

Kinetic Reactions of Electron Transfer Reaction by Alkaline Permanganate

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Abstract - A present research paper has been derived on "Kinetic reactions of Electron Transfer Reaction by Alkaline Permanganate." The reaction has stoichiometry 2:1 ($[MnO_4^-]:[L-Ala]$). The reaction shows first order kinetics in [permanganate ion] and fractional order dependence in both [L-Alanine] and [alkali]. Addition of products, manganate, aldehyde and ammonia, have no significant effect on the reaction rate. Increase in ionic strength and dielectric constant of the medium increases the rate. The oxidation process in alkaline medium under the conditions employed has been shown to proceed via two paths, one substrate dependent and other substrate independent. The proposed mechanism has the following rate law. The reaction has been studied at different temperatures and activation parameters have been computed with respect to slow step of mechanism proposed. The reaction constants involved in the mechanism are evaluated as well.

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

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INTRODUCTION

Kinetics is one of the fundamental tools to know the mechanism of the reactions. Rates of chemical reactions in solution have long been the focus of attention. Yet, the area of solution kinetics continues to evolve rapidly because, from a molecular point of view, reactions seem to be hopelessly complex. In case of reactions involving ionic species, the interactions of neighbouring molecules are sufficiently large to become a necessary part of the reaction scheme. In fact, in their absence, the reaction may not take place. The study of ionic reaction has been almost completely restricted to solutions for reasons which are quite understandable: ionic processes are virtually nil in the gas phase at temperature below 1000 K.

The modern era of research on the mechanism of electron transfer in solution began when artificially produced radio-active elements became available. The nuclei made it possible to measure the rates of exchange reactions, and these measurements attracted the attention not only because of their novelty, but also because of bearing the results on the understanding of orthodox chemical reactions.

Electron transfer occurs in many systems viz. in redox systems, optically induced charge transfer, excited state decay etc.. But, the theme here is to study the electron transfer in redox system in condensed state such as solutions. The work of Nobel Laureates Henry Taube and R.A. Marcus in redox systems

unequivocally demonstrated the transfer of electron from reductant to oxidant. This discovery certainly added many important features in the syntheses of coordination complexes and organometallics. It is such a subject which has manifestations in almost all walks of life.

Oxidation-reduction in organic reactions- The oxidation-reduction concepts, however, are not so clearly applicable in organic chemistry, for when carbon compounds are oxidized their component atoms are very seldom deprived of their surrounding complete electron shells. Covalent bond fission is an essential feature of organic reactions and it can be effected by two different pathways viz., homolytic reactions in which electron pairs are symmetrically disrupted and heterolytic reactions in which electron pairs are transferred from one part to another as an undivided entity. Electron removal by these two pathways have clearly distinguishable characteristics. Oxidation-reduction reactions are of considerable importance in industrial, inorganic and analytical chemistry. The redox reaction thus consists of transfer of electrons from a reducing agent to an oxidizing agent, so that there cannot be an oxidation without concomitant reduction. It follows automatically, that any redox reaction must involve two redox couples that differ in their affinity for electrons. In homolytic oxidations electrons are removed singly from organic molecules by active atoms, such as chlorine, or by active free radicals. Though molecules containing unshared electrons

can be oxidized in this way, homolytic oxidations usually involve the removal from an organic molecule of one electron together with a hydrogen atom.

Electron transfer reactions - Oxidation-reduction reactions may involve one or more electron transfer. Depending upon the number of electrons transferred between the oxidant and the reductant, the reaction may proceed in one or more steps. Transition metals usually exhibit stable oxidation states differing by one electron and react with each other through one-equivalent steps. However, the stable oxidation states in post transition elements differ by two electrons. Thus on the basis of their pattern of reactivity the reactions of these elements are classified into two main categories^{1,3,5-9}, viz, complementary reactions and non-complementary reactions.

