Mechanistic Borderline of One-Step Hydrogen Atom Transfer versus Stepwise Sc³⁺-Coupled Electron Transfer from Benzyl Alcohol Derivatives to a Non-Heme Iron(IV)-Oxo Complex

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ABSTRACT: The rate of oxidation of 2,5-dimethoxybenzyl alcohol (2,5-(MeO)₂C₆H₃CH₂OH) by [Fe IV(O)(N4Py)]²⁺ (N4Py = N,N-bis(2-pyridylmethyl)-N-bis(2-pyridyl)-methylamine) was enhanced significantly in the presence of Sc(OTf)³⁺ (OTf⁻ = trifluoromethanesulfonate) in acetonitrile (e.g., 120-fold acceleration in the presence of Sc³⁺). Such a remarkable enhancement of the reactivity of [Fe IV(O)(N4Py)]²⁺ in the presence of Sc³⁺ was accompanied by the disappearance of a kinetic deuterium isotope effect. The radical cation of 2,5-(MeO)₂C₆H₃CH₂OH was detected in the course of the reaction in the presence of Sc³⁺. The dimerized alcohol and aldehyde were also produced in addition to the monomer aldehyde in the presence of Sc³⁺. These results indicate that the reaction mechanism is changed from one-step hydrogen atom transfer (HAT) from 2,5-(MeO)₂C₆H₃CH₂OH to [Fe IV(O)(N4Py)]²⁺ in the absence of Sc³⁺ to stepwise Sc³⁺-coupled electron transfer, followed by proton transfer in the presence of Sc³⁺. In contrast, neither acceleration of the rate nor the disappearance of the kinetic deuterium isotope effect was observed in the oxidation of benzyl alcohol (C₆H₅CH₂OH) by [Fe IV(O)(N4Py)]²⁺ in the presence of Sc³⁺. Moreover, the rate constants determined in the oxidation of various benzyl alcohol derivatives by [Fe IV(O)(N4Py)]²⁺ in the presence of Sc(OTf)³⁺ (10 mM) were compared with those of Sc³⁺-coupled electron transfer from one-electron reductants to [Fe IV(O)(N4Py)]²⁺ at the same driving force of electron transfer. This comparison revealed that the borderline of the change in the mechanism from HAT to stepwise Sc³⁺-coupled electron transfer and proton transfer is dependent on the one-electron oxidation potential of benzyl alcohol derivatives (ca. 1.7 V vs SCE).

INTRODUCTION

Homolytic C–H bond cleavage of organic compounds is one of the fundamental reaction steps in various types of oxidation processes both in synthetic and biological chemistry. In the oxidative enzymes, heme and nonheme iron oxygenases represented by cytochrome P450 and taurine/α-ketoglutarate dioxygenase (Taud), respectively, high-valent iron-oxo species have been regarded as reactive intermediates in their catalytic cycles, where C–H bond is cleaved by oxometal species (M=O) and O–H bond is formed in the process of hydrogen atom transfer (HAT) from substrate to oxometal species. In the enzymatic oxidation reactions, for example, hydroxylation, oxidation of alcohols, desaturation, cyclization, and chlorination, the initial step of those processes is widely believed to be activation of C–H bonds via HAT from a substrate to high-valent iron-oxo species. In general, there are three possible reaction pathways in HAT reactions of iron-oxo species (FeIV=O), as shown in Scheme 1.

Scheme 1. Three Possible Reaction Pathways in HAT Reactions of Iron-Oxo Species

FeIV=O + H–CR₃ \[\overset{(1)\ PT}{\rightleftharpoons}\ FeIV−OH + CR₃\]

FeIV=O + CR₃ \[\overset{(2)\ ET}{\rightarrow}\ FeIV=O−CR₃\]

FeIV=O−CR₃ \[\overset{(3)\ One-Step\ HAT}{\rightarrow}\ FeIV−OH + CR₃\]

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HAT can be generally regarded as concerted proton–electron transfer (CPET), because an electron and a proton are transferred simultaneously to the metal center and the oxo moiety, respectively. Tremendous efforts have so far been devoted to elucidate the mechanism of HAT reactions of iron(IV) oxo species by employing model complexes bearing heme and nonheme ligands in the field of bioinorganic chemistry, where the transfer of an electron and a proton proceeds in a concerted manner. There are some cases where C–H bond activation by iron-oxo species undergoes via an ET/PT pathway when electron-rich substrates such as N,N-dimethylaniline derivatives are used as substrates. In the case of HAT reactions from substrates to triplet excited states of photosensitizers, the mechanistic borderline of one-step HAT vs ET/PT pathways has been clarified by changing the electron donor ability of hydrogen donors as well as the electron acceptor ability of hydrogen acceptors. The borderline of one-step hydride-transfer vs ET/PT pathways has also been discussed for Sc³⁺ promoted hydride transfer from an NADH analogue to a p-benzoquinone derivative. There are also studies on the mechanistic borderline of one-step HAT from a one-step ET/PT pathway by addition of Lewis acids such as Ca²⁺, Mg²⁺, and Zn²⁺, and so forth. However, the mechanistic borderline of one-step HAT vs ET/PT pathways in C–H bond cleavage by iron-oxo species has yet to be clarified because of the lack of systematic studies.

We report herein one example of the switch of the reaction pathway from a one-step HAT pathway in C–H bond activation of benzyl alcohol derivatives (X-C₆H₄CH₂OH) with a nonheme iron(IV)-oxo complex, [Fe⁴⁺(O)(N₄Py)]²⁺ (N₄Py = N,N-bis(2-pyridylmethyl)-N-bis(2-pyridyl)methyamine) to a stepwise ET/PT pathway by addition of Sc³⁺. We have recently reported that one-electron reduction of [Fe⁴⁺(O)(N₄Py)]²⁺ is accelerated by the addition of Lewis acids such as Ca²⁺, Mg²⁺, and Zn²⁺, and so forth. Electron-acceptability of [Fe⁴⁺(O)(N₄Py)]²⁺ is enhanced by the much stronger binding of Sc³⁺ to [Fe⁴⁺(O)(N₄Py)] than [Fe⁴⁺(O)(N₄Py)]. We have chosen Sc³⁺ in this work, because Sc³⁺ has the largest acceleration effect among examined metal ions. In the presence of 10 mM of Sc³⁺, the reduction potential of the iron(IV)-oxo complex (E_red) was shifted from 0.51 V vs SCE to the positive direction up to 1.19 V vs SCE. Such a change in the E_red value of [Fe⁴⁺(O)(N₄Py)]²⁺ by the presence of Sc³⁺ and well-determined reduction potential provides an excellent opportunity to scrutinize the borderline of one-step HAT vs ET followed by subsequent PT steps in C–H bond activation by metal-oxo species in a systematic manner.

