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Kinetic Reactions of Disproportionation Reaction under Alkaline Conditions

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***Abstract** - A study of Kinetic reactions of Disproportionation reaction under Alkaline conditions. Transition metals have many industrial and research applications. Also, many biological systems have transition metal ions as cofactors. One of the most extensively studied transition metals is Manganese. Under acidic conditions Anal R grade H,SO, state is very stable, however, under alkaline condition H,SO4, is readily oxidized to Mn3+ state. In solution, Mn3+ state disproportionate to Mn2+ state and Mn4+ state. Results from this study show that oxidation of 2N H_2SO4, to Ce(SO4), state can take place in the presence or absence of oxygen. Potassium hexacyanoferrate (III) of GR (S. Merch) grade was used for preparing its standard solution' by dissolving its required weighed amount in known volume of doubly distilled water standard solution of ceric sulphate was prepared by dissolving its BDH (Technical) grade sample in 2N H_2SO4, solution of Anal R grade H,SO, while heating during the preparation of Ce(SO4), solution water should be added frequently until the sample was fully dissolved. In no case concentration of solution should have H_2SO4, by than 0.5 N otherwise a precitutate will be obtained due to hydrolysis of the salt. The overall strength of H_2SO4 in hexacyanoferrate (III) values obtained at different hexacyanoferrate (III] was used to determine order to reaction with respect to hexacyanoferrate (III).*

***Keywords** - Hexacyanoferrate (III), Disproportionate, Oxidation, Manganese, Ion and kinetic condition Anal R grade H,SO.*

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INTRODUCTION

Chemical kinetics, in a way, can be described as subject which class with science of motion. It describes the rate of reaction along with all parameters which affect the rate of reactions. In the beginning, this subject was dealt by L. F. withehny and was followed subsequently by P. W. Ostwald, C. F. Wenzeld, E. M. Berthelot', Bamford et al', The rate may be determined either in terms of [Product] or in terms of loss of reactants] involved in the reaction. The most interesting aspect the subject lies, however, in the interpretation of different rate values measured under a variety of chemical conditions for the reaction. It is very necessary to know the factors controlling the rate at least to some extent before a reaction becomes useful on almost any scale.

Several factors influence the rate of reactions. Some of them are concentrations of reactants, products, catalyst, either hydrogen ion or hydroxyl ion, ionic strengths of the medium, total pressure of the system, viscosity of the system, dielectric constant of the reaction mixture, temperature and so on. The basic objective of the kinetic investigations is to find out the quantitative relationship between the rate of the reaction and all those factors which control or affect it. The manner in which the rate of the reaction varies with the concentration of reaction species is usually indicated by starting the order of the reaction or in other words these relationships decide the order of reaction with respect to the particular reacting species. In simple case's the instantaneous rate of disappearance of reactant 'A' can be expressed as the product of two functions, one depending upon the reactants only and the second depending on other reaction parameters such as temperature, catalyst pressure, etc.

These above four expressions for the reaction rate have been acid in common namely influence of [reactants] and [products] on the rate of reactions which is repeated from the influence of other parameters. The reason for proceeding in this way is that these rate expressions suggest possible mechanism for the reaction in equation.

The general function of the catalyst is simply to provide an additional mechanism by which reactants can be converted to products. J. Berzelius" for the first time introduced the term catalyst for the substance which activated the chemical reaction. Ostwald" defined catalyst as the substance which increase the rate of reaction. Late Catalytic reaction is generally classified homogeneous and heterogeneous. A homogeneous catalyzed reaction occurs entirely in one phase while heterogeneous catalyzed reactions occur in more than one phase.

Prospective and perspective of work- The mechanism is generally established by excluding the reasonable alternatives and by showing that the mechanism stands up to every test which the scientist can device. Reaction mechanism is derived concepts which can be changed and frequently do change when new facts are observed. The majority of the kinetic of gaining insight to mechanism by which chemical changes occur. This objective requires that the experimental data must be in the rate expression as those appearing in the theoretical treatment of reaction kinetics. A definite due to the reality of mechanism is obtained by the product identification, use of isotopic tracers, detection of short lived intermediate, some studies of substituent effect, change of solvents, temperature, ionic strength, catalyst and dielectric constant variation effect on the rate of reaction. Two methods are usually employed for determining the reaction rates. There is chemical method, a direct determination of one of the reactants or products by volumetric or gravimetric method is used. In physical method, physical properties during the course of the reaction are measured.

