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

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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.

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1. Introduction

Mononuclear nonheme iron(IV)-oxo species are implicated as key intermediates in oxidation reactions by nonheme iron enzymes, such as 2-oxoglutarate-dependent enzymes, isoprenicillin 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(phenylpyrrole)]+ [20], [Ni(cyclam)]2+ [21], [Ni(oxime)]2+ [22], Cu2+ [23], [Cu(dpmp)]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...
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)RuVI(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 H2Q (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 H2Q by a nonheme iron(IV)-oxo species, [(TMC)FeIV@O]2+. In this work, we demonstrate that quinones (Q) were produced as products and the oxidation of H2Q 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 · CH3CN 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 OptostatDN variable-temperature liquid-nitrogen cryostat (Oxford Instruments). Product analysis for the oxidation of hydroquinone (H2Q) 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 o xoiron(IV) complex with H2Q

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 o xoiron(IV) complex (λmax = 820 nm, 400 M–1 cm–1) was prepared by adding 1.2 equiv. of PhIO (2.4 mM, diluted in 50 μL of CH3OH) into an 1-cm UV cuvette containing 2 mM Fe(TMC)(OTf)2 in CH3CN (2 mL) [30]. Then, appropriate amounts of H2Q were added into the UV cuvette, and spectral changes in the o xoiron(IV) complex reaction solution were directly monitored by an UV–Vis spectrophotometer. Rate constants, kobs, were determined by pseudo-first-order fitting of the decrease of absorption bands at 820 nm.

2.3. Product analysis for the oxidation of H2Q

A reaction solution containing [(TMC)FeIV=O]2+ (2 mM) was prepared as described above. Then, 20 equiv. of hydroquinone (H2Q) (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, H2Q (40 mM) equilibrated with H2O or D2O (100 equiv., 0.2 M) in CH3CN was allowed to react with solutions containing the o xoiron(IV) intermediate (2 mM).

3. Results and discussion

The reaction of hydroquinone (H2Q) with [(TMC)FeIV=O]2+ was monitored at –30 °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)FeIV=O]2+ under pseudo-first-order conditions with excess H2Q. The first-order rate constants, kobs, were shown to vary linearly with the increase of H2Q concentration, yielding the second-order rate constant to be 0.51 ± 0.02 M–1 s–1 (Fig. 2). The oxidation of H2Q resulted in the formation of over 90% quinone (Q) as determined by GC. The yield was calculated based on [(TMC)FeIV=O]2+ acting as Mn+=O

Mn+-OH

M(n-1)+-OH

M(n-1)+=O

H2Q

HQ-

HQ+

- H

-e-

- H+

+.+

H2Q+.+

Scheme 1.

Fig. 1. Reactions of [(TMC)FeIV=O]2+ (2 mM) with hydroquinone in CH3CN at –30 °C. (a) Time-resolved UV–Vis spectral changes upon the addition of 20 equiv. hydroquinone. Inset shows absorbance traces monitored at 820 nm.
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$_2$Q or semiquinone radical under the reaction conditions [31].

From the studies of temperature effect on the oxidation of H$_2$Q by [(TMC)Fe IV@O]$^{2+}$ in the range of 233–263 K, activation parameters were obtained by plotting ln($k_{obs}$/T) against 1/T according to the Eyring equation (Fig. 3). The parameters thus obtained were $\Delta H^f = 6.9 \pm 0.2$ kJ/mol and $\Delta S^f = -38 \pm 1$ J/mol K. The activation enthalpy 6.9 kJ/mol is relatively higher than those obtained in the oxidation of H$_2$Q by trans-[(TMC)Ru VI(O)$_2$$]^{2+}$ (2.9 kJ/mol) [27] and in the oxidation of phenols with [(Cz)Mn V(O)] (1.5 kJ/mol) [32], but lower than that in the oxidation of phenols by trans-[(TMC)Ru VI(O)$_2$$]^{2+}$ (10 kJ/mol) [33].

To understand the mechanism of H$_2$Q oxidation by [(TMC)Fe IV@O]$^{2+}$, kinetic studies were performed with a series of substituted hydroquinone substrates (H$_2$Q–X; X = H, tBu, Me, Cl, Br). A decrease in the relative rates was observed with an increase in the electron-withdrawing nature of the substituents. The plot of log($k_X/k_H$) against $r_{meta}$ is reasonably linear for the reactions, providing the slope $\sigma_{meta}$ is reasonably linear for the reactions, providing the slope $q = 1.6 \pm 0.1$ (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 [(TMC)Ru VI(O)$_2$$]^{2+}$, [(Cz)Mn V(O)], and [(TMC)Fe IV@O(X)]$^{2+}$ (X=N$_3$, CF$_3$COO, and CH$_3$CN), such negative Hammett constants were provided with the $q$ 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
abstraction over other possible mechanisms including a concerted hydrogen abstraction. The plot of log(\(k_{\text{obs}}\)) against the O–H BDE of H₂Q–X in the oxidation by \([(\text{Fe}^\text{IV}=\text{O})^2]\) showed a linear correlation in which the relative rate decreases with increasing O–H bond strength (Fig. 4). The slope −0.26 obtained with \([(\text{Fe}^\text{IV}=\text{O})^2]\) is comparable to that reported in the oxidation of H₂Q–X with trans-[(\text{Ru}^\text{VI}(\text{O})_2)^2]\ (−0.27) \[27\] and those obtained in the oxidation of phenols by [(Cz)Mn V(O)] (−0.39) and \([(\text{Fe}^\text{IV}=\text{O}(\text{X}))^2]\) (−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 H₂Q–X. Further evidence for supporting the H-atom abstraction mechanism was obtained from the measurement of KIE. Substitution of deuteriums for the hydrogens in H₂Q led to a significant decrease in rate constant (Δ\(k_{\text{obs}}\), 1.1 V vs. NHE, pH 7.7, water) \[35,36\].

KIEs for H₂Q (1.1 V vs. NHE, pH 7.7, water) \[35,36\]. Substitution of deuteriums for the hydrogens in H₂Q afforded semiquinone radical (HQ) \[32\].

In summary, kinetic studies on the oxidation of H₂Q by an isolated mononuclear nonheme Fe IV-oxo species, \([(\text{Fe}^\text{IV}=\text{O})^2]\), have been reported, and based on the results presented here, the most reasonable mechanism for the initial reaction step in the H₂Q oxidation is a H-atom abstraction from H₂Q by the Fe IV-oxo species.

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Appendix A. Supplementary material


References
