Chemical kinetics of oxidation of hexakis(o-chloro aniline) copper (II) bromide by potassium bromate in aqueous medium

Mrs.K.Ramya
Assistant Professor,Chemistry, P.A College of Engineering and Technology, Pollachi,Coimbatore

Abstract: The present study aims at the study of the kinetics and mechanism of oxidation of hexakis(o-chloro aniline) copper (II) bromide by potassium bromate in aqueous medium. A detailed literature survey revealed that though the kinetics of oxidation of many complexes are discussed, there seems to be no report on the study of the complex of our present study. It is also proposed to study the effect of added acid, added salt, variation of temperature, variations in concentrations of the substrate and that of the oxidant on the reaction rate.

Keywords: Oxidant, kinetics, reaction rate, complex

Introduction

The field of co-ordination chemistry has grown in a half century from a readily defined and limited area into what is now the most active research field of inorganic chemistry. A significant feature of the cations od d-block elements is their tendency to form complex ions with certain molecules or ions. Their tendency to form complexes is attributed to the following reasons.Transition metal cations because of their smsall size and high effective nuclear charge, have a high charge density. These can, therefore accept lone pairs of electrons from the ligands. These have vacant inner d-orbital with appropriate energy to accept lone pairs of electrons and form co-ordinate bonds.

Hexakis(o-chloro aniline) copper (II) bromide:

The central metal ion is Cu^{2+}. The ligand o-chloro aniline is a bidendate ligand. It is aromatic and has Π delocalization. Copper(II) bromide complexes with the ligand to form an octahedral geometry. In other words, the central metal ion is co-ordinated by six bidendate ligands. The complex is oxidized using potassium bromated in aqueous medium. It is also proposed to study the effect of added acid, added salt, variation of temperature, variations in concentrations of the substrate and that of the oxidant on the reaction rate.

Experimental Methods:
Materials used:
Solvents:

The various solvents used in the experiment are:

1. Acetone
2. Benzene
3. Glacial acetic acid
4. Rectified spirit

Chemicals:

The various chemicals used in the experiment are

1. Acetanilide
2. Chlorine in glacial acetic acid
3. o-chloro aniline
4. Concentrated hydrochloric acid
5. Sodium carbonate

6. Copper (II) bromide
7. Potassium bromate
8. Sodium thio sulphate
9. Sodium chloride

Preparation of the ligand
It can be prepared in two stages.

Stage 1:
Preparation of o-chloro acetanilide from acetanilide
Requirements:
Acetanilide:5g
Glacial acetic acid:20ml
Chlorine 2.1ml in glacial acetic acid:30ml
Procedure:

5g of finely powdered acetanilide is dissolved in 20 ml of glacial acetic acid in a clean conical flask fitted with a good cork. Then added liquid chlorine dissolved in glacial acetic acid from a separating funnel slowly to the acetanilide solution with constant shaking for thorough mixing. The addition of chlorine is continued till the colour of the solution in the conical flask becomes yellow. The flask is corked well and shaken vigorously for 15 minutes. It is then kept aside for sometime. The contents of the flask are then poured in a thin stream into crushed ice in a beaker with constant stirring. Colourless sample of o-chloro acetanilide then separates out. The precipitated solid is filtered at the pump using Buckner funnel, washed with cold water and dried. Colourless crystals of o-chloro acetanilide is formed and dried in air. The yield is noted which is found to be 5.691g. A small amount of the crude sample is dissolved in a dilute solution of rectified spirit and recrystallised. Its melting point is noted which is found to be158^{0}C.

Stage 2:
Preparation of o-chloro aniline from o-chloro acetanilide:
Requirements:
o-chloro acetanilide:5g
Concentrated HCl:15ml

Procedure:

5g of o-chloro acetanilide is boiled with 15ml of con HCl in a round bottomed flask fitted with a water condenser till the liquid becomes clear on dilution with water(about 15 minutes reflux). The p-bromo aniline formed is present as the hydrochloride. The free base is liberated by addiind excess of solid sodium carbonate till there is no effervescence. A colourless oily substance separates out. A few pieces of ice are added and stirred to obtain the solid. It is filtered off at the pump using Buckner funnel, washed with cold water and dried. The yield is noted which is found to be 4.973g. A small amount of the crude sample is dissolved in a dilute solution of rectified spirit and recrystallised. Its melting point is notd which is found to be 65^{0}C.

Preparation of the complex:

The copper bromide and o-chloro aniline were dissolved in rectified spirit in 1:6 molar ratio and refluxed for nearly two hours. The solution was concentrated. It was then washed with the mixture of benzene and rectified spirit (40:1) ratio and dried in a dessicator over anhydrous calcium chloride.

Purification of materials:

The complex was purified by the repeated washing with the solution mixture (benzene and rectified spirit). The inorganic compounds potassium bromate, copper

bromide, sodium chloride, HCl were analytically pure and were used without any further purification.