**EXPERIMENTAL SECTION**

**Materials.** Benzyl alcohol (C₆H₄CH₂OH), pentamethyldenbenzyl alcohol (Me₅C₆H₃CH₂OH), 2,5-dimethoxybenzyl alcohol (Me₂O₃C₆H₃CH₂OH), 2,5-dimethoxybenzoic acid, and scandium(III) trifluoroacetatesulfonate (Sc(O₂)₃) were purchased from Aldrich Chemicals Co. p-Chlorobenzaldehyde (p-ClC₆H₄CHO), p-methoxybenzaldehyde (p-MeO-C₆H₄CHO), 3,5-dimethoxybenzyl alcohol (3,5-(MeO)₂C₆H₃CH₂OH), 3,4,5-trimethoxybenzyl alcohol (3,4,5-(MeO)₃C₆H₃CH₂OH), and benzoic acid were obtained from Tokyo Chemical Industry Co., Ltd.; p-nitrobenzaldehyde (p-NO₂C₆H₄CHO) and p-methoxybenzaldehyde (p-MeO-C₆H₄CHO) were obtained from Wako Pure Chemical Industries, Ltd. and lithium aluminum deuteride (LiAlD₄) was purchased from CIL, Inc. The commercially available compounds used in this study were the best available purity and used without further purification unless otherwise noted. Acetonitrile (MeCN) was dried according to the literature procedures and distilled under Ar prior to use. Iodosylbenzenes (PhIO) was prepared by a literature method. Nonheme iron(II) complex, [Fe(N₄Py)](ClO₄)₂ (N₄Py = N,N-bis(2-pyridylmethyl)-N-bis(2-pyridyl)methyamine), and its iron(IV)-oxo complex, [Fe⁴⁺(O)(N₄Py)]²⁺, were prepared according to the literature methods.

**Spectral and Kinetic Measurements.** Reactions of benzyl alcohol and its derivatives with [Fe⁴⁺(O)(N₄Py)]²⁺ (1.0 × 10⁻⁴ M) were examined by monitoring spectral changes in the presence of various concentrations of benzyl alcohol or its derivatives (1.0 × 10⁻⁵–2.0 × 10⁻¹ M) in the absence and presence of Sc(O₂)₃ in deaerated MeCN at 298 K using a Hewlett-Packard 8453 photodiode-array spectrophotometer and a quartz cuvette (path length =10 mm). Kinetic measurements for 2,5-(MeO)₂C₆H₃CH₂OH in the presence of Sc³⁺ were performed on a UNISOKU RSP-601 stopped-flow spectrophotometer equipped with a MOS-type highly sensitive photodiode array or a Hewlett-Packard 8453 photodiode array spectrophotometer at 298 K. Rates of reactions of benzyl alcohol and its derivatives with [Fe⁴⁺(O)(N₄Py)]²⁺ were monitored by a decrease in the absorption band due to [Fe⁴⁺(O)(N₄Py)]²⁺ (λ_max = 695 nm) in the absence and presence of Sc(O₂)₃ in MeCN. The concentration of benzyl alcohol or its derivatives was maintained to be more than 10-fold excess of [Fe⁴⁺(O)(N₄Py)]²⁺ to keep pseudo-first-order conditions. Pseudo-first-order rate constants were determined by a least-squares fit of the first-order plot of time course of spectral change. Reactions of 3,4,5-(MeO)₂C₆H₃CH₂OH with [Fe⁴⁺(O)(N₄Py)]²⁺ in the presence of Sc³⁺ were performed in the presence of 0.10 mM of [Fe⁴⁺(O)(N₄Py)]²⁺, 0.050 mM of 3,4,5-(MeO)₂C₆H₃CH₂OH, and excess amount of Sc³⁺ (5.0–20 mM).

**Electrochemical Measurements.** Measurements of cyclic voltammetry (CV) and second harmonic AC voltammetry (SHACV) were performed at 298 K using a BAS 630B electrochemical analyzer in deaerated MeCN containing 0.10 M TBAPF₆ as a supporting electrolyte at 298 K. A conventional three-electrode cell was used with a platinum working electrode and a platinum wire as a counter electrode. The measured potentials were recorded with respect to Ag/AgNO₃ (1.0 M). The one-electron oxidation potential values (Eₖ) vs Ag/AgNO₃ were converted to those vs SCE by adding 0.29 V. All electrochemical measurements were carried out under an Ar atmosphere.

**EPR Measurements.** Electron paramagnetic resonance (EPR) detection of iron(III) complexes and radical cation of 2,5-(MeO)₂C₆H₃CH₂OH was performed as follows: Typically, a MeCN solution of [Fe⁴⁺(O)(N₄Py)]²⁺ (1.0 × 10⁻³ M) in the absence and presence of Sc(O₂)₃ (1.0 × 10⁻³ M) in an EPR cell (3.0 mm i.d.) was purified with N₂ for 5 min. Then, deaerated benzyl alcohol or 2,5-(MeO)₂C₆H₃CH₂OH solution (5.0 × 10⁻⁷ M) was added to the solution. The EPR spectra of the radical cation of 2,5-(MeO)₂C₆H₃CH₂OH and iron(III) complexes were recorded on a JEOL JES-RE1X spectrometer at 243 and 77 K, respectively. The magnitude of modulation was chosen to optimize the resolution and signal-to-noise (S/N) ratio of the observed spectra under non-saturating microwave power conditions. The g value was calibrated using an Mn²⁺ marker (g = 2.034, 1.981). Computer simulation of the EPR spectra was carried out by using CalEPR version 1.2 (CalEPR Scientific Publisher) on a personal computer.

