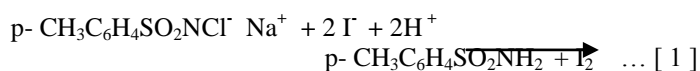
KEYWORDS: p – toluenesulphonamide, catalyst , acetic aci , plotted , medium , protonated

I. INTRODUCTION

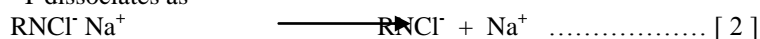
The diverse nature of chemistry of some n- halogeno and N- metallo reagents is consequence of their ability to act as a source of

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 Chattaway² 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.[2] 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. Chloramine – T has been used as a useful oxidant and it appears to be suitable for hypochlorides.[3] 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.

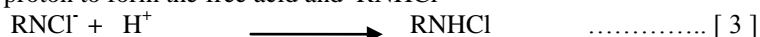


The reaction involves a two electron change and hence the equivalent weight is equal to its molecular weight / 2
Chloramine – T dissociates as



Where R = p- CH₃C₆H₄SO₂

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



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The free acid has not been isolated, but the evidence for its existence has been reported. The free acid then disproportionates giving to p-toluene sulphonamide [RNH₂] and dichloramine-T [RNCl₂]. [4]

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. [5] 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 result of interaction between DCT and HCl. [6]

III. EXPERIMENTAL

3.1. Preparation of Chloramine - T (CAT)

3.1.a) Preparation of Pure p-toluenesulphonamide

The procedure used was that of Vogel.⁷⁹ Ten grams of p-toluenesulphonylchloride 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. 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-toluenesulphonylchloride was recrystallised from boiling water and dried at 100 °C. The pure product melted at 138 °C. [7][8]

3.1.b) Preparation of Dichloramine - T (DCT)

This was prepared by the method of Kraus and Crede. p-toluenesulphonamide 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. [9] 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 °C. [10][11]

3.1.C) Preparation of Chloramine - T (CAT)

Forty five ml of 10% sodium hydroxide solution was heated to a temperature of about 80 ° and to which added 6 g of dichloramine - T in small quantities, stirring the mixture gently after each addition until a clear solution was 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 desiccator over anhydrous calcium chloride. It was recrystallised from water; m.p. 175 - 179 °C. [13]

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. [14]

The solutions were thermostated at least for one hour before the run. The kinetics was carried out by mixing the substrate and oxidant in an appropriate solvent mixture. [15] 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. [16]

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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 . 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.[17]

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

V.RESULTS AND DISCUSSINS

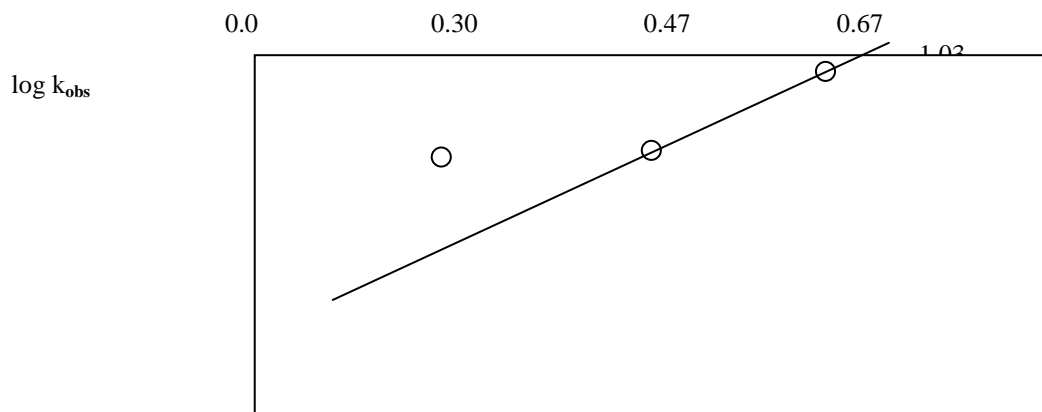
7.1.Effect of Perchloric Acid

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 [18](Table 4.5 ; Fig. 5)

