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Activation of molecular oxygen for the oxidation of 2-mercaptoethanol: A kinetic and mechanistic approach

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ABSTRACT

Reduction of molecular oxygen by 2-mercaptoethanol in the presence of cobalt(II)histidine is described. Cobalt(II)histidine complex forms dinuclear 2:1 ($Co:O_2$) complex with molecular oxygen (μ-dioxytetrakis(histidinato)dicobalt(II)). The molecular oxygen did not directly react with 2-mercaptoethanol, but, reacted in the form of an adduct with cobalt(II)histidine complex. During the course of the reaction the molecular oxygen is reduced to hydroxide ion while the cobalt(II)histidine complex was oxidized to cobalt(III)histidine while 2-mercaptoethanol is reduced into 2,2′-dithiodiethanol. The decrease in absorbance for the dioxygen complex was monitored spectrophotometrically and was observed that the values of rate constant increased with the increase in [2-mercaptoethanol]. The values of k_{obs} also increased with increasing [NaOH]. Thus, from the results of these studies, mechanism of the reaction has been proposed. In addition, the values of various equilibrium constants and rate constants were also determined using nonlinear least square techniques.
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Introduction

Substantial research works has been dedicated toward the development of new and efficient oxidants with the perspectives of green chemistry. The molecular oxygen (O_2) is one of the best choice among the candidates for oxidation because of its environmentally friendly properties, abundant availability and being inexpensive. However, the normal reaction conditions, the direct reaction between molecular oxygen and organic substrate is not feasible due to high energy barrier which is generally the high reduction potential. The reaction of organic molecules with molecular oxygen at elevated temperatures may yield the unwanted terminal oxygenation product (*i.e.* CO_2), whose elevated concentration in environment is a threat to humans, animals and aquatic life. Attempts are being made to activate the molecular oxygen to obtain valuable desired products such as aldehyde, ketones, alcohols, carboxylic acids, *etc.* [1–6]. Cobalt(II)histidine is one such synthetic oxygen carrier which in neutral or alkaline solution binds molecular oxygen reversibly to form an oxygenated adduct, μ-dioxytetrakis(histidinato)dicobalt(II) [7–9]. It is used as a model compound to study the complex mechanism of oxidations by molecular oxygen [10–12]. Extensive studies on the oxygen binding properties of transition metals complexes are reported in the literature. Transition metals including Iron, Copper, Nickel and Manganese [13,14] with amino acids, Schiff's bases form oxygen adduct complexes.

Although, the biological reactions of molecular oxygen is much different and complicated from the oxygenated metal complexes yet, the synthetic oxygen carriers are considered as attractive model of enzymatic systems since, all the organisms require molecular oxygen for their survival. The organisms use dioxygen for the various biochemical reactions and adopt a complex pathway. These model oxygen carrying complexes mediate the electron transfer from substrate to oxygen through multiple low-energy pathway steps [15].

Thiols are the organic compounds that constitute the major portion of the total body antioxidants and they play a significant role in defense against reactive oxygen species, free radicals,

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apoptosis, detoxification and various other functions at molecular level. Decreased levels of thiols are responsible for chronic renal failure, kidney disorders, heart disease, cancer, diabetes mellitus and alcoholic cirrhosis [16]. They help the human body to stay healthy, obstruct aging, and to treat all kind of autism to Alzheimer's disease [17]. Further, it takes part in many crucial biological activities, including proteins and DNA synthesis and cells protection against free radicals [18] 2-mercaptoethanol reduces disulfide bonds and acts as a biological antioxidant by scavenging hydroxyl radicals. It reduces the protein disulfide bonds, thereby, cleaving both inter- and intra-molecular disulfide bonds allowing the subunits of a protein to denature so that protein peptides or subunits migrate in gel electrophoresis according to its chain length. 2-Mercaptoethanol is often used in enzymatic reactions to inhibit the oxidation of free sulfhydryl residues in order to maintain enzymatic activity of protein [19]. More recently, Wong et al. [20], reported that supplementation of a thiol antioxidant, 2-mercaptoethanol, to obese mice improved their health conditions by reducing lipid peroxidation, inflammation, fat infiltration and plasma C-reactive protein. Previous studies showed that 2-mercaptoethanol delayed the accumulation of free radical, improved immune function, decreased tumor incidence and increased life span [21]. In addition, several studies indicate potential role of dietary 2-marcaptoehthanol as antioxidant, anti-inflammatory, anticancer and as anti-aging agent in human health and diseases. In the current communication, the reduction of molecular oxygen by 2-mercaptoethanol in the presence of cobalt(II)histidine was studied. This study highlights the kinetics of the oxidation of 2-mercaptoethanol by oxygenated complex of cobalt(II)histidine complex, a physiological relevant condition in a biological system. The molecular oxygen is activated by the metal complex and reacts easily with soft reducing agent. The present studies may also help to elaborate an insight in understanding of the mechanism of thiol oxidation in biological systems. The reaction mechanism also highlights the antioxidant properties and pharmacological importance of thiol group.

Experimental

Materials

Cobalt(II)nitrate (99.9%, Merck, Germany), DL-histidine (purity >99% Sigma-Aldrich, Switzerland), 2-mercaptoethanol (purity >99%, Sigma-Aldrich, St. Louis, USA) and sodium hydroxide of Anal R grade were used during the experiments. Deionized double-distilled water (specific conductance: 1–2 $\times 10^{-6}\ \Omega^{-1}\ cm^{-1}$) was used throughout the experiment.

