"**KINETIC STUDY OF OXIDATION OF SOME SCHIFF BASES BY $Ce^{+4} \rightarrow Ce^{+3}$ REDOX SYSTEM IN ACIDIC MEDIA**"

A MINOR RESEARCH PROJECT CARRIED OUT UNDER THE FINANCIAL ASSISTANCE OF UNIVERSITY GRANTS COMMISSION,WRO,PUNE.

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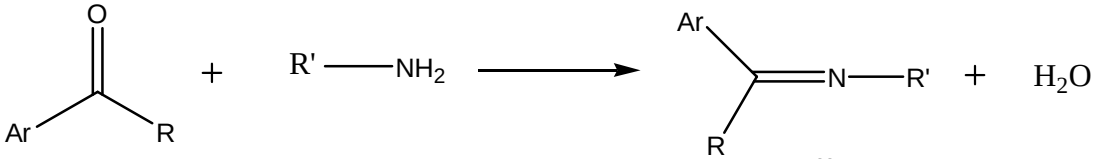
Executive Summary of the Project

INTRODUCTION AND ORIGIN OF THE RESEARCH PROBLEM:

Chemical kinetics deals with the rates of chemical reaction and it also includes the effect of concentration, temperature and hydrostatic pressure on reactions of various types. Such study provides essential evidence as to the mechanism of chemical processes. The valuable information about mechanism is also obtained from non-kinetic investigation, but knowledge of mechanism can be satisfactorily obtained only after careful kinetic investigations.

There are many types of chemical reactions and wide variety of experimental techniques available to investigate the chemical studies. Considerable amount of efforts has been taken to study the kinetics and mechanism of reaction in the gas phase. Also a large amount of work has been done on reaction in liquid phase, because of great interest of organic and inorganic chemist. A limited amount of work has been done on reactions in solid phase.

A compound formed by the reaction between an aromatic amine and an aldehyde or ketone is known as Schiff base. Schiff bases were first discovered by Hugo Schiff and hence they are referred as Schiff bases. In general a Schiff base can be prepared as follows.



A ketone An amine Schiff base

A number of reviews of the Schiff bases have been published.The kinetics of formation of Schiff bases in aqueous solution have been extensively studied. It has been formed that the reaction is of second order. This reaction proceeds by a two-step mechanism involving a carbinolamine intermediate.

Many types of reaction like hydrolysis, reduction oxidations, addition, substitution and metal complex formation have been studied with Schiff bases.

➢ OBJECTIVES OF THE STUDY

1. The literature survey pertaining to study of oxidation of the Schiff bases by using Ceric sulphate in sulphuric acid and varied study parameters viz. the effect of concentration of oxidant, substrate and sulphuric acid on the oxidation kinetics.
2. To prepare and characterize 5-Choloro-2-hydroxy-4-methyl acetophenone-anil and its bromo substituents.
3. To study the oxidation of the Schiff bases by using Ceric sulphate in sulphuric acid medium and the effect of concentration of oxidant, substrate, sulphuric acid on the oxidation kinetics.
4. Kinetic study will be carried out at five different temperatures to evaluate the thermodynamic parameters.
5. By using this kinetic study the suitable mechanism will be suggested.

➢ METHODOLOGY:

PREPARATION OF COMPOUNDS

In the First year the synthesis of the compounds was completed in the three steps viz. Ester formation, Ketone synthesis and Schiff bases synthesis from 5-Chloro-2-hydroxy-4-methyl acetophenone to its anil and the bromo derivatives, they were purified (by column chromatography) and analyzed (by elemental, TLC, UV and IR) and a representative 1H NMR is also recorded. Structures of these compounds were confirmed based on the analytical data.

In the second year the kinetics study of oxidation of the synthesized compounds was conducted, by employing following parameters.

1. **Effect of various concentration of Schiff Bases.(i.e. Substrate)**.
2. **Effect of various concentration of Ceric Sulphate.(i.e. Oxidant)**
3. **Effect of various concentration / ionic strength of different salts.**
4. **Effect of various concentration of Sulphuric acid.**
5. **Effect of various temperatures and determination of thermodynamic parameters.**

A short summary of kinetic study of Schiff base compound 5-Choloro-2-hydroxy-4-methyl acetophenone-anil is given below.

Effect of substrate:

In order to, determine the order of a reaction with respect to substrate. The titrations were carried out at different concentrations of the substrate. The concentrations of oxidant and sulphuric acid were kept constant. The temperature was maintained at 298 K. From the results following conclusion were obtained.

The k_1 values are found to be directly proportional to concentration of Schiff base studied indicating that reaction follows first order kinetics with respect to Schiff base[Substrate].The values of k_2 (Second order constant), calculated from k_1 / [Substrate], are practically constant which also proves first order dependence of reaction on the Schiff base. The plot of k_1^{-1} vs

$[Substrate]^{-1}$ which is linear making an intercept on rate axis indicating formation of equilibrium complex between Ce (IV) and [Substrate]. Similar results are also obtained for all substrate.