Table – 4.5

$$\begin{array}{ll}
 [\text{CAT}] = 1.0 \times 10^{-3} \text{ M} & [\text{Anil}] = 1.0 \times 10^{-2} \text{ M} \\
 [\text{OsO}_4] = 1.0 \times 10^{-5} \text{ M} & \text{AcOH} : \text{H}_2\text{O} = 60 : 40 \text{ (V/V)} \\
 & \text{Temp.} = 40^{\circ} \text{ c}
 \end{array}$$

[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



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7.2.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 x 10⁻³ M [Anil] = 1.0 x 10⁻² M
[OsO₄] = 1.0 x 10⁻⁵ M AcOH : H₂O = 60 : 40 (V/V)
[HCl O₄] 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

7.3.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]

Table – 4.7

[CAT] = 1.0 x 10⁻³ M [Anil] = 1.0 x 10⁻² M
[OsO₄] = 1.0 x 10⁻⁵ M AcOH : H₂O = 60 : 40 (V/V)
[HCl O₄] = 1.0 x 10⁻² M Temp. = 40⁰ c

[NaCl] x 10 ³ M	K _{obs.} X 10 ⁴ s ⁻¹
0.0	1.073
5.0	1.052
10.0	1.056
15.0	1.024

7.4.Effect of PTSA

It was observed that no change in the rate of oxidation while adding p – toluenesulphonamide by keeping other [reactants] constant.[19]

7.5.Test with Acrylonitrile

It was found that no turbidity observed while a drop of acrylonitrile in the reaction mixture . hence it indicates the absence of free radicals[20]

7.6.Effect of Temperature

The reaction was studied in the temperature range 35⁰ c to 45⁰ c . The rate increased with increase in Temperature as shown by the table 4.8 .[Table 4.8 ; Fig.6]

Table – 4.8

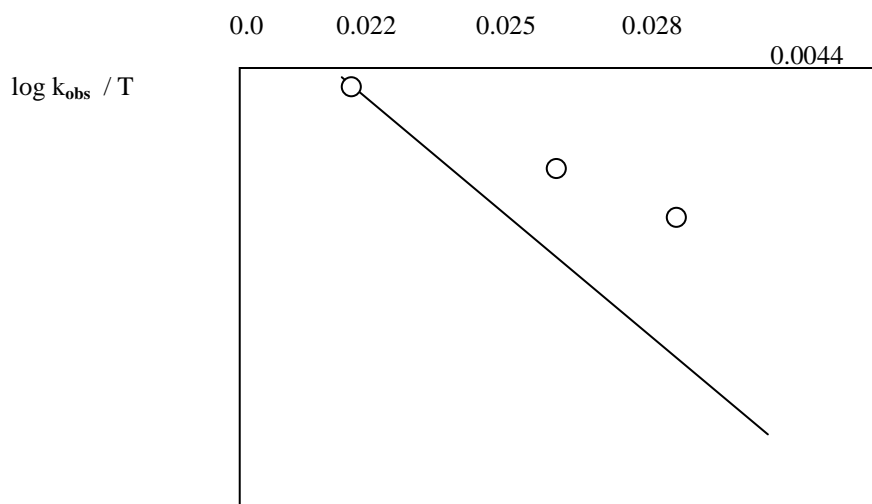
[CAT] = 1.0 x 10⁻³ M [Anil] = 1.0 x 10⁻² M
[OsO₄] = 1.0 x 10⁻⁵ M AcOH : H₂O = 60 : 40 (V/V)
[HCl O₄] = 1.0 X 10⁻² M Temp. = 40⁰ c

Temp. ⁰ c	K _{obs.} X 10 ⁵ s ⁻¹
35	2.65
40	10.73
45	24.04

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