Fundamental Electron-Transfer Properties of Non-heme Oxoiron(IV) Complexes

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Non-heme oxoiron(IV) intermediates have merited attention ever since they were identified as active oxidizing species in the catalytic cycles of *Escherichia coli* taurine: α-ketogultarate dioxygenase (TauD), prolyl-4-hydroxylase, and halogenase CytC3.[1−4] The successful isolation and structural characterization of a mononuclear non-heme oxoiron(IV) complex bearing a macrocyclic ligand[5] have stimulated extensive studies on the reactivities of mononuclear non-heme oxoiron(IV) complexes bearing tetradentate N4 and pentadentate N5 and N4S ligands in the oxidation of various substrates, such as PPh₃, thioanisoles, *N,N*-dialkylanilines, aromatic compounds, olefins, alcohols, and alkanes.[6,7] However, fundamental electron-transfer (ET) properties of non-heme oxoiron(IV) complexes, which would provide valuable mechanistic insight into the catalytic activities, have yet to be reported.[8,9]

We report herein the kinetic data for the ET reduction of non-heme oxoiron(IV) complexes by a series of electron donors. The driving force dependence of the ET rate is analyzed in light of the Marcus theory of electron transfer,[10] leading to the evaluation of the fundamental ET properties for the first time, that is, the reorganization energies and the one-electron reduction potentials of non-heme oxoiron(IV) complexes.

The investigated non-heme oxoiron(IV) complexes are presented as $[(L)Fe^{IV}(O)]^{2+}$, where L = TMC, (1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane); Bn-TPEN, (*N*-benzyl-*N*,*N*′,*N*′-tris(2-pyridylmethyl)ethane-1,2-diamine); N4Py, (*N*,*N*-bis(2-pyridylmethyl)-*N*-bis(2-pyridyl)methylamine) (Chart 1).[8a] A series of

Chart 1

$[(TMC)Fe^{IV}(O)(NCCH_3)]^{2+}$ $[(Bn\text{-}TPEN)Fe^{IV}(O)]^{2+}$ $[(N4Py)Fe^{IV}(O)]^{2+}$
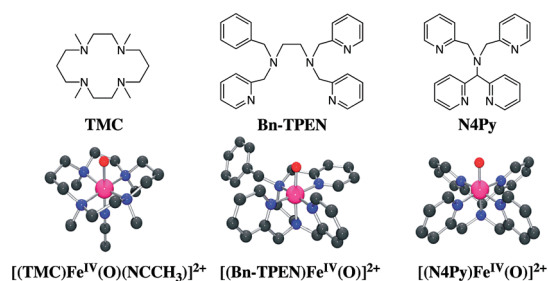
ferrocene derivatives were selected as one-electron reductants for use in acetonitrile (MeCN).[11,12] Although the reduction peak potential, $E_{p,c}$, of $[(TMC)Fe^{IV}(O)]^{2+}$ was reported to be 0.1 V (vs SCE) in MeCN,[8a] $[(TMC)Fe^{IV}(O)]^{2+}$ is readily reduced by ferrocene (Fc). The visible spectral changes in electron transfer from ferrocene to $[(TMC)Fe^{IV}(O)]^{2+}$ are shown in Figure 1a, where the absorption band at 820 nm due to $[(TMC)Fe^{IV}(O)]^{2+}$ decreases, accompanied by an increase in the absorption band at 615 nm due to the ferricenium ion (Fc⁺). The stoichiometry of the electron transfer was confirmed to be 1:1 by spectral redox titration. The spin state
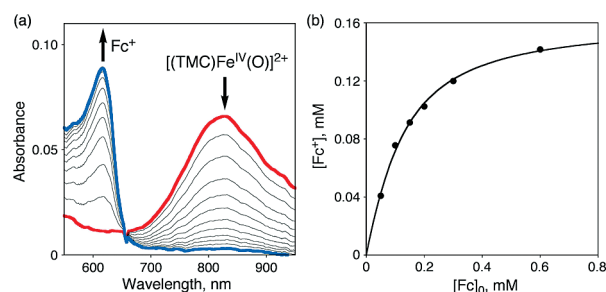
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Figure 1. (a) Spectral changes observed in electron transfer from ferrocene (Fc: 6.0×10^{-4} M) to $[(TMC)Fe^{IV}(O)]^{2+}$ (1.7×10^{-4} M) in deaerated MeCN at 298 K. (b) Plot of concentration of ferricenium ion [Fc⁺] produced in electron transfer from Fc to $[(TMC)Fe^{IV}(O)]^{2+}$ (1.7×10^{-4} M) in deaerated MeCN at 298 K vs initial concentration of Fc, [Fc]₀.

