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Efficient Epoxidation of Styrene Derivatives by a Nonheme Iron(IV)-Oxo Complex via Proton-Coupled Electron Transfer with Triflic Acid

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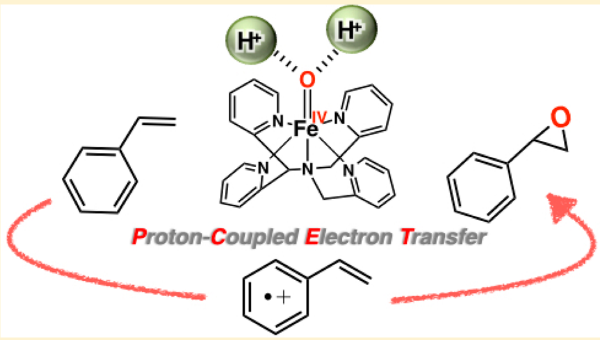
Supporting Information

ABSTRACT: Styrene derivatives are not oxidized by $[(N4Py)Fe^{IV}(O)]^{2+}$ (N4Py = *N*,*N*-bis(2-pyridylmethyl)-*N*-bis(2-pyridyl)methylamine) in acetonitrile at 298 K, whereas epoxidation of styrene derivatives by the iron(IV)-oxo complex occurs efficiently in the presence of triflic acid (HOTf) via proton-coupled electron transfer (PCET) from styrene derivatives to the diprotonated species of $[(N4Py)Fe^{IV}(O)]^{2+}$ with HOTf. Logarithms of the first-order rate constants of HOTf-promoted expoxidation of styrene derivatives with $[(N4Py)Fe^{IV}(O)]^{2+}$ and PCET from electron donors to $[(N4Py)Fe^{IV}(O)]^{2+}$ in the precursor complexes exhibit a remarkably unified correlation with the driving force of PCET in light of the Marcus theory of electron transfer when the differences in the formation constants of precursor complexes are taken into account. The same PCET driving force dependence is obtained for the first-order rate constants of HOTf-promoted oxygen atom transfer from thioanisols to $[(N4Py)Fe^{IV}(O)]^{2+}$ and HOTf-promoted hydrogen atom transfer from toluene derivatives to $[(N4Py)Fe^{IV}(O)]^{2+}$ in the precursor complexes. Thus, HOTf-promoted epoxidation of styrene derivatives by $[(N4Py)Fe^{IV}(O)]^{2+}$ proceeds via the rate-determining electron transfer from styrene derivatives to the diprotonated species of $[(N4Py)Fe^{IV}(O)]^{2+}$, as shown in the reactions of HOTf-promoted oxygen atom transfer from thioanisols to $[(N4Py)Fe^{IV}(O)]^{2+}$ and HOTf-promoted hydrogen atom transfer from toluene derivatives to $[(N4Py)Fe^{IV}(O)]^{2+}$.



INTRODUCTION

There are nonheme iron enzymes that can catalyze substrate oxidations, similar to those observed in the oxidation reactions by heme enzymes (e.g., cytochrome P450).[1−4] Inspired by these enzymes, extensive efforts have been devoted to developing biomimetic iron porphyrin catalysts[5,6] and also to the design of new families of nonheme iron catalysts.[7−14] It has been shown that the biomimetic iron compounds act as efficient catalysts in various oxidation reactions, such as alkane hydroxylation, olefin epoxidation, and the oxidation of heteroatom compounds.[7,9] In particular, nonheme iron complexes catalyze not only epoxidation but also *cis*-dihydroxylation of olefins.[15,16] The olefin epoxidation and *cis*-dihydroxylation are in closely related transformations that have been carried out by presumed $HO\text{-}Fe^{V}(O)$ species.[17]

Addition of acetic acid to nonheme iron-catalyzed olefin oxidation reactions by H_2O_2 resulted in an increase in both catalytic activity and selectivity toward epoxidation.[18,19] The acetic acid enhanced olefin epoxidation with $[(TPA)Fe(OTf)_2]$ (TPA = tris(2-pyridylmethyl)amine, OTf^- = triflate) has been proposed to be mediated by $[(TPA)Fe^{V}(O)(OOCCH_3)]^{2+}$, generated from O−O bond heterolysis of the $[(TPA)Fe^{III}(OOH)(CH_3COOH)]^{2+}$ intermediate, which is promoted by the protonation of the terminal oxygen atom of the hydroperoxide by the coordinated carboxylic acid.[12] Peracetic acid used as an acid as well as an oxidant has also been reported to promote olefin epoxidation.[20] Perchloric acid and triflic acid have been reported to remarkably promote oxidation of toluene and thioanisole derivatives by $[(N4Py)Fe^{IV}(O)]^{2+}$.[21−24] However, there has been no report on acid-promoted epoxidation of olefins by nonheme iron(IV)-oxo complexes.

We report herein efficient epoxidation of styrene derivatives by $[(N4Py)Fe^{IV}(O)]^{2+}$ in the presence of triflic acid (HOTf) in acetonitrile (MeCN) at 298 K, although $[(N4Py)Fe^{IV}(O)]^{2+}$ is not able to oxidize styrene derivatives efficiently without HOTf under the same reaction conditions. The mechanism of HOTf-promoted epoxidation of styrene derivatives is clarified by comparing the reactivity of $[(N4Py)Fe^{IV}(O)]^{2+}$ toward styrene derivatives in the presence of HOTf with that of proton-coupled electron transfer (PCET) from various electron donors to $[(N4Py)Fe^{IV}(O)]^{2+}$ in the presence of HOTf in light of the

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Marcus theory of electron transfer.[21−26] This is the first observation of the PCET pathway for epoxidation of styrene derivatives with a nonheme iron(IV)-oxo complex.

