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Note

Oxidation of hydroquinones by a nonheme iron(IV)-oxo species

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Received 22 August 2007; received in revised form 18 December 2007; accepted 22 December 2007

Available online 3 January 2008

Abstract

The reactivity of an isolated, well-characterized nonheme iron(IV)-oxo complex, [(TMC)Fe^{IV}=O]²⁺ (TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane), has been examined in the oxidation of hydroquinones. This complex has been shown to oxidize a series of hydroquinones, resulting in the production of the corresponding quinone products. Kinetic studies performed with substituted hydroquinones revealed a good correlation between reaction rates of the iron(IV)-oxo complex and the electron-donating ability of the substituents and the bond dissociation energy (BDE) of substrate O–H bonds. These results with a kinetic isotope effect (KIE) of 2.7 led us to propose a hydrogen-atom abstraction mechanism for the oxidation of hydroquinones by the nonheme iron(IV)-oxo species. © 2008 Elsevier B.V. All rights reserved.

Keywords: Nonheme iron enzymes; High-valent iron-oxo species; Oxidation; Hydroquinone; Hydrogen-atom abstraction

1. Introduction

Mononuclear nonheme iron(IV)-oxo species are implicated as key intermediates in oxidation reactions by non-heme iron enzymes, such as 2-oxoglutarate-dependent enzymes, isopenicillin N synthase, pterin-dependent aromatic amino acid hydroxylases, and halogenases [1–6]. Such enzymes are involved in various oxidation reactions, not only for the functionalization of unactivated C–H bonds but also for other oxidative processes such as cyclization, ring expansion, desaturation, *N*-dealkylation, and halogenation reactions. Recently, much work has been done to understand the chemical properties of nonheme

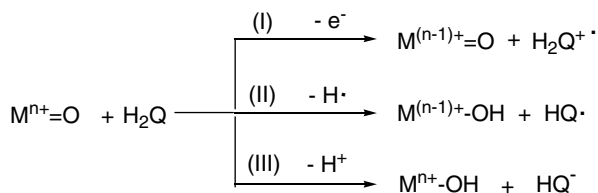
iron(IV)-oxo species in the oxygenation reactions. Indeed, a number of synthetic nonheme iron(IV)-oxo species bearing nitrogen-rich ligand environments were isolated and studied in the oxygenation reactions of various substrates, such as triphenylphosphine, thioanisole, olefins, alkanes, alcohols, *N,N*-dimethylanilines, and alkylaromatic compounds [7–17].

The oxidation of hydroquinones (H₂Q) by transition metal complexes, such as VO²⁺ [18], [Mn(EDTA)][−] [19], [Fe(porphyrin)]⁺ [20], [Ni(cyclam)]³⁺ [21], [Ni(oxime)]²⁺ [22], Cu²⁺ [23], [Cu(dmp)₂]²⁺ [24], [Ru(CN)₆]^{3−} [25], [(bpy)(py)Ru^{IV}=O]²⁺ [26], [(TMC)Ru^{VI}(O)₂]²⁺ [27], and [Rh₂(O₂CCH₃)₄(OH₂)₂]⁺ [28], has been extensively studied as an overall two-electron process. Among the initial steps proposed for the oxidation of H₂Q by metal-oxo species (Mⁿ⁺=O), the oxidation of H₂Q was reported to involve simple outer-sphere electron transfer from H₂Q to metal species (Scheme 1, pathway I). However, in the oxidation of H₂Q by [(bpy)(py)Ru^{IV}=O]²⁺, Meyer and coworkers proposed a proton-coupled electron transfer mechanism based on detailed mechanistic studies including a pH dependence of oxidation reactions and large H₂O/D₂O

Abbreviations: TMC, 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane; EDTA, ethylenediaminetetraacetic acid; cyclam, 1,4,8,11-tetraazacyclotetradecane; oxime, 3,14-dimethyl-4,7,10,13-tetra-azahexadeca-3,13-diene-2,15-dione dioxime; dmp, bis(2,9-dimethyl-1,10-phenanthroline); bpy, bipyridine; py, pyridine; Cz, 2,3,7,8,12,13,17,18-octakis-(4-*tert*-butylphenyl) corrolazine; N4Py, *N,N*-bis(2-pyridylmethyl)-bis(2-pyridyl)-methylamine; BDE, bond dissociation energy.