of the resulting Fe(III) complex was determined to be $S = \frac{3}{2}$ on the basis of the data obtained with the ESR spectrometer and the Evans NMR method (Supporting Information (SI), Figures S1 and S2).[13,14]

The ET reduction of $[(TMC)Fe^{IV}(O)]^{2+}$ is found to be in equilibrium (eq 1), where the final concentration of Fc⁺ produced in the ET reduction of $[(TMC)Fe^{IV}(O)]^{2+}$ increases with the increase in initial Fc concentration. The equilibrium constant (K_{et}) in eq 1 is determined to be 2.0 at 298 K by fitting the plot in Figure 1b (SI, Figure S3).

$$Fc + [(TMC)Fe^{IV}(O)]^{2+} \overset{K_{et}}{\rightleftharpoons} Fc^+ + [(TMC)Fe^{III}(O)]^+ \quad (1)$$
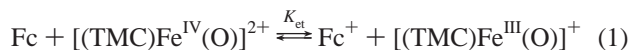
The apparent one-electron reduction potential, E_{red}, of $[(TMC)Fe^{IV}(O)]^{2+}$ is then determined with the K_{et} value and the E_{ox} value of Fc (0.37 V vs SCE) (eq 2).[12] The value of 0.39 V (vs SCE) agrees well with the half-wave potential between the anodic and cathodic peak potentials of cyclic voltammogram (CV) of $[(TMC)Fe^{IV}(O)]^{2+}$ ($E_{1/2} = 0.39$ V vs SCE), although the peak separation is as large as 0.69 V at the scan rate of 0.10 V s⁻¹ (SI, Figure S4). Such a large peak separation suggests extremely slow electron transfer. This is indeed confirmed by the kinetic analysis of the ET reduction of oxoiron(IV) complexes by ferrocene derivatives (vide infra).

$$E_{red} = E_{ox} + (RT/F) \ln K_{et} \quad (2)$$

ET rates were also determined from the decrease in the absorption band at 820 nm due to $[(TMC)Fe^{IV}(O)]^{2+}$ or the increase in the absorption band at 615 nm due to Fc⁺ (see Figure 1a). The ET rates obey pseudo-first-order kinetics in a large excess of reductants (SI, Figure S5). The pseudo-first-order rate constants (k_{obs}) increase linearly with increasing concentrations of reductants. The second-order ET rate constants (k_{et}) were determined from the slopes of linear plots of k_{obs} vs concentrations of ferrocene derivatives. The k_{et} values thus obtained are listed in the SI, Table S1, together with the E_{ox} values of ferrocene derivatives, the E_{red} values of oxoiron-
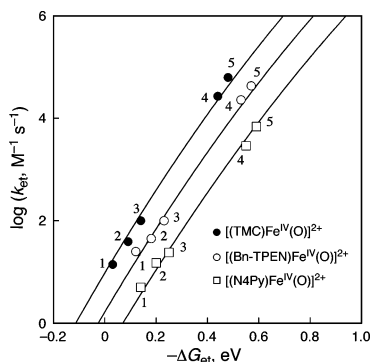
Figure 2. Driving force dependence of rate constants (log k_{et}) for ET from ferrocene derivatives (1, ferrocene; 2, *n*-amylferrocene; 3, dimethylferrocene; 4, octamethylferrocene; 5, decamethylferrocene) to oxoiron(IV) complexes in deaerated MeCN at 298 K.

Table 1. One-Electron Reduction Potentials (E_{red}) and Reorganization Energies (λ) of ET Reduction of Oxoiron(IV) Complexes

complex	E_{red}, V vs SCE	λ, eV
$[(TMC)Fe^{IV}(O)]^{2+}$	$0.39 \pm 0.01^{a,b}$	2.37 ± 0.04
$[(Bn\text{-}TPEN)Fe^{IV}(O)]^{2+}$	0.49 ± 0.02^{b}	2.55 ± 0.05
$[(N4Py)Fe^{IV}(O)]^{2+}$	0.51 ± 0.02^{b}	2.74 ± 0.06

a Determined from the spectral redox titration. *b* Determined from the half-wave potentials of CV (SI, Figure S4).