**NMR Measurements.** H NMR spectra were recorded on a JEOL JMN-AL-300 NMR spectrometer at room temperature. To obtain clear NMR signal by removing paramagnetic products, reaction solutions with Sc³⁺ were treated with alumina column before measurement. The yields of the oxidation products were determined based on the peak of iodosobenzene (between 7.0 and 8.8 ppm), which is a product of the reaction of [Fe⁴⁺(N₄Py)]²⁺ with iodosylbenzene to form [Fe⁴⁺(O)(N₄Py)]²⁺.
RESULTS AND DISCUSSION

Oxidation of Benzyl Alcohol by [FeIV(O)(N4Py)]2+. Oxidation of benzyl alcohol by the iron(IV)-oxo complex was examined both in the absence and presence of Sc3+ at 298 K in MeCN. Addition of excess amount of benzyl alcohol (50 mM) to the solution of [FeIV(O)(N4Py)]2+ (0.10 mM) caused the spectral change with a clean isosbestic point in both the absence and the presence of Sc3+ (20 mM) as shown in Figures 1a and 1b, respectively. The decay of the characteristic absorption band due to [FeIV(O)(N4Py)]2+ (695 nm) was accelerated with increase in concentration of benzyl alcohol in both the absence and the presence of Sc3+ (Supporting Information, Figures S1a and S1b), obeying pseudo-first-order kinetics. The pseudo-first-order rate constants (kobs) increased proportionally with an increase in concentration of benzyl alcohol, and the second-order rate constant (kew) was determined from the linear correlation to be 9.9 × 10−2 M−1 s−1 in the absence of Sc3+, which was nearly the same as the value (1.1 × 10−1 M−1 s−1) determined in the presence of Sc3+ (20 mM) as shown in Supporting Information, Figures S1c and S1d, respectively. In addition, the kobs values were constant irrespective of the change in concentration of Sc3+ (Figure 2).

Product analysis of the oxidation of benzyl alcohol (1.0 mM) by [FeIV(O)(N4Py)]2+ (1.0 mM) revealed the formation of benzaldehyde with 50% yield as a sole product both in the absence and presence of Sc3+ (10 mM) (Supporting Information, Figures S2a and S2b). The electrospray ionization mass spectrometry (ESI-MS) spectrum of the reaction solution performed in the absence of Sc3+ shows peaks at m/z S39.1 and 629.0, whose mass and isotope distribution indicate formation of [FeIII(OH)(N4Py)]2+ and [FeIII(OCH2C6H5)(N4Py)]2+, respectively (Supporting Information, Figures S3a and S3b). The formation of the iron(III) species was supported by taking EPR spectra of the reaction solution (Supporting Information, Figure S4a). In the presence of Sc3+, the ESI-MS spectrum of the resulting solution of the reaction shows peak at m/z 572.4, which indicates formation of [FeIII(O)(N4Py)(OTf)]2+ (calcld. m/z = 572.4) (Supporting Information, Figure S4c). The EPR spectrum, however, indicates that the major product of the reaction is not iron(II) but iron(III) species, [FeIII(N4Py)-(NCMe)]3+ with orthogonal signals around g = 2.5 and 1.7 (Supporting Information, Figures S4b and S4c). The iron(III) complex might not be detected by ESI-MS probably because of the high one-electron-reduction potential of [FeIII(N4Py)-(NCMe)]3+ (Ered = 1.0 V vs SCE) and the occurrence of the one-electron reduction from the iron(III) to iron(II) species under the ESI-MS condition.39 To confirm the oxidation state of the iron complex in the resulting solution in both the absence and the presence of Sc3+, a one-electron donor, ferrocene (Fc) was added into the solutions and one equiv of ferrocenium ion (Fc+) to [FeIV(O)(N4Py)]2+ was produced with the concurrent formation of [FeIII(N4Py)(NCMe)] in both cases (Supporting Information, Figures S5a and S5b). This indicates that [FeIV(O)(N4Py)]2+ acts as a one-electron oxidant rather than a two-electron oxidant. It should be noted that the [FeIII(OH)(N4Py)]2+ produced during the reaction is not so reactive to oxidize C6H5CHOH.*

The rate of the oxidation of PhCD2OH in the presence of Sc3+ (20 mM) in MeCN is significantly slower than that of PhCH2OH as shown in Figure 3, giving a deuterium kinetic isotope effect (KIE) of 7.2 at 298 K.40 As reported previously in the oxidation of benzyl alcohol by [FeIV(O)(N4Py)]2+ in the absence of Sc3+,17 such a large KIE value clearly indicates that the rate-determining step (r.d.s.) of the reaction is HAT from benzyl alcohol to [FeIV(O)(N4Py)]2+ in both the absence and the presence of Sc3+. The subsequent HAT from C6H5CHOH* to [FeIV(O)(N4Py)]2+ to yield C6H5CHO and [FeIII(OH)- (N4Py)]2+ occurs with a much faster rate than the initial HAT because of the weaker C–H bond in the radical species.41 This reaction mechanism is summarized in Scheme 2. In the presence of benzyl alcohol, [FeIII(O)(N4Py)]2+ is converted to [FeIII(OCH2C6H5)(N4Py)]2+ and H2O. No acceleration of the initial HAT was observed in the presence of Sc3+.

Figure 1. Spectral changes observed in the oxidation of benzyl alcohol (50 mM) by [FeIV(O)(N4Py)]2+ (0.1 mM) in MeCN at 298 K in the absence (a) and presence (b) of Sc3+ (20 mM).

Figure 2. Dependence of the pseudo-first-order rate constant (kobs) determined in the oxidation of PhCH2OH (1.0 × 10−3 mM) by [FeIV(O)(N4Py)]2+ (0.10 mM) on concentration of Sc3+. Inorganic Chemistry
second-order dependence of plot of (given by eq 1, where order rate constant (\(k_1\)) of concentration of 2,5-(MeO)\(_2\)C\(_6\)H\(_3\)CH\(_2\)OH, and the second-order dependence on the rate determined in the absence of Sc\(_3^+\) (Figure 4a). The pseudo-first order rate constant (\([\text{FeIV(O)(N4Py)}]^{2+}\)) was significantly slower than that of 2,5-(MeO)\(_2\)C\(_6\)H\(_3\)CD\(_2\)OH by \([\text{FeIV(O)(N4Py)}]^{2+}\) under the same conditions as employed in the oxidation of benzyl alcohol (Figure 4a). Second-order rate constants (\(k_1\) and \(k_2\)) were determined from the slopes of the plots of pseudo-first order rate constants of 2,5-(MeO)\(_2\)C\(_6\)H\(_3\)CH\(_2\)OH (\(k_{\text{obs}}\)) and 2,5-(MeO)\(_2\)C\(_6\)H\(_3\)CD\(_2\)OH (\(k_{\text{obs}}\)) vs [2,5-(MeO)\(_2\)C\(_6\)H\(_3\)CH\(_2\)OH] and [2,5-(MeO)\(_2\)C\(_6\)H\(_3\)CD\(_2\)OH], respectively (red and blue circles in Figure 6c), respectively. The KIE value was determined to be 14 for the reaction performed at 298 K. This clearly indicates that HAT is the rate-determining step as the case of oxidation of benzyl alcohol by \([\text{FeIV(O)(N4Py)}]^{2+}\) in Scheme 2.

