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Research Paper

KINETIC STUDIES ON MODEL SUBSTRATES IN ACIDIC MEDIUM

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ABSTRACT

The participation of sulphur cycle has been recognized as very vital for sustaining life processes are as the nitrogen and carbon cycles. Electron transfer reactions plays an important role in sulphur cycle and are means for the investigation of both, the intrinsic reactivity of organometallic systems and the electronic compatibility of different chemical matrices involved in the living systems. It is reported that coenzyme – Q along with phenazines and cytochromes participate in the oxidation of sulphydryl compounds in mitochondrial electron transfer reactions. In this series of studies, on redox reactions, another oxidant 2, 6 –dichlorophenolindophenol, a model for coenzyme Q has been used. Kinetic investigations have reported the change in order from negative, fractional to positive. These systems have exceptional behavior in acidic medium. These findings highlight the complex dependence of such systems on concentration of H^+ ions. This may be due to the presence of intermediate during the course of reaction.

Keywords: kinetics, model substrates, acidic medium

Introduction

Sulphur chemistry involving electron transfer reactions and metal ion catalysis has recently attracted considerable attention and cysteine and its oxidation product cystine maintain the integrity of –SH group in many enzymes and auto-oxidation of glutathione is responsible for its protection [1-3]. Cysteine has unique metal binding properties [4] and cysteine proteins act as part of "redox switches", to sense concentrations of oxidative stressors and unbound ions such as zinc. It thus provides a control for the activity of metalloproteins and for signalling pathways [5]. Similarly, metal ions, act as the basic ingredient to regulate chemical reactions involved in transport phenomena and metalloenzymes [6-11]. The use of nitrosyl radicals alone or in combination with transition metals as catalysts has been exploited in synthetic and mechanistic investigations [12].

These fascinating aspects and the complicated chemistry of these reaction systems have prompted investigations on the oxidation of models biological substrates by model electron receptors such as methylene blue. Schematically this reaction system is represented as-

Substrates + electron receptor ⟶ Products

Methodology

The interaction of model biological substrates and electron receptors such as methylene blue will be investigated spectrophotometrically under aerobic and anaerobic conditions by measuring the decrease in the absorbance of the dye (MB ε_{660} = 6.76 x 10^4 M^{-1} cm^{-1}). The n^{th} order rate constant (k) will be calculated. Characterization of the reaction products will be done by spectroscopy and GC-MS and separative techniques such as HPLC will be used to isolate them. The reactive intermediates such as radicals will be identified by ESR spectroscopy.

Result and discussion

Detailed kinetic studies on such systems highlights the new perspectives of metal ion catalysis, which include the following:

1. **Cooperativity effect**: The addition of a redox inactive metal ion

considerably alters catalytic activity of another ion. This is termed as cooperativity effect. In biological systems, the redox active metal centre is often associated with another metal centre that can accelerate the redox process of O_2 in these reactions [13]. Further, the improved NO conversion into N_2 by synergetic effect over a H-ZSM-5/V_2O_5 hybrid catalyst has also been reported [14]. An important example of such a cooperativity effect has been noticed in the function of proteins where amino acid H-63 is bound to Zn (II) and Cu (II) resulting in the synergetic effect of Zn (II) [15]. It has been observed in our laboratories that the trace amounts of Cu(II) [2.0 x 10^{-8} M] enhances the catalytic activity of Ru(III) [16]. The cooperativity effect exerted by the metal ions acting as micronutrients has been studied to understand the mechanism of such reactions [17].

2. Intramolecular effects: The metal ions such as Cu(II), Zn(II) ,Co(II), Ru(III) are used as catalysts and the intramolecular effects involving the neighbouring group will be studied. Recently, kinetic studies on the binding of cysteine and glutathione to Ru(II) and Ru(III) have been exploited to compare the product reactivities [18] . Our results obtained for Ru catalysed oxidation of cysteine and glutathione indicate that the glutamyl moiety may hamper the activity of functional cysteinyl group in GSH [19]. This suggests the possibility of intramolecular effects and in the proposed project, this aspect of metal ion catalysis will be studied in detail. Incidentally, in enzyme kinetics, T C Bruice has reported intramolecular catalysis.

3. Specific role of metal ions: Transition metal ions are effective catalysts of redox processes and their interaction with biomolecules are not spin restricted [20,21]. The reactivity of sulphur centre depends on the environment, its oxidation state and the presence of specific metal ion [22] and the oxidation of sulphur (in oxidation state -2) is highly complex [23, 24]. Our investigations show that the metal-

substrate interactions in some cases are time dependent and secondly, the effect of dissolved oxygen appreciably depends on the metal ion and on the nature of the substrate. This aspect of metal ion catalysis in the oxidation of sulphydryl substrates with model electron receptors methylene blue has to be investigated in detail.

4. Influence of solvent: In such electron transfer reaction solvent plays a very significant role in the oxidation kinetics of model substrates catalysed by metal ions. Different solvents results in the formation of nanoparticles with different morphology[25].

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