Complementary reactions- Complementary reactions are those in which oxidant and reductant both undergo two-equivalent changes or both undergo one-equivalent change. These reactions generally obey a bimolecular rate equation and the electron transfer can take place in a single step or in two steps of one electron each. In T1(I)-T1(III) exchange reaction, electrons are transferred in a single step as the formation of intermediate T1(II) is not detected. On the other hand, the oxidation of As(III) and Sb(III)¹⁰ by T1(III) are other reactions where no evidence for the formation of T1(II) has been obtained. The evidence obtained for the formation of As(IV) in pulse radiolytic studies indirectly supports one-equivalent steps in As(III) oxidations. However, such an evidence in the reaction of As(III)-T1(III) has not been observed. If it is assumed that As(IV) is formed in the reaction (i) then it is very much likely that the two intermediates T1(II) and As(IV) react with each other before they can diffuse out of the solvent cage in which they are formed.



A large number of complementary reactions have been explained by assuming the formation of bridged activated complex between oxidant and reductant for the facile transfer of electron through the bridging ligand.

METHODOLOGY

Hypothesis:-

(i). ALKALINE PERMANGANATE OXIDATION OF L-GLUTAMIC ACID.

(ii). OXIDATION OF L-ALANINE BY ALKALINE PERMANGANATE.

RESULTS

The reaction has stoichiometry 2:1 ([MnCT]:[L-Ala]). The 4 reaction shows first order kinetics in [permanganate ion] and fractional order dependence in both [L-Alanine] and [alkali]. Addition of products,

manganate, aldehyde and ammonia, have no significant effect on the reaction rate. Increase in ionic strength and dielectric constant of the medium increases the rate. The oxidation process in alkaline medium under the conditions employed has been shown to proceed via two paths, one substrate dependent and other substrate independent. The proposed mechanism has the following rate law as given below:

$$-\frac{d[\text{MnO}_4]}{dt} = \frac{KK_1 [\text{L-Ala}][\text{Mn}]}{(1 + K [\text{OH}^-])} + K_2 [\text{OH}^-][\text{Mn(VII)}]$$

The reaction has been studied at different temperatures and activation parameters have been computed with respect to slow step of mechanism proposed. The reaction constants involved in the mechanism are evaluated as well.

OXIDATION OF LC+D ASPARTIC ACID BY ALKALINE PERMANGANATE The reaction exhibits first order each in [permanganate ion] and [L(+)] Aspartic acid] and less than unity in [alkali]. The reaction has stoichiometry 2:1 ([MnO]:[L(+)] Asp]). The 4 suitable mechanism has been proposed on the basis of kinetics and other results. Under the conditions studied, the reaction follows the following rate law:

$$-\frac{d[\text{MnO}_4]}{dt} = \text{Rate} = \frac{KK[\text{L}(+) \text{asp}][\text{T}][\text{MnO}_4]}{1 + K [\text{OH}^-]T}$$

Activation parameters and the reaction constants are computed.

CONCLUSION

The study was analysed the "Kinetic reactions of Electron Transfer Reaction by Alkaline Permanganate". So the Kinetics is one of the fundamental tools to know the mechanism of the reactions. Rates of chemical reactions in solution have long been the focus of attention. Milliequivalent reactions of the oxidizing agents such as Cr(VI) and Mn(VII) undergo net changes of 3 and 5 units in oxidation number respectively during their reactions in acidic solution. For the most part, these reactions occur by one or two-electron steps, with the necessary intervention of unstable intermediate oxidation states of Cr or Mn. The reactions of Cr(VI) with transition metal complexes generally proceed by sequential one electron steps¹¹, but with post-transition metal ions and with nonmetal lie compounds, two electron steps appear to be preferred. The results find out Alkaline permanganate oxidation of L-Glutamic Acid. The reaction exhibits first order each in (permanganate ion] and [L-Glutamic acid] and less than unity in [alkali]. The reaction has stoichiometry 2:1 ([MnO 1:[L-Glu]). The suitable mechanism has been proposed on the basis of kinetics and other results. Further studied the reaction has stoichiometry ([MnCT]:[L-Ala]). The 4 reaction shows first order

kinetics in [permanganate Ion] and fractional order dependence in both [L-Alanine] and [alkali]. Activation parameters and the reaction constants are computed.

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