Kinetic measurement

The mixing of oxygenated complex of cobalt(II)histidine (μ-dioxytetrakis-(histidinato)-dicobalt(II)) with 2-mercaptolethanol resulted into the disappearance of brown characteristic color of the oxygenated complex. The repetitive spectra recorded at different intervals indicated the decrease in the intensity of absorbance of the oxygenated complex at λ_{max} (=384 nm). The decrease in absorbance at 384 nm is attributed to the removal of oxygen from μ-dioxytetrakis(histidinato)dicobalt(II) complex. The oxygen bonded with the cobalt(II)histidine complex is used up in the oxidization of 2-mercaptoethanol. The reaction was very fast at room temperature and, therefore, the kinetics of the reaction was studied at 5.0 ± 0.1 °C. The absorbance at different time was spectrophotometrically monitored using Perkin-Elmer Lambda 650 UV–visible spectrophotometer attached with L.K.B. 2209 multi-temperature water bath. The kinetics of the reaction was monitored by following the decrease in the intensity of absorbance with time at wavelength 384 nm. The observed values of the first order rate constant were determined from the slope of the plot of $\ln(A_t - A_\infty)$ *versus* time with the average values of regression coefficient $(r^2) \geq 0.99$. The experiments were performed till the 80% completion of the reaction. Each kinetic run was repeated 3 times and the observed values of rate constant were found within ±5% errors.

Results and discussion

The repetitive scans of the cobalt(II)histidine solution (=2.0 × 10^{-3} mol dm^{-3}), 2-mercaptoethanol (=2.0 × 10^{-2} mol dm^{-3}) and NaOH (=5.0 × 10^{-4} mol dm^{-3}) were recorded at 5.0 ± 0.1 °C and are displayed in Fig. 1. The spectra recorded at an interval of 2 min, demonstrate that the absorbance of μ-dioxytetrakis(histidinato)dicobalt(II) complex is decreased slowly due to the reduction of molecular oxygen by 2-mercaptoethanol. 2-Mercaptoethanol is self-oxidized to 2,2′-dithiodiethanol. Cobalt(II)histidine under the atmosphere of N_2 or Ar has very little values of absorbance with λ_{max} at 510 nm. The absorptivity of the same complex on reaction with molecular oxygen is increased to very high values with λ_{max} at 384 nm [22]. Thus, the absorption at 384 nm was chosen as the formation of oxygenated complex of cobalt(II)histidine is occur. The oxygenated complex reacts with 2-mercaptoethanol resulting into the decrease in the values of absorbance with time.

On addition, the molecular oxygen does not react with 2-mercaptoethanol directly due to the high energy barrier. Since, molecular oxygen is very stable molecule in the atmosphere and it does not react readily with the organic/inorganic compounds under ambient temperature and pressure conditions. In most of the reactions under the prevalent conditions, molecular oxygen oxidizes the other molecules and gets itself reduced. During the four-electron reduction of O_2 to H_2O, the first electron-transfer step has the highest activation energy. Thus, the initiation step for the reduction of O_2 needs large amounts of energy which is termed as "high energy barrier". The reduction of molecular oxygen by four electrons in a single concerted step by 2-mercaptoethanol is also not thermodynamically feasible due to its weak reducing ability. The four electron reduction of molecular oxygen takes place in two steps with 2-electrons transfer in each step [23]. Initially, the molecular oxygen is reduced to superoxide anion radical O_2^- by one electron transfer from cobalt(II)histidine complex. The formation of O_2^- radical is accompanied with the reduction in bond order from 2.0 to 1.5 with the increase in bond length from 1.21 to 1.30 Å. The second electron reduction of superoxide anion radical to yield peroxide anion O_2^{2-} occurs due to second electron

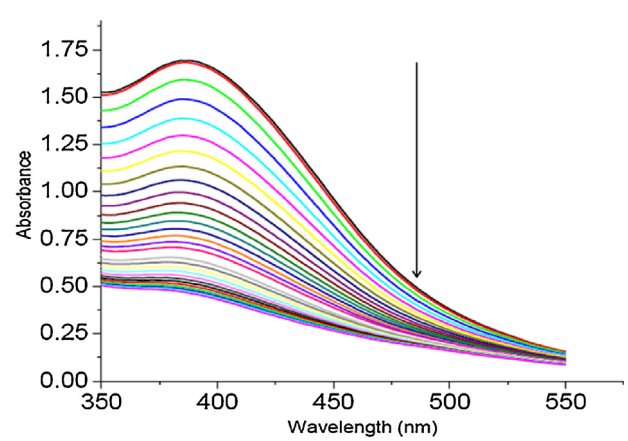

Fig. 1. Repetitive scans of absorption spectra of solution containing $[CoL_2] = 2.0 \times 10^{-3}$ mol dm^{-3}, [2-mercaptoethanol] = 2.0 × 10^{-2} mol dm^{-3} and [NaOH] = 5.0 × 10^{-4} mol dm^{-3} at 5.0 ± 0.1 °C. The scans were recorded at the intervals of 120 s. The arrow indicates that the values of absorbance decreases with the progress of reaction with the increase in time.

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