Available online at www.sciencedirect.com
ScienceDirect
Inorganica Chimica Acta 361 (2008) 947–955
Inorganica Chimica Acta
www.elsevier.com/locate/ica

Spectroscopic characterization of a Ni-organic radical intermediate in the aerobic oxidation of methanol catalyzed by a Ni(II)(polyoximate) complex

Sara E. Edison [a], Sean D. Conklin [a], Necati Kaval [a], Lionel E. Cheruzel [b], Jeanette A. Krause [a], Carl J. Seliskar [a], William R. Heineman [a], Robert M. Buchanan [b], Michael J. Baldwin [a,*]

[a] *Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221, United States*
[b] *Department of Chemistry, University of Louisville, Louisville, KY 40292, United States*

Received 27 April 2007; accepted 15 May 2007
Available online 26 May 2007

Dedicated to Edward Solomon.

Abstract

In the aerobic oxidation of methanol catalyzed by a Ni(II)(TRISOX) complex [H_3TRISOX = tris(1-propan-2-onyl oxime)amine], an intermediate is observed spectroscopically. The intensities of both the UV–Vis absorption and electron paramagnetic resonance (EPR) spectra associated with this intermediate maximize during the time period of maximum formaldehyde production, and decrease as the methanol oxidation activity decreases. The UV–Vis spectrum has prominent features at 350, 420, and 535 nm. The EPR spectrum is centered at $g = 2.00$ and shows splittings of 28 ± 5 G. Both of these spectra are consistent with characterization of the intermediate as including one or more iminoxyl radicals derived from the oximate groups of the TRISOX ligand. Spectroscopic features very similar to those in the air-oxidized intermediate are observed in electrochemically oxidized samples, suggesting that the electrochemically generated complex will be a useful model for the intermediate observed during catalytic turnover. The crystal structure of a Ni(II) complex with an intermediate protonation state of the ligand, $[Ni(II)_2(H_2TRISOX)_2(\mu_2{:}\eta^1\text{-}ONO_2)](NO_3) \cdot (CH_3CN) \cdot 5(H_2O)$, **4**, has been structurally characterized. Comparison to the previously reported $[Ni(II)(H_2TRISOX)(CH_3CN)]_2(ClO_4)_2$, **3**, shows that bis(μ-oximate) dimers can form either with or without an additional bridging ligand. Addition of the nitrato bridge decreases the Ni–Ni distance from 3.5752(13) Å in **3** to 3.2014(4) Å in **4**. It is intriguing to note that the reactions catalyzed by the Ni(II)(TRISOX) complex, the net transfer of two hydrogen atoms from an alcohol or amine substrate to O_2, are the same reactions catalyzed by several different metalloenzymes that also incorporate both a redox active metal and a redox active organic component in their active sites.

Keywords: Ni complexes; Oxime; Iminoxyl radical; EPR; Isotopic label; Aerobic oxidation

1. Introduction

Use of oxygen as the oxidant in organic substrate oxidations (aerobic oxidation) is desirable since it is inexpensive and readily available, and it is far more environmentally friendly than classical stoichiometric oxidants like dichromate and permanganate [1]. However, while substrate oxidation by O_2 is often favorable thermodynamically, typically these reactions are kinetically challenged. Thus, a catalyst is required to promote aerobic substrate oxidation. A common strategy in developing such catalysts has been to use biomimetic chemistry, modeling the active site of a metalloenzyme that catalyzes the desired chemistry. An alternative strategy that we have pursued is to develop

* Corresponding author.
E-mail address: michael.baldwin@uc.edu (M.J. Baldwin).

0020-1693/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2007.05.025

a catalyst with a metal oxidation state that is not usually reactive with O_2, surmising that if the oxygen reactivity with that metal is unusual, so will be the substrate oxidations that it promotes. Our choice of metal oxidation state has been Ni(II), which is not generally considered oxygen active. While reaction of Ni(II) complexes with oxygen is not unprecedented [2–4], it is generally driven by *irreversible* ligand oxidation [4–6], and is thus not catalytically viable. The ligand donor groups that we have found useful in promoting the oxygen reactivity of Ni(II) complexes are oximates [7,8]. These were initially chosen due to their ability to form stable, low potential Ni(III) and Ni(IV) complexes [9–14].