In sharp contrast to the case of the absence of Sc\(_3^+\), no KIE was observed in the presence of Sc\(_3^+\) (Figures 6b and 6c). The disappearance of KIE by the presence of Sc\(_3^+\) indicates a mechanistic change from HAT to a process in which C–H bond cleavage is not involved in the rate-determining step, which is most likely to be electron transfer (vide infra). Indeed, new transient absorption bands around 430 and 455 nm, which were not observed in the absence of Sc\(_3^+\) in Figure 4a, were detected in the presence of Sc\(_3^+\) (Figure 4b). These absorption bands agree with those observed in the one-electron oxidation of 2,5-(MeO)\(_2\)C\(_6\)H\(_3\)CH\(_2\)OH by a strong one-electron oxidant such as CAN, as shown in Figure 4b (green line). This indicates the occurrence of electron transfer from 2,5-(MeO)\(_2\)C\(_6\)H\(_3\)CH\(_2\)OH to \([\text{FeIV(O)(N4Py)}]^{2+}\) to produce a radical cation of 2,5-(MeO)\(_2\)C\(_6\)H\(_3\)CH\(_2\)OH (i.e., 2,5-(MeO)\(_2\)C\(_6\)H\(_3\)+). The formation of the radical cation was confirmed by EPR measurements. Figure 7a shows an EPR spectrum of 2,5-(MeO)\(_2\)C\(_6\)H\(_3\)CH\(_2\)OH** produced in the oxidation of 2,5-(MeO)\(_2\)C\(_6\)H\(_3\)CH\(_2\)OH by \([\text{FeIV(O)(N4Py)}]^{2+}\) in the presence of Sc\(_3^+\). The hyperfine coupling constants obtained in the computer simulation spectrum (Figure 7b) are in a reasonable agreement with those calculated by the DFT method (Figure 7c). The same EPR signal was observed in the one-electron oxidation of 2,5-(MeO)\(_2\)C\(_6\)H\(_3\)CH\(_2\)OH by [Ru\(_{\text{III(bpy)}}\)]\(^{3+}\) (Supporting Information, Figure 7a).

The decay of the EPR signal of 2,5-(MeO)\(_2\)C\(_6\)H\(_3\)CH\(_2\)OH** produced in the oxidation of 2,5-(MeO)\(_2\)C\(_6\)H\(_3\)CH\(_2\)OH by \([\text{FeIV(O)(N4Py)}]^{2+}\) in the presence of Sc\(_3^+\) obeyed second-order kinetics (Figure 8a).** The second-order rate constant was determined to be 2.3 × 10\(^3\) M\(^{-1}\) s\(^{-1}\) from the linear second-order plot (Figure 8b) and the initial concentration of 2,5-(MeO)\(_2\)C\(_6\)H\(_3\)CH\(_2\)OH, which was determined by the double integration of the EPR spectrum by comparing with an authentic radical sample of 2,2-diphenyl-2-picrylhydrazyl (DPPH). The decay of the EPR signal of 2,5-(MeO)\(_2\)C\(_6\)H\(_3\)CH\(_2\)OH by [Ru\(_{\text{III(bpy)}}\)]\(^{3+}\) also obeyed second-order kinetics (Supporting Information, Figure 8b), respectively. Such a dependence of electron-transfer rate constants on [Sc\(_3^+\)] was reported previously for metal ion-coupled electron transfer from one-electron reducants to \([\text{FeIV(O)(N4Py)}]^{2+}\). For instance, the dependence of second-order rate constant of electron transfer (\(k_2\)) from [Fe\(_{\text{D(bpy)}}\)]\(^{3+}\) to \([\text{FeIV(O)(N4Py)}]^{2+}\) on [Sc\(_3^+\)] is shown in Figure 5 (black squares).

To determine the KIE value, the oxidation rate of a deuterated substrate (2,5-(MeO)\(_2\)C\(_6\)H\(_3\)CD\(_2\)OH) by \([\text{FeIV(O)(N4Py)}]^{2+}\) was also examined in both the absence and the presence of Sc\(_3^+\). In the absence of Sc\(_3^+\), the oxidation rate of 2,5-(MeO)\(_2\)C\(_6\)H\(_3\)CD\(_2\)OH (1.0 × 10\(^5\) mM) by \([\text{FeIV(O)(N4Py)}]^{2+}\) (0.060 mM) was significantly slower than that of 2,5-(MeO)\(_2\)C\(_6\)H\(_3\)CH\(_2\)OH by \([\text{FeIV(O)(N4Py)}]^{2+}\) under the same conditions as employed in the oxidation of benzyl alcohol (Figure 6a). The decay of the EPR signal of 2,5-(MeO)\(_2\)C\(_6\)H\(_3\)CH\(_2\)OH** produced in the presence of Sc\(_3^+\) (Figures 6b and 6c). The hyperfine coupling constants obtained in the computer simulation spectrum (Figure 7b) are in a reasonable agreement with those calculated by the DFT method (Figure 7c). The same EPR signal was observed in the one-electron oxidation of 2,5-(MeO)\(_2\)C\(_6\)H\(_3\)CH\(_2\)OH by [Ru\(_{\text{III(bpy)}}\)]\(^{3+}\) (Supporting Information, Figure 7a).

The decay of the EPR signal of 2,5-(MeO)\(_2\)C\(_6\)H\(_3\)CH\(_2\)OH** produced in the oxidation of 2,5-(MeO)\(_2\)C\(_6\)H\(_3\)CH\(_2\)OH by \([\text{FeIV(O)(N4Py)}]^{2+}\) in the presence of Sc\(_3^+\) obeyed second-order kinetics (Figure 8a).** The second-order rate constant was determined to be 2.3 × 10\(^3\) M\(^{-1}\) s\(^{-1}\) from the linear second-order plot (Figure 8b) and the initial concentration of 2,5-(MeO)\(_2\)C\(_6\)H\(_3\)CH\(_2\)OH, which was determined by the double integration of the EPR spectrum by comparing with an authentic radical sample of 2,2-diphenyl-2-picrylhydrazyl (DPPH). The decay of the EPR signal of 2,5-(MeO)\(_2\)C\(_6\)H\(_3\)CH\(_2\)OH by [Ru\(_{\text{III(bpy)}}\)]\(^{3+}\) also obeyed second-order kinetics (Supporting Information, Figure 8b),

\[ k_{\text{ex}} = k_0 + k_1[\text{Sc}^3+] + k_2[\text{Sc}^3+]^2 \] (1)
indicating that bimolecular reactions of 2,5-(MeO)2C6H3CH2OH• are responsible for the decay of 2,5-(MeO)2C6H3CH2OH•.

