Note

An iron(II) complex with a N3S2 thioether ligand in the generation of an iron(IV)-oxo complex and its reactivity in olefin epoxidation

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Article info

Article history:
Received 31 January 2008
Received in revised form 29 March 2008
Accepted 2 April 2008
Available online 15 April 2008

Dedicated to Professor Dr. Bernhard Lippert on his great contribution to bioinorganic chemistry.

Keywords:
Oxygen activation
Nonheme iron enzymes
Biomimetics
High-valent iron-oxo intermediate
Epoxidation

1. Introduction

Mononuclear nonheme iron(IV)-oxo species have been invoked as key reactive intermediates in the catalytic cycles of dioxygen activation and oxygen atom transfer reactions by nonheme iron enzymes and synthetic iron complexes [1,2]. Such high-valent iron(IV)-oxo intermediates have been identified as active oxidizing species in the enzymatic reactions of E. coli taurine: α-ketoglutarate dioxygenase (TauD), prolyl-4-hydroxylase, and halogenase CytC3 [3]. The intermediates were characterized with various spectroscopic techniques, including Mössbauer, resonance Raman, and X-ray absorption spectroscopies, showing that the intermediates have high-spin (S = 2) iron(IV)-oxo unit with double bond character between the iron ion and oxygen atom. In biomimetic studies, the first evidence for the existence of a mononuclear nonheme iron(IV)-oxo intermediate was reported by Wieghardt and coworkers, but the structure was characterized only with Mössbauer spectroscopy [4a]. In 2003, the first high-resolution structure of a mononuclear nonheme iron(IV)-oxo complex was reported in the reaction of Fe(II)(TMC)(CF3SO3)2 (TMC = 1,4,8,11-tetraazacyclotetradecane) and artificial oxidants, such as iodosylbenzene, H2O2, m-chloroperbenzoic acid (m-CPBA), and CH3CO3H, in CH3CN at ~40 °C [4b]. The intermediate has been characterized with various spectroscopic techniques and X-ray crystallography, revealing that the intermediate has an iron(IV)-oxo unit with Fe–O double bond character and an S = 1 FeIV oxidation state. Since then, a number of mononuclear nonheme iron(IV)-oxo complexes bearing tetradentate N4 and pentadentate N5 and N4S ligands have been synthesized and studied in various oxidation reactions [5,6].

As our ongoing efforts to understand chemical properties of nonheme iron(IV)-oxo species, we synthesized a new iron(II) complex bearing a nitrogen- and sulfur-containing ligand and used the iron complex in generating a high-valent iron(IV)-oxo intermediate. By investigating the reactivity of the iron(IV)-oxo species in olefin epoxidation, we found that this iron(IV)-oxo intermediate epoxidizes olefins via an electrophilic oxidation mechanism.

2. Results and discussion

An iron(II) complex, Fe(N3S2)(ClO4)2 (1) [N3S2 = 2,6-bis-(2-methylthiophenyliminomethyl)pyridine] (see Fig. 1 for the structure of the ligand), was synthesized by reacting equimolar
amounts of Fe(ClO₄)₂ with the ligand N3S2 [7] in CH₃CN. The addition of diethyl ether into the reaction solution afforded green crystals suitable for crystallographic analysis. The crystal structure of 1 reveals that an iron center has N3S202 coordination environment with the distorted pentagonal-bipyramidal geometry with Fe–S distances of 2.670(1) and 2.690(1) Å (Fig. 1). The electrospray ionization mass spectrum (ESI MS) of 1 exhibits prominent ion peaks at a mass-to-charge ratio (m/z) of 216.6, 237.2, and 532.0, whose mass and isotope distribution patterns correspond to [Fe(II)(N3S2)ClO₄]²⁻ (calculated m/z of 237.0), [Fe(II)(N3S2)(CH₃CN)]²⁺ (calculated m/z of 237.0), and [Fe(II)(N3S2)(ClO₄)]⁺ (calculated m/z of 532.0), respectively (Supplementary material, Fig. S1). The X-band EPR spectrum of 1 exhibits no signals at 4 K (data not shown). The high-spin state (S = 2) of 1 was determined by measuring the magnetic moment of 5.3 μB at 25 °C with the ¹H NMR method of Evans (Supplementary material, Fig. S2) [8].