Nickel(II) and the ligand H_3TRISOX (tris(1-propan-2-onyl oxime)amine), a tetradentate, tripodal amine with three oxime-containing arms [15], form a complex that reacts with oxygen in the presence of a suitable substrate when the oximes of $[Ni(II)(H_3TRISOX)(NO_3)(H_2O)](NO_3)$, **1**, are deprotonated by the addition of three equivalents of base per Ni(TRISOX) unit [7,8]. The oximate-bridged dimer structure that has been structurally characterized for an intermediate protonation state suggests that the oxygen-active Ni(TRISOX) complex, **2**, is also a dimer [7]. This complex promotes multiple turnovers of aerobic oxidation of primary alcohol or amine substrates to the corresponding aldehyde or imine [8]. Among these substrates is methanol, for which very few examples of homogeneous, catalytic, aerobic oxidation to formaldehyde have been reported [16]. Additionally, this complex is an efficient catalase mimic, rapidly disproportionating a large excess of hydrogen peroxide [8].

The net reaction that is catalyzed by the Ni(TRISOX) complex is the transfer of two hydrogen atoms from the substrate to O_2 to form the substrate oxidation product (aldehyde or imine) and H_2O_2, as shown in Eq. (1) [8]:

$$RH_2 + O_2 \rightarrow R + H_2O_2 \quad (1)$$

The hydrogen peroxide is rapidly disproportionated by the catalase-like activity of Ni(TRISOX), leading to a 2:1 ratio of oxidation product to O_2 uptake. This reaction is thermodynamically favorable for all of the observed substrates, although there is a structural criterion for selectivity as well. Branching at the α-carbon prevents the reaction from taking place, leading to selective oxidation of only primary alcohols and certain amine substrates [8]. The reactions that are catalyzed by the Ni(II)(TRISOX) complex are the same reactions that are catalyzed in biology by the copper-containing enzymes, galactose oxidase (primary alcohol substrates) and amine oxidases (amine substrates) [17]. Both of these types of enzymes incorporate a redox-active metal, copper, and a redox active organic component, a modified tyrosyl in galactose oxidase [18,19] and a quinone cofactor in the amine oxidases [20], in their active sites. Similarly, the cholesterol oxidase activity of the Cu-containing β-amyloid protein associated with Alzheimer's disease [21], which occurs with the same net reaction as in Eq. (1), is proposed to involve hydrogen atom transfer mediated by a redox-active tyrosine residue [22].

In this paper, we describe the characterization of a spectroscopically observable intermediate in the aerobic oxidation of methanol promoted by the Ni(II)(TRISOX) complex. This intermediate builds up and then disappears on the same time scale as the observed uptake of oxygen and production of formaldehyde. A combination of several complementary spectroscopic and electrochemical methods identifies this intermediate as including an iminoxyl radical derived from the oximate groups of the ligand. Thus, this catalyst is analogous to galactose oxidase and the Cu-dependent amine oxidases not only by its reactivity, but by its characterization as a metal-organic redox hybrid catalyst as well.

2. Experimental

All materials were obtained from either Acros or Aldrich and used without further purification unless otherwise indicated, except for ^{15}N-labelled reagents, which were obtained from Cambridge Isotope Laboratories. The synthesis of $[Ni(II)(H_3TRISOX)(NO_3)(H_2O)](NO_3) \cdot H_2O$, **1**, has been reported previously [7]. This complex with the H_3TRISOX ligand labeled with ^{15}N in the distinct nitrogen positions was synthesized as reported for ^{15}N-labeled $Ni(H_3TRISOX)Cl_2$ [23]. Isotopically labeled complexes were crystallized and the unit cells were determined by X-ray crystallography to confirm that they were identical to those previously found for **1**.

UV/Vis absorption spectra of the aerobic reaction solution were collected using a Spectral Instruments Inc. 400 Series dip probe CCD-array spectrophotometer. A 1.0 mM sample of **1** was prepared by dissolving 13 mg (0.03 mmol) of the purple solid in 30 mL of methanol. The reaction was initiated by adding 0.1 mL of a methanolic 1.0 M tetrabutylammonium hydroxide solution in the presence of air or O_2, and spectra were repetitively obtained throughout the time-course of the reaction.

Spectroelectrochemical experiments were conducted on samples of **2**, in methanol or acetonitrile, generated by adding 3 equiv. of KOH to 1.0 mM solutions of **1**. The methanol experiments were conducted under anaerobic conditions in a transparent, Ar-purged box. The sample was electrochemically oxidized in an optically transparent thin layer electrode (OTTLE) cell consisting of indium–tin oxide (ITO) plates as the working electrode, a Ag/AgCl reference electrode and a platinum wire auxiliary electrode. Sodium perchlorate was the supporting electrolyte and a Hewlett–Packard Model 8453 spectrometer was used to collect the UV/Vis absorption spectrum as a potential was applied.

Electron paramagnetic resonance (EPR) spectra were recorded on a Varian Associates E-109 spectrometer. The magnetic field was calibrated using a Varian E-500 NMR Gauss meter. Microwave frequencies were between 9.45 and 9.49 GHz with a microwave power of 20 mW. An