(IV) complexes, and the driving force of electron transfer $[-\Delta G_{et} = e(E_{red} - E_{ox})$ in eV].

The driving force dependence of the rate constants of the ET reduction of oxoiron(IV) complexes in MeCN at 298 K is shown in Figure 2, where the log k_{et} values are plotted against the $-\Delta G_{et}$ values. Each curve is well fitted by the solid line in Figure 2 in light of the Marcus theory of adiabatic outer-sphere electron transfer:

$$k_{et} = Z \exp[-(\lambda/4)(1 + \Delta G_{et}/\lambda)^2/k_B T] \qquad (3)$$

where Z is the collision frequency taken as 1×10^{11} M^{-1} s^{-1}, λ is the reorganization energy of electron transfer, k_B is the Boltzmann constant, and T is the absolute temperature.[10,15] The λ values thus obtained are listed in Table 1, together with the E_{red} values of oxoiron(IV) complexes.[16]

As shown in Table 1, the λ value of the ET reduction of $[(L)Fe^{IV}(O)]^{2+}$ becomes larger (L = TMC, 2.37 eV < Bn-TPEN, 2.55 eV < N4Py, 2.74 eV),[17] as the E_{red} value is more positively shifted (L = TMC, 0.39 V < Bn-TPEN, 0.49 V $\approx$ N4Py, 0.51 V vs SCE). This suggests that the higher E_{red} of $[(L)Fe^{IV}(O)]^{2+}$ is attained by compensation of the larger reorganization energy including the structural change required for the electron transfer. In addition, it is of interest to note that the λ value (2.37 eV) of the ET reduction of $[(TMC)Fe^{IV}(O)]^{2+}$ is comparable to the reported λ value (2.34 eV) of the ET oxidation of $[(OETPP)Fe^{III}(Ph)]$ (OETPP = 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraphenylporphyrin),[18] but significantly larger than the λ value (2.04 eV) of the ET reduction of $[(TPFPP)Fe^{IV}(O)]$ (TPFPP = *meso*-tetrakis-(pentafluorophenyl)porphyrin; E_{red} = 1.6 V vs SCE).[19] Judging from the comparison of the driving force dependence of log k_{et} of the ET reduction of $[(L)Fe^{IV}(O)]^{2+}$ with that of heme oxoiron(IV) complexes,[19,20] the λ values of the ET reduction of non-heme oxoiron(IV) complexes are generally larger and the E_{red} values are smaller than those of heme oxoiron(IV) complexes. The larger λ values may result from the flexible non-heme ligand that allows more significant bond reorganization upon the ET reduction as compared with the rigid heme ligand.[21]

In conclusion, we have determined for the first time the fundamental ET properties of non-heme oxoiron(IV) complexes, which are featured by the large reorganization energies of electron transfer and the low reduction potentials as compared with the heme oxoiron(IV) complexes. Detailed investigations aimed at understanding the correlation between the ET properties of the non-heme and heme oxoiron(IV) complexes and their reactivities in oxidation reactions are currently underway in our laboratory.

Supporting Information Available: Experimental details, ESR spectrum (Figure S1), NMR spectra (Figure S2), plot for determination of K_{et} (Figure S3), CV data (Figure S4), kinetic data (Figure S5), and rate constants (Table S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) The λ values of the electron self-exchange between $[(L)Fe^{IV}(O)]^{2+}$ and $[(L)Fe^{III}(O)]^{+}$ (L = TMC, Bn-TPEN, and N4Py) were evaluated using the λ values of electron self-exchange between Fc and Fc^{+} (1.0 eV)[11] as 3.7, 4.1, and 4.5 eV, respectively. Such large λ values result in the large peak separation (SI, Figure S4).
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(21) Since the one-electron reduction of Fe(IV) ($S = 1$) to Fe(III) ($S = {}^3/_2$) in oxoiron complexes is spin-allowed, the contribution of change in the spin state to the large λ values may not be important.

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