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Scheme 1.

kinetic isotope effects (i.e., electron transfer followed by the next rapid proton transfer; Scheme 1, pathway I) [26]. In the study with *trans*-dioxoruthenium(VI) complex, $[(TMC)Ru^{VI}(O)_2]^{2+}$, a hydrogen-atom abstraction mechanism was suggested from a large solvent kinetic isotope effect and a good correlation between reaction rates and bond dissociation energy (BDE) of H_2Q (Scheme 1, pathway II). The proton transfer pathway (Scheme 1, pathway III) was ruled out because stringent energetic demands on metal-oxo complexes at a transition state were required based on the calculation from thermodynamic data [26,27]. In the continuation of our reactivity studies with nonheme iron(IV)-oxo species, we have investigated the oxidation of H_2Q by a nonheme iron(IV)-oxo species, $[(TMC)Fe^{IV}=O]^{2+}$. In this work, we demonstrate that quinones (Q) were produced as products and the oxidation of H_2Q by the iron(IV)-oxo species occurs via a hydrogen-atom abstraction mechanism.

2. Materials and methods

2.1. Materials and instrumentation

All chemicals obtained from Aldrich Chemical Co. were of the best available purity and used without further purification unless otherwise indicated. Solvents were dried according to published procedures and distilled under Ar prior to use [29]. $Fe(TMC)(OTf)_2 \cdot 2CH_3CN$ was prepared in a glove box according to literature methods [11,30].

UV–Vis spectra were recorded on a Hewlett Packard 8453 spectrophotometer equipped with *Optostat*^{DN} variable-temperature liquid-nitrogen cryostat (Oxford Instruments). Product analysis for the oxidation of hydroquinone (H_2Q) was performed either on Agilent Technologies 6890N gas chromatograph (GC) or Thermo Finnigan Focus DSQ mass spectrometer interfaced with Focus gas chromatography (GC–MS).

2.2. Reactions of the oxoiron(IV) complex with H_2Q

In general, reactions were run at least in triplicate, and the data represent average of these reactions. All reactions were followed by monitoring spectral changes of reaction solutions with an UV–Vis spectrophotometer. The nonheme oxoiron(IV) complex ($\lambda_{max} = 820$ nm, $400 M^{-1} cm^{-1}$) was prepared by adding 1.2 equiv. of PhIO (2.4 mM, diluted in 50 μL of CH_3OH) into an 1-cm UV cuvette con-

taining 2 mM $Fe(TMC)(OTf)_2$ in CH_3CN (2 mL) [30]. Then, appropriate amounts of H_2Q were added into the UV cuvette, and spectral changes in the oxoiron(IV) complex reaction solution were directly monitored by an UV–Vis spectrophotometer. Rate constants, k_{obs} , were determined by pseudo-first-order fitting of the decrease of absorption bands at 820 nm.

2.3. Product analysis for the oxidation of H_2Q

A reaction solution containing $[(TMC)Fe^{IV}=O]^{2+}$ (2 mM) was prepared as described above. Then, 20 equiv. of hydroquinone (H_2Q) (40 mM) was added to the reaction solution under air. Product analysis was performed by injecting reaction solutions directly into GC and/or GC–MS. Product yields were determined by comparison with standard curves of known authentic samples.

In kinetic isotope effect study, H_2Q (40 mM) equilibrated with H_2O or D_2O (100 equiv., 0.2 M) in CH_3CN was allowed to react with solutions containing the oxoiron(IV) intermediate (2 mM).