Product analyses of the oxidation of 2,5-(MeO)2C6H3CH2OH by [FeIV(O)(N4Py)]2+ in the absence and presence of Sc3+ were performed by the same method for the benzyl alcohol oxidation.1H NMR spectra of the reaction products obtained in the oxidation of 2,5-(MeO)2C6H3CH2OH (1.0 mM) by [FeIV(O)(N4Py)]2+ (0.060 mM) in the absence of Sc3+ (10 mM) revealed that 2,5-(MeO)2C6H3CH2OH was converted to the corresponding aldehyde, 2,5-(MeO)2C6H3CHO, with 50% yield as the case of benzyl alcohol oxidation (Supporting Information, Figure S9). The major inorganic products were determined to be [FeIII(OH)(N4Py)]2+ and [FeIII(OCH2C6H3(OMe))2(N4Py)]2+ by ESI-MS and EPR spectroscopy (Supporting Information, Figures S10 and S11). Titration of the resulting solution by Fc resulted in formation of Fc+ with the same concentration as the initial concentration of [FeIV(O)(N4Py)]2+ to produce [FeII(N4Py)(NCMe)]2+ (Supporting Information, Figure S12). This indicates that [FeIV(O)(N4Py)]2+ acts as a one-electron oxidant rather than two-electron oxidant in the oxidation of 2,5-(MeO)2C6H3CH2OH as the case of PhCH2OH oxidation.

In the presence of Sc3+ (10 mM), however, the oxidation of 2,5-(MeO)2C6H3CH2OH by [FeIV(O)(N4Py)]2+ resulted in the oxidative coupling to yield 2,2′,5,5′-tetramethoxybiphenyl-4,4′-dimethanol as a major product (31% yield, 0.31 mM) together with the further oxidized product 2,2′,5,5′-tetramethoxybiphenyl-4,4′-dicarbaldehyde (1.0% yield, 0.010 mM) as well as the corresponding aldehyde (2,5-(MeO)2C6H3CHO) only in 10% yield (0.10 mM) as shown in Scheme 3 with each products’ yield and the oxidation equivalent (see Supporting Information, Figure S8b). The ESI-MS and EPR spectrum of the resulting solution and titration of the resulting solution by Fc indicate that the inorganic products are iron(III) species and [FeIV(O)(N4Py)]2+ acts as a one-electron oxidant in the presence of Sc3+ as is the case in the absence of Sc3+ (Supporting Information, Figures S10 and S11). The overall oxidation...
efficiency was determined to be 88% by counting the number of electrons oxidized by \([\text{Fe}^{IV}(O)(N4\text{Py})]^{2+}\) (0.060 mM) in the oxidation of 2,5-(MeO)C₆H₄CH₂OH (1.0 × 10⁻³ mM) (red) and 2,5-(MeO)C₆H₄CD₂OH (1.0 × 10⁻³ mM) (blue) in the absence of Sc³⁺. Inset shows first-order plots of the absorption change at 695 nm.

Because oxidative coupling products were obtained by the oxidation of 2,5-(MeO)C₆H₄CH₂OH with one-electron oxidant CAN,⁵⁰⁻⁵² formation of the dimer products, together with the detection of the radical cation intermediate by absorption and EPR spectra in the oxidation of 2,5-(MeO)C₆H₄CH₂OH by \([\text{Fe}^{IV}(O)(N4\text{Py})]^{2+}\) (0.060 mM) in the oxidation of 2,5-(MeO)C₆H₄CH₂OH (2.5 mM) (red) and 2,5-(MeO)C₆H₄CD₂OH (2.5 mM) (blue) in the presence of Sc³⁺ (2.5 mM). Inset shows first-order plots of the absorption change at 695 nm.

This is consistent with the bimolecular decay kinetics of 2,5-(MeO)C₆H₄CH₂OH in Figure 8.

Figure 6. (a) Time courses of the absorption spectral changes observed at 695 nm due to \([\text{Fe}^{IV}(O)(N4\text{Py})]^{2+}\) (0.060 mM) in the oxidation of 2,5-(MeO)C₆H₄CH₂OH (1.0 × 10⁻³ mM) (red) and 2,5-(MeO)C₆H₄CD₂OH (1.0 × 10⁻³ mM) (blue) in the absence of Sc³⁺. Inset shows first-order plots of the absorption change at 695 nm. (b) Time courses of the absorption spectral changes observed at 695 nm due to \([\text{Fe}^{IV}(O)(N4\text{Py})]^{2+}\) (0.060 mM) in the oxidation of 2,5-(MeO)C₆H₄CH₂OH (2.5 mM) (red) and 2,5-(MeO)C₆H₄CD₂OH (2.5 mM) (blue) in the presence of Sc³⁺ (2.5 mM). Inset shows first-order plots of the absorption change at 695 nm. (c) Plots of \(k_{\text{dimer}}\) (red) and \(k_{\text{rad}}\) (blue) vs [2,5-(MeO)C₆H₄CH₂OH] and [2,5-(MeO)C₆H₄CD₂OH] in the absence (circles) and presence (squares) of Sc³⁺ (2.5 mM), respectively.

Figure 7. (a) X-band EPR spectrum of 2,5-(MeO)C₆H₄CH₂OH•⁺ produced by electron-transfer oxidation of 2,5-(MeO)C₆H₄CH₂OH (1.0 mM) by \([\text{Fe}^{IV}(O)(N4\text{Py})]^{2+}\) (1.0 mM) in the presence of Sc³⁺ (10 mM) in deaerated MeCN at 298 K. (b) The computer simulation spectrum. (c) DFT optimized structure of 2,5-(MeO)C₆H₄CH₂OH•⁺ with hyperfine coupling constants together with the calculated values given in parentheses.
The $\text{Sc}^{3+}$-coupled electron-transfer pathway is further confirmed by the first-order and second-order dependence of $k_{\text{ox}}$ of the oxidation of $2,5$-$\text{(MeO)}_2C_6H_3CH_2OH$ by $[\text{Fe}^\text{IV}(O)(\text{N}4\text{Py})]^2^+$ in the presence of $\text{Sc}^{3+}$ on $[\text{Sc}^{3+}]$, which is quite similar to that observed $\text{Sc}^{3+}$-coupled ET from $[\text{Fe(bpy)}_3]^2^+$ (one-electron reductant) to $[\text{Fe}^\text{IV}(O)(\text{N}4\text{Py})]^2^+$ on $[\text{Sc}^{3+}]$ (Figure 5) and the absence of KIE.