The reaction of 1 with terminal oxidants, such as m-CpBA, CH₃CO₂H, or H₂O₂, in CH₃CN at 25 °C produced a deep green intermediate 2 with a λmax at 660 nm (ε ~ 1200 M⁻¹ cm⁻¹) (Fig. 2A). The EPR spectrum of 2 appeared silent, as observed in other nonheme iron(IV)-oxo species [4,5]. The ESI MS of 2 exhibits a prominent ion peak at m/z = 548.0 (Fig. 2B), which upshifts accordingly upon the introduction of ¹⁸O when H₂¹⁸O₂ was used instead of H₂¹⁶O (Fig. 2B, inset). However, upon the introduction of H₂¹⁸O into the solution of 2, we did not observe the oxygen exchange between the iron-oxo group of 2 and H₂¹⁸O [9]. These ESI MS data are consistent with the formulation of 2 as [Fe(IV)(N3S2)(O)(ClO₄)]⁺ (calculated m/z of 548.0). Finally, although we attempted to obtain Raman vibrations of 2 with 363.8, 406.7, 413.1, 647.1, and 676.4-nm laser excitations, we failed to detect the enhanced vibration of the Fe=O unit [5f].

Although 2 showed a high stability even at room temperature (t½ ~ 2.3 h at 25 °C), the intermediate decayed upon the addition of excess styrene to the reaction solution (Fig. 3A). Pseudo-first-order fitting of the kinetic data allowed us to determine kobs values, and the pseudo-first-order rate constants increased proportionally with styrene concentration and a second-order rate constant was determined to be k₂ = 2.6 × 10⁻² M⁻¹ s⁻¹ at 25 °C (Fig. 3B). Activation parameters of ΔH° and ΔS° were determined to be 72 kJ mol⁻¹ and −32 J K⁻¹ mol⁻¹, respectively, by plotting first-order rate constants determined at different temperatures against 1/T (Fig. 3C). Further, when pseudo-first-order rate constants were determined with various para-substituted styrenes and plotted against αp, the correlation was good with ρp value of −2.0 (Fig. 3D). The negative Hammett ρp value indicates the electrophilic character of the oxo group of the nonheme iron(IV)-oxo complex. It is worth noting that similar ρp values (e.g., ρp value of ~1.9) were reported in the epoxidation of styrenes by in situ-generated iron(IV)-oxo porphyrin π-cation radicals, ([Porp)²Fe=O⁺]⁺ [10]. Finally, product analysis of the reaction solution of styrene epoxidation by 2 revealed the formation of styrene oxide (~60%) with a small amount of benzoaldehyde formation (~20%), and the styrene oxide contained ¹⁸O when ¹⁸O-labeled 2 was used as an oxidant under inert atmosphere [5a]. The latter result indicates that the source of oxygen in the epoxide product was the iron(IV)-oxo species, not molecular oxygen.

In conclusion, we have synthesized a new iron(II) complex bearing an N3S2 thioether ligand, with the previous reports stating that the thioether sulfur ligatation in metal complexes (M = Cu and Ni) plays an important role in tuning dioxygen activation and effecting C–H bond hydroxylation reactions [11]. We have also shown the generation of a mononuclear nonheme iron(IV)-oxo intermediate in the reaction of the iron(II) complex with various terminal oxidants. The iron(IV)-oxo shows the capability of epoxidizing olefins, and we have demonstrated that the olefin epoxidation occurs via an electrophilic oxidation mechanism.