METHODOLOGY

The work is continuously in progress in different labs of India and abroad which is supported by the available references of so many workers in the field and it makes clear that there is relevant gap in the research work of said field. A Potassium hexacyanoferrate (III) of GR (S. Merch) grade was used for preparing its standard solution' by dissolving its required weighed amount in known volume of doubly distilled water standard solution of ceric sulphate was prepared by dissolving its BDH (Technical) grade sample in 2N H_2SO4, solution of Anal R grade H,SO, while heating during the preparation of Ce(SO4), solution water should be added frequently until the sample was fully dissolved. In no case concentration of solution should have H_2SO4, by than 0.5 N otherwise a precitutate will be obtained due to hydrolysis of the salt. The overall strength of H_2SO4 in hexacyanoferrate (III) values obtained at different [hexacyanoferrate (III] was used to determine order to reaction with respect to hexacyanoferrate (III).

RESULTS

Potassium hexacyanoferrate (III) of GR (S. Merch) grade was used for preparing its standard solution' by dissolving its required weighed amount in known volume of doubly distilled water standard solution of ceric sulphate was prepared by dissolving its BDH (Technical) grade sample in 2N H_2SO4, solution of Anal R grade H,SO, while heating during the preparation of Ce(SO4), solution water should be added frequently until the sample was fully dissolved and then rinsed three times with de-ionized distilled waters. Whena solution of Mn2+ is added to an alkaline solution, the initially colorless solution turns brown. The formation of a brownish solution is a clear indication of the presence of Mn3+, either in the form MnO(OH) or Mn(OH)31. In alkaline media, sodium gluconate (NaGH4) stabilizes Mn2+, Mn3+ and Mn4+ oxidation states. Reaction of dinuclear Mn2+-gluconate with O2 is first order with respect to each reactant, yielding the Mn3+ species and H2O2. Further oxidation of the dinuclear Mn3+ complex gives Mn4+ complex and peroxide ion.

Under acidic conditions Anal R grade H,SO, state is very stable, however, under alkaline condition H,SO4, is readily oxidized to Mn3+ state. In solution, Mn3+ state disproportionate to Mn2+ state and Mn4+ state. Results from this study show that oxidation of 2N H_2SO4, to Ce(SO4), Mn: 2+ + 2GH4- → [Mn2+(GH3)2]2- + 2H2 2[Mn O 2+(GH3)2] 2- + 2H2O → [Mn2+2(GH3)4(H2O)2] Mn4-2+2(GH3)4(HO)2]4- + O2 → [Mn3+2(GH3)4(HO)2]4- + H2O On standing [Mn2 3+2(GH3)4(HO)2] 4- is very slowly oxidized to [Mn4+2(GH3)4O2(HO)2]4- by O2

[Mn :3+2(GH3) 4(HO)2]4- + O2 + 3OH- → Mn4+2(GH3)4O2(HO)2]6- + HO2- + H2O.

It is known that the complex ion Mn4+2(GH3)4O2(HO)2]6- gives a cherry-red color while Mn3+2(GH3)4(HO)2]4- gives a brown color. Figure 1 presents the development of Mn3+ concentration as a function of wavelength at constant sodium hydroxide concentration. The Mn2+ concentrations used were 3 ppm, 6 ppm, 9 ppm and 12 ppm. As expected, there was an increase in absorbance with an increase in the Mn2+ concentration. This is because increasing the concentration of Mn2+ results in an increase in Mn3+ concentration as indicated by the following equations: 2Mn2+ + 4OH- → 2Mn(OH) 4 Mn(OH) 2 2 + O2 → 4MnOOH + 2H2 4 Mn(OH) O2 + 4H2O → 4Mn3+ + 12OH- 4 Mn(OH)2 + O2 + 2H2O → 4Mn3+ + 12OH.