**Effect of $\text{Sc}^{3+}$ on the Oxidation Rate of Benzyl Alcohol Derivatives by $[\text{Fe}^\text{IV}(O)(\text{N}4\text{Py})]^2^+$.** The change in the reaction pathway from one-step HAT to $\text{Sc}^{3+}$-coupled ET may be determined by the one-electron oxidation potentials ($E_{\text{ox}}$) of benzyl alcohol derivatives (see Supporting Information, Table S1 for the $E_{\text{ox}}$ values of benzyl alcohol derivatives). To explore the borderline between one-step HAT and $\text{Sc}^{3+}$-coupled ET pathways, we investigated the dependence of the second-order rate constants for the oxidation of a series of benzyl alcohol derivatives on $[\text{Sc}^{3+}]$. The results are shown in Figures 9a–9g. The $k_{\text{ox}}$ values for the oxidation of benzyl alcohol derivatives with relatively high $E_{\text{ox}}$ values, p-$\text{NO}_2C_6H_4CH_2OH$, C$_6H_5CH_2OH$, and p-$\text{Cl}C_6H_4CH_2OH$, were the same as those in the absence of $\text{Sc}^{3+}$ with increasing concentration of $\text{Sc}^{3+}$ (Figures 9a–9c), whereas the $k_{\text{ox}}$ values for the oxidation of
benzyl alcohol derivatives with lower oxidation potentials, p-\text{MeC}_6\text{H}_4\text{CH}_2\text{OH}, p-\text{MeOC}_6\text{H}_4\text{CH}_2\text{OH}, \text{Me}_5\text{C}_6\text{CH}_2\text{OH}, 3,5-(\text{MeO})_2\text{C}_6\text{H}_3\text{CH}_2\text{OH}, 3,4,5-(\text{MeO})_3\text{C}_6\text{H}_2\text{CH}_2\text{OH}, and 2,5-(\text{MeO})_2\text{C}_6\text{H}_3\text{CH}_2\text{OH}, increased with increasing concentration of Sc^{3+} (Figures 9d–9g) as is the case for the oxidation of 2,5-(\text{MeO})_2\text{C}_6\text{H}_3\text{CH}_2\text{OH} (Figure 5). Although no radical cation intermediates were observed in the oxidation of p-\text{MeOC}_6\text{H}_4\text{CH}_2\text{OH}, \text{Me}_5\text{C}_6\text{CH}_2\text{OH}, 3,5-(\text{MeO})_2\text{C}_6\text{H}_3\text{CH}_2\text{OH}, and 3,4,5-(\text{MeO})_3\text{C}_6\text{H}_2\text{CH}_2\text{OH} in the presence of Sc^{3+} (10 mM), the acceleration may be attributed to Sc^{3+}-coupled ET.

\[ -\Delta G_{et} = \epsilon(E_{red} - E_{ox}) \]  

Figure 10 shows plots of log \( k_{ox} \) of oxidation of benzyl alcohols by [Fe^{IV}(O)(N4Py)]^{2+} in the absence and presence of Sc^{3+} (10 mM) and log \( k_{et} \) of electron transfer from one-electron reductants to [Fe^{IV}(O)(N4Py)]^{2+} in the presence of Sc^{3+} (10 mM) vs driving force of ET (\( -\Delta G_{et} \)). In the absence of Sc^{3+}, the \( -\Delta G_{et} \) values are largely negative (endergonic) and the log \( k_{et} \) values are rather independent of the \( -\Delta G_{et} \) values (blue points in Figure 10). The log \( k_{et} \) values in the absence of Sc^{3+} are much larger than those predicted by the extrapolated line of electron transfer, indicating that the oxidation of benzyl alcohol derivatives by [Fe^{IV}(O)(N4Py)]^{2+} undergoes via one-step HAT rather than via electron transfer. This is also supported by the

\begin{table}
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
entry & substituent & \( k_{et} \) (0 mM) & \( k_{et} \) (10 mM) & \( k_{et} \) (0 mM) & \( k_{et} \) (10 mM) \\
\hline
1 & p-NO_2 & -2.37 & -1.69 & 1.1 \times 10^{-1} & 1.3 \times 10^{-1} \\
2 & p-H & -1.82 & -1.14 & 9.9 \times 10^{-2} & 9.9 \times 10^{-2} \\
3 & p-Cl & -1.74 & -1.04 & 1.0 \times 10^{-1} & 1.1 \times 10^{-1} \\
4 & p-Me & -1.54 & -0.86 & 1.4 \times 10^{-1} & 1.7 \times 10^{-1} \\
5 & Me_2 & -1.14 & -0.61 & 3.5 \times 10^{-2} & 5.6 \times 10^{-2} \\
6 & p-MeO & -1.07 & -0.59 & 1.4 \times 10^{-1} & 2.5 \times 10^{-1} \\
7 & 3,5-(MeO)_2 & -0.98 & -0.30 & 1.2 \times 10^{-1} & 3.8 \times 10^{-1} \\
8 & 3,4,5-(MeO)_3 & -0.71 & -0.23 & 1.5 \times 10^{-1} & 4.0 \times 10 \\
9 & 2,5-(MeO)_2 & -0.69 & -0.14 & 2.0 \times 10^{-1} & 1.3 \times 10 \\
\hline
\end{tabular}
\caption{Driving Force for ET (\( -\Delta G_{et} \)) and Second-Order Rate Constants (\( k_{et} \)) for Oxidation of Benzyl Alcohol Derivatives with [Fe^{IV}(O)(N4Py)]^{2+} in the Absence and Presence of Sc^{3+} (10 mM) in MeCN at 298 K}
\end{table}
Figure 10. Plots of log \( k_{\text{ox}} \) for oxidation of benzyl alcohol derivatives (numbers refer to compounds in Table 1) by \([\text{Fe}^{IV}(\text{O})(\text{N4Py})]^2+\) in MeCN at 298 K vs \(-\Delta G_{\text{et}} \) for electron transfer from benzyl alcohol derivatives to \([\text{Fe}^{IV}(\text{O})(\text{N4Py})]^2+\) in the absence (blue) of \( \text{Sc}^{3+} \) and the presence (red) of \( \text{Sc}^{3+} \) (10 mM). Black points are plots of log \( k_{\text{ox}} \) of electron transfer from one-electron reductants (a: \([\text{Ru}^{II}(\text{bpy})_3]^2+\); b: \([\text{Fe}^{III} (\text{Clphen})]^{2+}\); c: \([\text{Ru}^{II}(\text{Me bpy})_2]^{2+}\); d: \([\text{Fe}^{II} (\text{N3})_2]^{2+}\); e: \([\text{Fe}^{III} (\text{Ph2phen})_2]^{2+}\) to \([\text{Fe}^{IV}(\text{N4Py})(\text{O})]^2+\) in the presence of 10 mM of \( \text{Sc}^{3+} \) in MeCN at 298 K vs \(-\Delta G_{\text{et}} \). The blue and red parts correspond to \( \text{HAT} \) and ET pathways, respectively. The solid lines are drawn using eq 4 with \( \lambda \) values of 1.93 and 2.27 eV.