Effect of oxidant:

In order to determine the order of a reaction with respect to oxidant, the reaction was studied at different concentration of the oxidant while keeping all other parameters constant. The reaction follows first order kinetics with respect to Ce (IV). From the results following conclusion were obtained.

The value of k_1 decreases with increase in concentration of oxidant which is contrary to our expectation. This fact shows the formation of an equilibrium complex between the reactants prior to the rate determining step. A plot of k_1 against $[Ce(IV)]^{-1}$ is linear with an intercept on the rate axis provides a positive evidence for the formation of complex. Similar results are also obtained for all substrate.

Effect of ionic strength:

The reaction was carried out at five different values of ionic strength for each studied salt and at a constant temperature of 298 K. The concentrations of sulphuric acid, oxidant and substrate were kept constant. The ionic strength of the solution was varied separately with the addition of different salts viz. KCl, NaCl and NH_4Cl. From the results following conclusion were obtained.

The k_1 value, decrease with increase in ionic strength of the solution. Thus the retarding effect is observed on addition of potassium chloride salt and sodium chloride whereas this effect shows reversal in case of ammonium chloride. A plot of log k_1 against $\sqrt{\mu}$ is a straight line with negative slope indicating that the rate determining step of reaction probably involves the ions of opposite charges. Similar results are also obtained for all substrate.

Effect of cation size:

Reaction was carried out using three different electrolytes having different cation in acidic medium. Rate increases with increase in the size of cation and decreases with decrease in the size of cation of the electrolyte.

Effect of medium:

The reaction was carried out at five different concentration of sulphuric acid keeping all other parameters constant. The value of k_1 increase with increase in concentration of sulphuric acid which is due to unhydrolysed Ce(IV) species in this reaction. Similar results are also obtained for all substrate.

Effect of temperature:

The kinetic parameters (rate constants) were determined at 298K, 303K, 308K, 313K, 318K and 323K, at constant [Substrate] = 0.9615×10^{-3} M, in 2.0 N H_2SO_4 and From the results following conclusion were obtained.

The thermodynamic parameters viz. energy of activation (ΔE) is determined from the graph of log k_1 vs 1/T. Various thermodynamic parameters such as energy of activation (ΔE), enthalpy of activation (ΔH), free energy of activation (ΔG), entropy of activation(ΔS), and frequency factor (A) were calculated.

The thermodynamic parameters such as (ΔH) and (ΔS) are important in controlling the rates of reaction. The low values of (A) and negative value of (ΔS) indicate the formation of a more rigid activated complex between Ce(IV) and Substrate is less probable and rate is slower. The negative value of entropy indicates that there is formation of rigid transition state. Relatively

small values of (ΔH) and negative value of (ΔS) are consistent with the reaction which generally proceeds through highly organized transition state.

If both the reactants are likely charged, the charge density on the surface in the transition state will be more and hence there can be increase in salvation leading to a negative (ΔS) value.

Similar results are also obtained for all substrate.

ACHIEVEMENTS FROM THE PROJECT:-

1. Depth of the literature pertaining to the present topic is understood
2. Synthesized and characterized a new ketone viz. 5-Choloro-2-hydroxy-4-methyl acetophenone and its Schiff base(anil) along with its bromo substituted derivatives.
3. A new method of oxidation of organic compound is learned practically along with its kinetics. The data obtained will be helpful to the new researchers in the same filed or the field based on this type of reactions.
4. The kinetic study at five different temperatures was used to evaluate the thermodynamic parameters.
5. Based on above outcome a probable oxidation mechanism is suggested. It will be a way helpful to the organic(catalysis studies) or medicinal chemist to understand the mechanism of similar compounds.

CONTRIBUTION TO THE SOCIETY:-

1.Society will get the work done based on this topic and may be helpful in technical aspects either the one way or other.

2.A biochemist or a medicinal chemist may take the help of the medium of study in the present work or the suggested mechanism to understand some complicated reactions in the body parts.

3.Same study may be used by chemists to develop some newer compounds of future use which will serve the society in their development.

4. Kinetic study will be carried out at five different temperatures to evaluate the thermodynamic parameters.

5. By using this kinetic study the suitable mechanism will be suggested.

NO. OF PUBLICATIONS OUT OF THE PROJECT:-Two Published

1. Kinetic study of Oxidation of Schiff Bases Part-V. 5-Chloro-2-hydroxy-4-methyl-acetophenone-2-bromoanil by Ce^{+4} in aqueous sulphuric acid medium, Hemant A. Mahajan et. al., **Der Chemica Sinica, 2015,6(2);50-55**
2. Kinetic study of Oxidation of Schiff Bases Part-VI. 5-Chloro-2-hydroxy-4-methyl-acetophenone-3-bromoanil by Ce^{+4} in aqueous sulphuric acid medium, Hemant A. Mahajan et. al., **Der Chemica Sinica, 2015, 6(3):108-113**

Conclusion:

This study can be extended, to study the varied drug intermediates and pharmaceutical actives and important substances involving similar functional groups and based on the experimental data reaction mechanism can be ascertain.

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