3. Results and discussion

The reaction of hydroquinone (H_2Q) with $[(TMC)Fe^{IV}=O]^{2+}$ was monitored at $-30^\circ C$ by UV–Vis spectroscopy and revealed a smooth conversion of the iron(IV)-oxo species to the Fe(II) complex (Fig. 1). The kinetics were followed by the disappearance of $[(TMC)Fe^{IV}=O]^{2+}$ under pseudo-first-order conditions with excess H_2Q . The first-order rate constants, k_{obs} , were shown to vary linearly with the increase of H_2Q concentration, yielding the second-order rate constant to be $0.51 \pm 0.02 M^{-1} s^{-1}$ (Fig. 2). The oxidation of H_2Q resulted in the formation of over 90% quinone (Q) as determined by GC. The yield was calculated based on $[(TMC)Fe^{IV}=O]^{2+}$ acting as

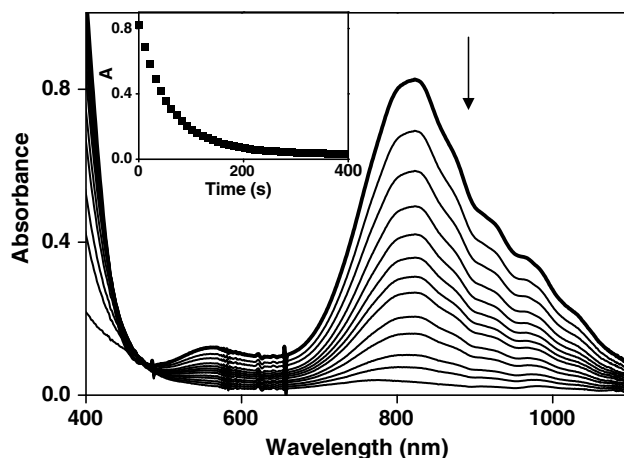


Fig. 1. Reactions of $[(TMC)Fe^{IV}=O]^{2+}$ (2 mM) with hydroquinone in CH_3CN at $-30^\circ C$. (a) Time-resolved UV–Vis spectral changes upon the addition of 20 equiv. hydroquinone. Inset shows absorbance traces monitored at 820 nm.

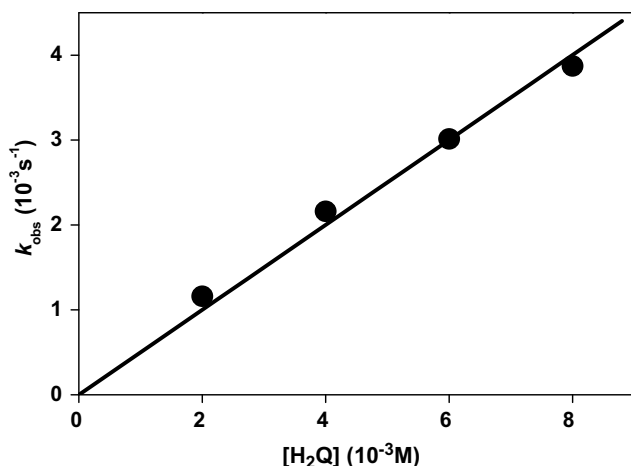
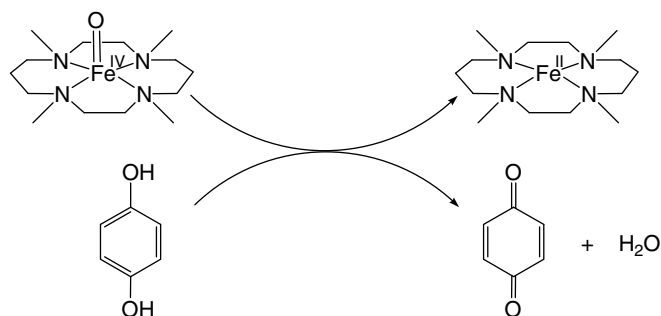


Fig. 2. Second-order rate constant determined in the reaction of $[(\text{TMC})\text{Fe}^{\text{IV}}=\text{O}]^{2+}$ (2 mM) in CH_3CN at -30°C with hydroquinone.

a two-electron oxidant, and no other organic products were detected (Scheme 2). The product yield was independent on the presence of O_2 , indicating that O_2 does not oxidize H_2Q or semiquinone radical under the reaction conditions [31].