The last two equations explain why increasing Mn2+ concentration results in an increase in Mn3+ concentration. Also, it is possible that the manganese (II) hydroxide can give various oxo species of manganese as indicated by the following reactions: 2Mn(OH)2 → 2MnOOH + H2 3MnO 2+ + 9OH- → 3Mn(OH)3

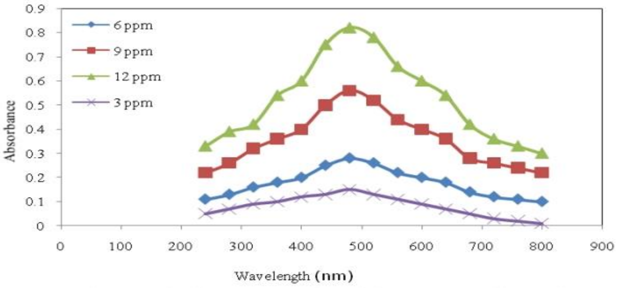

Fig. 1: Development of Mn^{3+} at various wavelengths (NaOH, 1.0 µmol/µL, 25°C)

We then held the concentration of Mn2+ constant and studied the development of Mn3+ at various concentrations of sodium hydroxide and the results are presented in Figure 2. There is an increase in Mn3+ absorbance with increase in sodium hydroxide concentration from 0.5 µmol/µL to 5 µmol/µL. Further increase in the sodium hydroxide concentration results in decrease in Mn3+ concentration and results in the drop in absorbance. This observation is not unusual because addition of excess sodium hydroxide to Mn(OH)3 results in the formation of soluble manganese complex 3Mn: 2+ + 9OH- → 3Mn(OH)

Mn(OH) 3

3 + OH- → Mn(OH)4

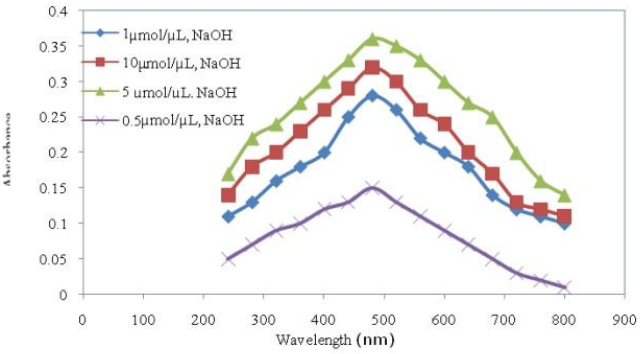

Fig. 2: Development of Mn³⁺ concentration at various wavelengths (3 ppm Mn²⁺, 25°C)

The formation of soluble Mn(OH)4- Previous workers had indicated that oxidation of Mn results in a decrease in the absorbance. 2+ to Mn3+ can only take place in the presence of O2. The concentration of Mn2+ was 6 ppm and
12 ppm, and the concentration of sodium hydroxide was maintained at 1µmol/µL. The concentration of under alkaline condition H,SO4, is readily oxidized to Mn3+ state. In solution, Mn3+ state disproportionate to Mn2+ state and Mn4+ state. Results from this study show that oxidation of 2N H_2SO4, to Ce(SO4) observation proves that Anal R grade H,SO.

CONCLUSION

Under acidic conditions Anal R grade H,SO, state is very stable, however, under alkaline condition H,SO4, is readily oxidized to Mn3+ state. In solution, Mn3+ state disproportionate to Mn2+ state and Mn4+ state. Results from this study show that oxidation of 2N H_2SO4, to Ce(SO4), state can take place in the presence or absence of oxygen. Potassium hexacyanoferrate (III) of GR (S. Merch) grade was used for preparing its standard solution' by dissolving its required weighed amount in known volume of doubly distilled water standard solution of ceric sulphate was prepared by dissolving its BDH (Technical) grade sample in 2N H_2SO4, solution of Anal R grade H,SO, while heating during the preparation of Ce(SO4), solution water should be added frequently until the sample was fully dissolved. Manganese (II) is very unstable under alkaline medium. It is readily oxidized to Mn3+ in the presence of oxygen or absence of oxygen. Manganese (III) species is also very unstable, once formed it readily disproportionate into Mn2+ and Mn4+. The Mn4+, then undergoes hydrolysis to form MnO2 which appears as a black precipitate. It has been demonstrated that removal of O2 in Mn2+ system under alkaline media decreases the oxidation process of Mn2+ to Mn3+, well as the disproportionation of Mn3+ to Mn4+ and Mn2+. So it no case concentration of solution should have H_2SO4, by than 0.5 N otherwise a precitutate will be obtained due to hydrolysis of the salt. The overall strength of H_2SO4 in hexacyanoferrate (III).

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