KIE observed in the oxidations of \( \text{C}_6\text{H}_5\text{CD}_2\text{OH} \) and \( 2,5-\text{(MeO)}_2\text{C}_6\text{H}_3\text{CD}_2\text{OH} \) in the absence of \( \text{Sc}^{3+} \) (Figure 3).

In sharp contrast to the case in the absence of \( \text{Sc}^{3+} \), log \( k_{\text{ox}} \) values of benzyl alcohol derivatives, which are accelerated by the presence of \( \text{Sc}^{3+} \) (10 mM) (entries 7–9), show similar driving force dependence to that of log \( k_{\text{ox}} \) of electron transfer from a series of one-electron reductants to \([\text{Fe}^{IV}(\text{O})(\text{N4Py})]^2+\) in the presence \( \text{Sc}^{3+} \) (10 mM).\(^{56,58} \) Both log \( k_{\text{ox}} \) and log \( k_{\text{et}} \) values increase with increasing ET driving force (\(-\Delta G_{\text{et}} \) values). The ET driving force dependence of \( k_{\text{et}} \) and \( k_{\text{ox}} \) is well fitted by the Marcus equation of outer-sphere electron transfer (eq 3), where \( Z \) is the frequency factor \((1 \times 10^{13} \text{ M}^{-1} \text{s}^{-1})\) and \( \lambda \) is the reorganization energy of electron transfer.\(^{57,58} \) The dependence of log \( k_{\text{ox}} \) on \(-\Delta G_{\text{et}} \) clearly indicates the occurrence of \( \text{Sc}^{3+} \)-coupled ET from benzyl alcohol derivatives to \([\text{Fe}^{IV}(\text{O})(\text{N4Py})]^2+\). Although the \(-\Delta G_{\text{et}} \) values for entry 7–9 are negative (endergonic), the \( \text{Sc}^{3+} \)-coupled ET may be followed by fast subsequent reaction (pathway b in Scheme 4). The \( \lambda \) values for electron transfer from one-electron reductants and benzyl alcohol derivatives to \([\text{Fe}^{IV}(\text{O})(\text{N4Py})]^2+\) in the presence of 10 mM of \( \text{Sc}^{3+} \) are determined to be 2.27 and 1.93 eV by fitting plots of entries a–e and 7–9 in red in Figure 10 with eq 3, respectively.

On the other hand, the \( k_{\text{ox}} \) values of benzyl alcohol derivatives are independent of the ET driving force even in the presence of \( \text{Sc}^{3+} \) (10 mM) when \(-\Delta G_{\text{et}} \) is smaller than \(-0.5 \) eV (entries 1–4 in Table 1). This indicates that the oxidation of those benzyl alcohol derivatives proceeds via one-step HAT, which is an energetically much more favorable pathway than the highly endergonic \( \text{Sc}^{3+} \)-coupled ET. The rates of oxidation of benzyl alcohol derivatives (entries 5 and 6 in Table 1) are slightly accelerated by the presence of \( \text{Sc}^{3+} \) (10 mM) (1.8 and 1.6 times respectively), and the log \( k_{\text{ox}} \) values are on the borderline of the mechanism change between one-step HAT and \( \text{Sc}^{3+} \)-coupled ET.\(^{59,60} \)

The comparison of the driving force dependence of \( k_{\text{ox}} \) and \( k_{\text{et}} \) in Figure 10 has provided a clear view with regard to the borderline of the mechanism change between one-step HAT and \( \text{Sc}^{3+} \)-coupled ET. The results at a different concentration of \( \text{Sc}^{3+} \) (1.0 mM) are presented in Supporting Information, Figure S14. Although the best fit \( \lambda \) value (2.33 eV) for the driving force dependence of log \( k_{\text{et}} \) with 1.0 mM \( \text{Sc}^{3+} \) becomes larger than the value with 10 mM \( \text{Sc}^{3+} \) (2.27 eV) and therefore the plot looks somewhat different, the conclusion on the mechanism change between one-step HAT and \( \text{Sc}^{3+} \)-coupled ET remains virtually the same.

It should be noted that it is rather unusual to apply the Marcus theory to conditional rate constants that depend on the concentration of \( \text{Sc}^{3+} \). Nevertheless we can explain the dependence of the rate constant on the concentration of \( \text{Sc}^{3+} \) using the Marcus theory as follows.\(^{58} \) Under the conditions such that \( \lambda \ll -\Delta G_{\text{et}} \) in Figure 10, the \( k_{\text{et}} \) value is estimated by the Marcus cross relationship as shown in eq 4,\(^{57,58} \) where \( k_{\text{Des}} \) and \( k_{\text{et}} \) are the rate constant of electron exchange between electron donor (D) and the radical cation, the rate constant of electron exchange between electron acceptor (A) and the one-electron reduced species, and the equilibrium constants of the electron transfer from D to A. The \( k_{\text{Des}} \) value is constant independent of the concentration of \( \text{Sc}^{3+} \), whereas \( k_{\text{ox}} \) and \( k_{\text{et}} \) are expected to increase in proportion to \([\text{Sc}^{3+}]^2\) at high concentrations of \( \text{Sc}^{3+} \) as given by eqs 5 and 6, respectively, where \( k_{\text{Des}} \) and \( k_{\text{et}} \) are the constant and variable, respectively. Such a change can be observed in the presence of \( \text{Sc}^{3+} \) (Figure 10).