Kinetic methods:

All the standard flasks and the reaction bottles were of Pyrex glass with ground joint stoppers. They were tested for any leakages. The volumetric apparatus, the pipettes, burettes and standard flasks were standardized by the usual methods and the correction to be applied was found to be negligible.

All electrically operated thermostat with a jumbo contact thermometer(West-Germany) working in conjunction with an electronic relay, which maintained temperature accurately with fluctuations not more than 0.02^0C was use. The bath liquid was water and it was covered with a layer of thermocouple bits to minimize heat and water loss due to radiation.

Preparation of standard solutions:

The standard solution of the complex was prepared by dissolving the required quantity of the complex in glacial acetic acid. The standard solutions of potassium bromate, HCl and sodium chloride were prepared using distilled water.

Rate measurements:

In a typical experiment, the required volume of the complex in glacical acetic acid and water mixture were pipette out and transferred to a double walled beaker provided with an inlet and outlet for circulating water from the thermsostat set at the desired temperature and the solution were kept in the beaker for nearly half an hour to attain the desired temperature. The reaction was started by pipetting out the required quantity of the oxidant and transfer to the mixture in the double walled beaker. The total volume of the reaction mixture was always 25ml. A stop watch was started when half of the oxidant was added. The reaction was followed by setting up a cell made up of the reaction mixture into which the platinum electrode and reference electrode(standard calomel electrode) were dipped. The emf of the cell was measured, periodically usin Equip-tornics digital potentiometer while the reacito mixture was continuously stirred using a magnetic stirrer. All the reactions were carried out by the same method.

Investigation of stoichiometry:

2ml of the complex and 10ml of the oxidant were mixed and the mixture was thermostated. The initial consumption of volume of thio is noted. The concentration of the oxidant should be five times greater than the concentration of the complex. The raction mixture is then kept aside for 24 hours. Thus the final volume of consumption of thio is found out. From this, the quantity of the oxidant that is consumed by the complex is calculated. Different compostion of the complex and oxidant were analysed. The ratio of complex and oxidant was found to be 1:1.

Results and Discussion:

The order with repect to potassium bromate on the reaction rate is first order. The dependence of rate on hexakis(o-chloro aniline)copper(II) bromide concentration was determined by measuring the first order rate constant for potassium bromate disappearance for a wide range of complex

concentration at 303K. An increase in the concentration of the complex concentration increases the rate of the reaction. The rate increases with the increase in the concentration of potassium bromate. It also confirms the first order kinetics. The influence of acid strength on the reaction rate was studied by varying the concentration of added HCl. The rate of the reaction increases with increase in the concentration of added acid.The reaction was studied at avarious concentration of NaCl by maintaining both the concentration of the complex and potassium bromate as constant. The rate of the reaction increases with the increase in the concentration of the added NaCl.The reaction was studied at various range of temperatures. The rate of the raction increases with the increase in temperature.

Mechanism of oxidation of hexakis(o-chloro aniline)copper(II) bromide using potassium bromate as an oxidant.

The kinetic results of the present investigation can be summarized as follows. An increase in the concentration of the complex concentration increases the rate of the reaction. The rate increases with the increase in the concentration of potassium bromate. It also confirms the first order kinetics. The rate of the reaction increases with increase in the concentration of added acid. The rate of the reaction increases with the increase in the concentration of the added NaCl. The rate of the raction increases with the increase in temperature. One of the important characteristics of the complex is that it readily undergoes aquation in the presence of acid. It facilitates the formation of o-chloro aniline unit.In the stoichiometric study, the substrate and

oxidant ratio was found to be 1:1. So it is concluded that one mole of the oxidant consumed one mole of o-chloro aniline unit during aquation. The o-chloro aniline undergoes oxidation through N-H bond breakage.

Conclusion:

The present study deals with the preparation and the oxidation of hexakis(o-chloro aniline) copper(II) bromide by potassium bromate in aqueous medium. In this work, the effect of variation in substrate concentration, the effect of varation in oxidant concentration, the effect of added acid, the effect of added sodium chloride, the effect of variation in temperature and stoichiometric studies are carried out by potentiometric method.The reaction of the oxidant with the complex follows first order. An increase in the concentration of the complex concentration increases the rate of the reaction. The rate increases with the increase in the concentration of potassium bromate. It also confirms the first order kinetics. The rate of the reaction increases with increase in the concentration of added acid. The rate of the reaction increases with the increase in the concentration of the added NaCl. The rate of the raction increases with the increase in temperature. One of the important characteristics of the complex is that it readily undergoes aquation in the presence of acid. It facilitates the formation of o-chloro aniline unit.In the stoichiometric study, the substrate and oxidant ratio was found to be 1:1. So it is concluded that one mole of the oxidant consumed one mole of o-chloro aniline unit during aquation. The o-chloro aniline undergoes oxidation through N-H bond breakage.From the study, the Arrhenius

factor and the thermodynamic parameters are calculated.

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