From the studies of temperature effect on the oxidation of H_2Q by $[(\text{TMC})\text{Fe}^{\text{IV}}=\text{O}]^{2+}$ in the range of 233–263 K, activation parameters were obtained by plotting $\ln(k_{\text{obs}}/T)$ against $1/T$ according to the Eyring equation (Fig. 3). The



Scheme 2.

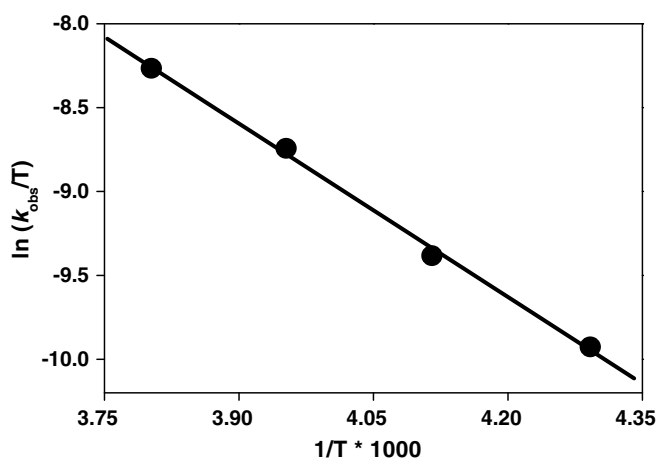


Fig. 3. Eyring plot for the reduction of $[(\text{TMC})\text{Fe}^{\text{IV}}=\text{O}]^{2+}$ (2 mM) by 20 equiv. hydroquinone (233–263 K) in CH_3CN .

parameters thus obtained were $\Delta H^\ddagger = 6.9 \pm 0.2$ kJ/mol and $\Delta S^\ddagger = -38 \pm 1$ J/mol K. The activation enthalpy 6.9 kJ/mol is relatively higher than those obtained in the oxidation of H_2Q by $\text{trans}[(\text{TMC})\text{Ru}^{\text{VI}}(\text{O})_2]^{2+}$ (2.9 kJ/mol) [27] and in the oxidation of phenols with $[(\text{Cz})\text{Mn}^{\text{V}}(\text{O})]$ (1.5 kJ/mol) [32], but lower than that in the oxidation of phenols by $\text{trans}[(\text{TMC})\text{Ru}^{\text{VI}}(\text{O})_2]^{2+}$ (10 kJ/mol) [33].

To understand the mechanism of H_2Q oxidation by $[(\text{TMC})\text{Fe}^{\text{IV}}=\text{O}]^{2+}$, kinetic studies were performed with a series of substituted hydroquinone substrates ($\text{H}_2\text{Q}-\text{X}$; $\text{X} = \text{H}, \text{tBu}, \text{Me}, \text{Cl}, \text{Br}$). A decrease in the relative rates was observed with an increase in the electron-withdrawing nature of the substituents. The plot of $\log(k_{\text{X}}/k_{\text{H}})$ against σ_{meta} is reasonably linear for the reactions, providing the slope $\rho = -1.6 \pm 0.1$ (Supporting Information, Table S1 and Fig. S1). Such a negative correlation can be expected with the formation of an electron-deficient quinone radical in the first step of the reaction and gives a hint to propose a H-atom abstraction as the rate-determining step (*vide infra*). As an evidence for the hydrogen abstraction mechanism in the oxidation of para-substituted phenols by $[(\text{TMC})\text{Ru}^{\text{VI}}(\text{O})_2]^{2+}$, $[(\text{Cz})\text{Mn}^{\text{V}}(\text{O})]$, and $[(\text{TMC})\text{Fe}^{\text{IV}}=\text{O}(\text{X})]^{2+}$ ($\text{X} = \text{N}_3, \text{CF}_3\text{COO}, \text{and CH}_3\text{CN}$), such negative Hammett constants were provided with the ρ values in a range -1.5 to -3.2 [12,32,34].