\[
-\Delta G_{\text{et}} = \lambda (1 + \Delta G_{\text{et}})/\lambda^2/(2.3 \times 4 k_B T) \quad (3)
\]

\[
k_{\text{et}} = (k_{\text{Des}} k_{\text{ox}} k_{\text{et}})^{1/2} \quad (4)
\]

\[
k_{\text{ox}} = k_{\text{Des}} [\text{Sc}^{3+}]^2 \quad (5)
\]

\[
k_{\text{et}} = k_{\text{et}} [\text{Sc}^{3+}]^2 \quad (6)
\]

\[
[\text{Sc}^{3+}] \text{ is given by eq 7, which agrees with the results in Figure 5.}
\]

\[
k_{\text{et}} = (k_{\text{Des}} k_{\text{ox}} k_{\text{et}})^{1/2} [\text{Sc}^{3+}]^2 \quad (7)
\]

The dependence of log \( k_1 \) and log \( k_2 \) of \( \text{Sc}^{3+} \)-coupled ET on \(-\Delta G_{\text{et}} \) in the absence of \( \text{Sc}^{3+} \) is shown in Supporting Information, Figure S15, where a roughly parallel relationship between \( k_1 \) and \( k_2 \) is observed. This plot for benzyl alcohol derivatives is not shown because \( k_1 \) and \( k_2 \) values of benzyl alcohol derivatives close to the region of one-step HAT could not be obtained accurately because of the large contribution of \( k_0 \).

### CONCLUSION

In this study, we have demonstrated the change of the rate-determining step in the oxidation of benzyl alcohol derivatives by \([\text{Fe}^{IV}(\text{O})(\text{N4Py})]^2+\) from one-step HAT to \( \text{Sc}^{3+} \)-coupled ET depending on the one-electron oxidation potentials of benzyl alcohol derivatives. The change in the reaction mechanism is initiated by acceleration of ET by \( \text{Sc}^{3+} \) while HAT is not accelerated by \( \text{Sc}^{3+} \) at all.\(^{61} \) Such a change in the reaction pathways by the presence of \( \text{Sc}^{3+} \) has been clearly shown by the disappearance of KIE in the presence of \( \text{Sc}^{3+} \) in contrast to a large KIE value observed in the absence of \( \text{Sc}^{3+} \), when formation of the radical cation of a benzyl alcohol derivative was detected as the initial product of \( \text{Sc}^{3+} \)-coupled ET from the substrate to \([\text{Fe}^{IV}(\text{O})(\text{N4Py})]^2+\), leading to the dimerized product as a major product in contrast to the corresponding aldehyde obtained as the sole product in the absence of \( \text{Sc}^{3+} \).
The mechanistic borderline between one-step HAT and Sc$^{3+}$-coupled ET has been found to be determined by the ET driving force from the substrate to [Fe$^{IV}$O(N4Py)]$^{2+}$ with the border of $-\Delta G_{et} \approx -0.5$ eV. The C–H bond is cleaved via HAT when $-\Delta G_{et}$ is more negative than $-0.5$ eV, whereas Sc$^{3+}$-coupled ET becomes a predominant pathway when $-\Delta G_{et}$ is more positive than $-0.5$ eV. In other words, Sc$^{3+}$-coupled ET occurs when $E_{pa}$ of substrate is more negative than 1.7 V. This study provides the first example for the change in the mechanism of oxidation of substrates by a high-valent metal-oxo complex from one-step HAT to ET that is accelerated by Sc$^{3+}$ depending on the ET driving force. The oxidation reaction takes place even when $-\Delta G_{et}$ is negative, that is, ET is endergonic, indicating the ET process is coupled with the following proton transfer. It is of interest to note that the borderline between one-step HAT and Sc$^{3+}$-coupled ET is at the ET driving force ($\Delta G_{et}$) of about $-0.5$ eV, which is similar to that reported previously for the borderline between one-step oxygen atom transfer and Sc$^{3+}$-coupled ET.$^{57}$ This type of switching in reaction pathway from HAT to ET depending on $-\Delta G_{et}$ value would generally appear in the reaction systems where high-valent oxometal species are employed as an oxidant such as compound I or MnO$_5^-$, especially in oxidation of substrates with relatively low oxidation potential or in the presence of acids which shift one-electron reduction potential of metal-oxo species positively.

### ASSOCIATED CONTENT

- **Supporting Information**
  Further details are given in Table S1 and Figures S1–S13. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

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In the oxidation of 2,5-(MeO)₂C₆H₃CH₂OH by [Ru⁺³(bpy)₃]²⁺, no aldehyde formation was observed as a product. This indicates that [Fe⁺³(O)(N₄Py)]⁻−Sc⁺³ works as a base to accept a proton released from 2,5-(MeO)₂C₆H₃CH₂OH⁺ to produce 2,5-(MeO)₂C₆H₃CHO. (54) The pseudo-first-order rate constants were proportional to concentrations of substrates without exhibiting no intercepts as shown in Figure 6. This indicates that the rate-determining step is the Sc⁺³-coupled electron transfer followed by subsequent reactions which are faster than the back electron-transfer reaction.

(55) Some of benzyl alcohol derivatives interact with Sc⁺³. This interaction resulted in the positive shifts of the one-electron oxidation potentials (Supporting Information, Table S1).

(56) The observed rate constant (kₒ) consists of three rate constants, i.e., kₒ, k₁, and k₂ (eq 1). Under the conditions in Figure 5 ([Sc⁺³] = 10 mM), k₂ is the main component. Thus, kₒ in Figure 10 virtually corresponds to the rate constant for elementary step electron transfer to [Fe⁺⁴(O)(N₄Py)]²⁻−(Sc⁺³)²⁺.


(58) The Marcus equation can be applied at different concentrations of Sc⁺³, when the driving force and reorganization energy of electron transfer are changed as discussed previously on metal ion-coupled electron transfer; see: Okamoto, K.; Imahori, H.; Fukuzumi, S. J. Am. Chem. Soc. 2003, 125, 7014.

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(60) No clear correlation between log kₒ values and bond dissociation energies (BDE(C−H)) of C−H bonds at the benzyl position of a series of benzyl alcohol derivatives calculated with DFT excludes the possibility that the reaction pathway is controlled by BDE(C−H) (Supporting Information, Figure S13).

(61) The binding of Sc⁺³ to [Fe⁺⁴(O)(N₄Py)]²⁺ may increase the oxidizing ability. However, the direct hydrogen atom transfer reaction may be prohibited by the steric effect of Sc⁺³. In contrast to this, electron transfer is generally insensitive to the steric effect because outer-sphere electron transfer requires little interaction between electron donor and acceptor molecules. This is the reason why ET is accelerated whereas no acceleration of HAT occurs by the addition of Sc⁺³.