3. Experimental

3.1. Materials and instrumentation

All chemicals obtained from Aldrich Chemical Co. were of the best available purity and were used without further purification unless otherwise indicated. H₂¹⁸O₂ (90% ¹⁸O-enriched, 2% H₂¹⁶O₂ in water) was purchased from ICON Services Inc. (Summit, NJ, USA). m-Chloroperbenzoic acid (m-CpBA) purchased from Aldrich.
was purified by washing with phosphate buffer (pH 7.4) followed by water and then dried under reduced pressure. Peracetic acid (CH₃CO₃H, 32 wt.% solution containing < 6% H₂O₂) and H₂O₂ (30 wt.% solution in water) were obtained from Aldrich Chemical Co. The ligand N₃S₂ was prepared according to the reported procedures [7]. Iron(II) complex, Fe(N₃S₂)(ClO₄)₂ (1), was synthesized by stirring equimolar amounts of Fe(ClO₄)₂ and N₃S₂ in CH₃CN under inert atmosphere at room temperature. Crystals were obtained by vapor diffusion of diethyl ether into the reaction solutions (ca. 70–80% yield). Elemental Anal. Calc. for 1, C₂₁H₁₉Cl₂FeN₃O₈S₂: C, 39.9; H, 3.0; N, 6.7. Found: C, 38.8; H, 3.2; N, 6.5%.

**Caution!** Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great care.

UV–Vis spectra were recorded on a Hewlett–Packard 8453 spectrophotometer equipped with a circulating water bath. Electrospray ionization mass spectra (ESI MS) were collected on a Thermo Finnigan (San Jose, CA, USA) LCQ™ Advantage MAX quadrupole ion trap instrument, by infusing samples directly into the source at 20 µL/min using a syringe pump. The spray voltage was set at 4 kV and the capillary temperature at 70 °C. Elemental Analysis was done on a Thermo Finnigan Italia SpA (Flash EA™ 1112) CHN analyzer. 2,5-Bis(5-tert-butyl-2-benzoxazol-2-yli)thiophene (BBOT) was used as a reference standard. EPR spectra were obtained on a JEOL JES-FA200 spectrometer. ¹H NMR spectra were measured with Bruker DPX-400 spectrometer. Crystallographic analysis was conducted with an SMART APEX CCD equipped with a Mo X-ray tube at the X-ray Crystallographic Laboratory of Ewha Womans University. Product analysis for the epoxidation of styrene was performed on DIONEX Pump Series P580 equipped with a variable wavelength UV-200 detector (HPLC). Products were separated on Waters Symmetry C18 reverse phase column (4.6 × 250 mm), and detection was made at 215 and 254 nm.

### 3.2. Crystallographic studies

Crystals suitable for crystallographic analysis were obtained from the layer diffusion of CH₃CN/ether in a glove box. Pertinent crystallographic data and selected bond distances and angles are summarized in Tables S1 and S2 in Supplementary material. The structures were solved by using SHELX-86 and SHELX-97 programs [12]. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in ideal positions with isotropic displacement parameters. Complete crystallographic data of 1 are provided in CIF format (Supplementary material).

#### 3.3. Generation and reactivity of an iron(IV)-oxo intermediate

All reactions were followed by monitoring spectral changes of reaction solutions with a UV–Vis spectrophotometer. A nonheme iron(IV)-oxo complex, [Fe(IV)(O)(N₃S₂)]²⁺ (2), was prepared by reacting 1 with oxidants, such as 1.2 equiv. of m-CPBA, 1.2 equiv. of CH₃CO₃H, or 2 equiv. of H₂O₂, in CH₃CN at 25 °C. Complex 2 was then used in the epoxidation of styrenes under stoichiometric conditions in CH₃CN at the given temperatures. The disappearance of 2 was followed by UV–Vis spectral changes of the reaction solution. Product analysis of the resulting solution was performed by HPLC, and product yields were determined by comparison against standard curves prepared with a known authentic sample.

### Acknowledgements

This research was supported by KOSEF/MOST through Creative Research Initiative Program (to W.N.) and the Korea Research Foundation (KRF-2005-217-C00006 to M.S.S).
Appendix A. Supplementary material

Supplementary data (Tables S1 and S2, Figs. S1 and S2, crystallographic data of 1 in CIF format.) associated with this article can be found, in the online version, at doi:10.1016/j.ica.2008.04.018.

References