We then studied the correlations between rate constants and O–H BDE, providing supporting evidence for H-atom

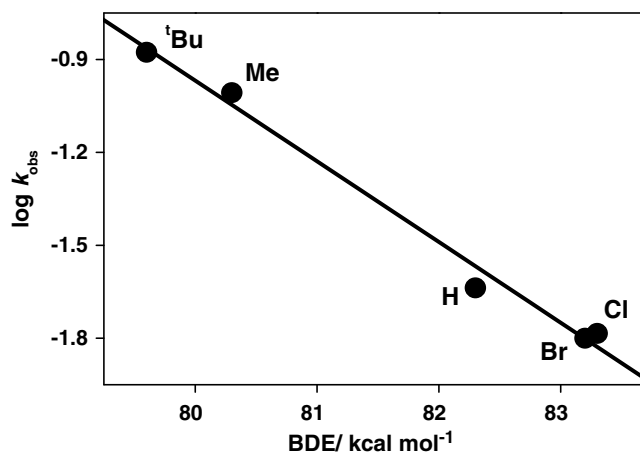


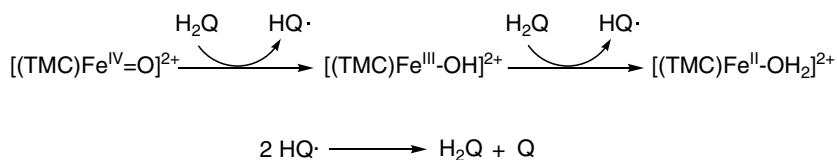
Fig. 4. Plot of rate constants versus O–H BDE for the oxidation of substituted hydroquinones ($\text{H}_2\text{Q}-\text{X}$) by $[(\text{TMC})\text{Fe}^{\text{IV}}=\text{O}]^{2+}$ in CH_3CN at -30°C .

Table 1

Reaction rates determined in the reactions of $[(\text{TMC})\text{Fe}^{\text{IV}}=\text{O}]^{2+}$ (2 mM) with various substituted hydroquinones in CH_3CN at -30°C

X	k_{obs} (s^{-1})	BDE (kcal mol^{-1})	Refs. ^a
tBu	$1.3(1) \times 10^{-1}$	76.9	[27]
Me	$1.1(1) \times 10^{-1}$	80.3	[27]
H	$2.1(2) \times 10^{-2}$	82.3	[27]
Cl	$1.6(3) \times 10^{-2}$	83.3	[27]
Br	$1.5(2) \times 10^{-2}$	83.2	[41]

^a References are for literature BDE of substrates.



Scheme 3.

abstraction over other possible mechanisms including a concerted hydrogen abstraction. The plot of $\log(k_{\text{obs}})$ against the O–H BDE of $\text{H}_2\text{Q-X}$ in the oxidation by $[(\text{TMC})\text{Fe}^{\text{IV}}\text{=O}]^{2+}$ showed a linear correlation in which the relative rates decrease with increasing O–H bond strength (Fig. 4). The slope -0.26 obtained with $[(\text{TMC})\text{Fe}^{\text{IV}}\text{=O}]^{2+}$ is comparable to that reported in the oxidation of $\text{H}_2\text{Q-X}$ with *trans*- $[(\text{TMC})\text{Ru}^{\text{VI}}(\text{O})_2]^{2+}$ (-0.27) [27] and those obtained in the oxidation of phenols by $[(\text{Cz})\text{Mn}^{\text{V}}(\text{O})]$ (-0.39) and $[(\text{TMC})\text{Fe}^{\text{IV}}\text{=O}(\text{X})]^{n+}$ (-0.36 to -0.55 depending on X) [32], in which their reaction mechanisms were proposed to be a hydrogen-atom abstraction mechanism from the –OH group of $\text{H}_2\text{Q-X}$. Further evidence for supporting the H-atom abstraction mechanism was obtained from the measurement of KIE. Substitution of deuteriums for the hydrogens in H_2Q led to a significant decrease in rate constant (D_2Q , $1.0(1) \times 10^{-2} \text{ s}^{-1}$; H_2Q , $2.7(1) \times 10^{-2} \text{ s}^{-1}$, Fig. S2). The resulting KIE of 2.7 provides a strong evidence that the rate-determining step involves O–H bond cleavage by a hydrogen-atom abstraction (see Table 1).

Considering the mechanism for the oxidation of H_2Q by $[(\text{TMC})\text{Fe}^{\text{IV}}\text{=O}]^{2+}$, an initial electron transfer pathway is not plausible due to a low redox potential ($\sim 0.51 \text{ V}$ vs NHE) for $[(\text{TMC})\text{Fe}^{\text{IV}}\text{=O}]^{2+}$ relative to oxidation potentials for H_2Q (1.1 V vs. NHE, pH 7.7, water) [35,36]. $[(\text{TMC})\text{Fe}^{\text{IV}}\text{=O}]^{2+}$ was reported as a much weaker oxidant than $[(\text{N4Py})\text{Fe}^{\text{IV}}\text{=O}]^{2+}$ ($E_{1/2} = 0.9 \text{ V}$ obtained from spectropotentiometric experiments) [37], based on the comparative study in hydrocarbon oxidations and in electron transfer rates from *N,N*-dimethylanilines [11,12]. Also, an initial proton transfer pathway can be eliminated for the mechanism as $[(\text{TMC})\text{Fe}^{\text{IV}}\text{=O}]^{2+}$ is unlikely basic enough to deprotonate the H_2Q substrates. Indeed, $[(\text{TMC})\text{Fe}^{\text{IV}}\text{=O}]^{2+}$ was stable upon the treatment of 1–3 equiv. HClO_4 dissolved in CH_3CN , based on the measurement of the absorption band of $[(\text{TMC})\text{Fe}^{\text{IV}}\text{=O}]^{2+}$ (see Supporting Information, Fig. S3). Additionally, if the proton transfer was the mechanism, an opposite correlation of $\log(k_{\text{X}}/k_{\text{H}})$ against σ would be expected, since the pK_{a} of $\text{H}_2\text{Q-X}$ is estimated to decrease with σ , causing an increase in k_{obs} [32].

Therefore, we propose that the initial hydrogen abstraction from H_2Q affords semiquinone radical ($\text{HQ}\cdot$) which can subsequently undergo disproportionation to H_2Q and Q at a very rapid rate ($k_{\text{disp}} = 1.1 \times 10^{-9} \text{ M}^{-1} \text{ s}^{-1}$) [38]. Considering the almost quantitative formation of Q based on the iron(IV)-oxo species ($>90\%$) and O_2 -independent oxidation results, we propose that the $\text{Fe}(\text{III})\text{-OH}$ species

generated from the first hydrogen abstraction abstract a hydrogen atom from H_2Q to afford $\text{HQ}\cdot$ (Scheme 3). Further work to elucidate the exact mechanism is under way in our laboratory. Recently, such $\text{Fe}(\text{III})\text{-OR}$ and $\text{Mn}(\text{III})\text{-OH}$ species were reported to achieve H-atom abstraction from hydrocarbons [39,40].

In summary, kinetic studies on the oxidation of H_2Q by an isolated mononuclear nonheme $\text{Fe}^{\text{IV}}\text{-oxo}$ species, $[(\text{TMC})\text{Fe}^{\text{IV}}\text{=O}]^{2+}$, have been reported, and based on the results presented here, the most reasonable mechanism for the initial reaction step in the H_2Q oxidation is a H-atom abstraction from H_2Q by the $\text{Fe}^{\text{IV}}\text{-oxo}$ species.

Acknowledgements

This work was supported by the SRC/ERC program of MOST/KOSEF (R11-2005-008-000-0 to J.K.), Seoul R&BD program (to J.K.), STAR program (2005–2007 to J.K. and F.D.), and the Ministry of Science and Technology of Korea through Creative Research Initiative Program (to W.N.).

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2007.12.027.

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