■ EXPERIMENTAL SECTION

Materials. All chemicals, which were the best available purity, were purchased from Aldrich Chemical Co. and Tokyo Chemical Industry and used without further purification unless otherwise noted. Solvents, such as acetonitrile (MeCN) and diethyl ether, were dried according to the literature procedures and distilled under Ar prior to use.[27] Nonheme iron(II) complex $[(N4Py)Fe^{II}(MeCN)](ClO_4)_2$ and its corresponding iron(IV)-oxo complex $[(N4Py)Fe^{IV}(O)]^{2+}$ were prepared by the literature methods.[28,29] Iodosylbenzene (PhIO) was prepared by a literature method.[30] Triflic acid was purchased from Tokyo Chemical Industry.

The detailed instrumentation and the experimental procedures of kinetic studies and product analyses are given in the Supporting Information.

■ RESULTS AND DISCUSSION

Triflic Acid-Promoted Epoxidation of Styrene Derivatives by $[(N4Py)Fe^{IV}(O)]^{2+}$. No oxidation of *α*-methylstyrene (6.3 mM) by $[(N4Py)Fe^{IV}(O)]^{2+}$ (0.25 mM) occurred in MeCN in 1 h at 298 K. However, addition of HOTf (10 mM) to an MeCN solution of $[(N4Py)Fe^{IV}(O)]^{2+}$ and *α*-methylstyrene resulted in efficient oxidation of *α*-methylstyrene by $[(N4Py)Fe^{IV}(O)]^{2+}$ within 200 s as shown in Figure 1, where the absorption band at 695 nm due to $[(N4Py)Fe^{IV}(O)]^{2+}$ disappeared upon addition of HOTf. The oxidized products were identified as the epoxides by ^{1}H NMR in the reactions of *α*-methylstyrene and *trans*-stilbene with $[(N4Py)Fe^{IV}(O)]^{2+}$ in the presence of HOTf (Figures S1 and S2 in Supporting Information, respectively).[31] The yields of epoxides of *α*-methylstyrene and *trans*-stilbene were 42 ± 4% and 45 ± 4%, respectively.

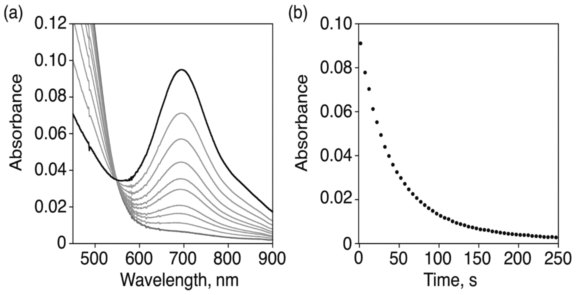
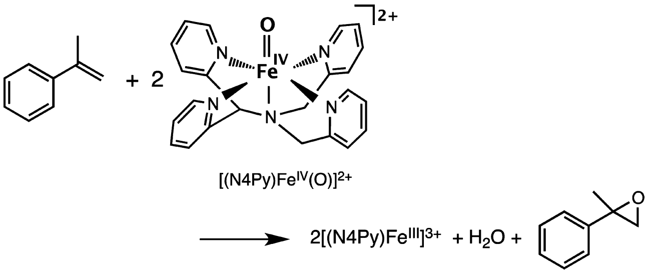


Figure 1. (a) Visible spectral changes observed in the oxidation of *α*-methylstyrene (6.3 mM) by $[(N4Py)Fe^{IV}(O)]^{2+}$ (0.25 mM) in the presence of 10 mM of HOTf in MeCN at 298 K. (b) Time course monitored by absorbance at 695 nm due to the decay of $[(N4Py)Fe^{IV}(O)]^{2+}$.

The $[(N4Py)Fe^{III}]^{3+}$ species was the metal product, which was confirmed by EPR (Figure S3 in Supporting Information). No EPR signal due to the high-spin Fe(III) species was observed at the low magnetic field region. The formation of 2 equiv of $[(N4Py)Fe^{III}]^{3+}$ has been confirmed by the EPR quantification and titration (Supporting Information Figure S3). Acetonitrile may be coordinated as the sixth ligand to $[(N4Py)Fe^{III}]^{3+}$. The stoichiometry of the reaction of styrene derivatives with $[(N4Py)Fe^{IV}(O)]^{2+}$ in the presence of HOTf to yield epoxides is given by Scheme 1, where *α*-methylstyrene is taken as an example and the maximum yield based on $[(N4Py)Fe^{IV}(O)]^{2+}$ was 50%; 50% of *α*-methylstyrene unreacted should remain if 1 equiv of *α*-methylstyrene is used (Supporting Information Figure S1). Styrene and *p*-substituted styrene derivatives were also oxidized by $[(N4Py)Fe^{IV}(O)]^{2+}$ in the presence of HOTf to produce the corresponding epoxides, which were not stable in the reaction solutions containing HOTf.[32]

Scheme 1



The rate of oxidation of *α*-methylstyrene by $[(N4Py)Fe^{IV}(O)]^{2+}$in the presence of HOTf (10 mM) in MeCN was monitored by the change of the absorbance at 695 nm due to $[(N4Py)Fe^{IV}(O)]^{2+}$ (Figure 1b), obeying first-order kinetics with large excess *α*-methylstyrene and HOTf (Figure S4 in Supporting Information). The pseudo-first-order rate constant (k_f) increased with increasing concentration of styrene ([S]) linearly up to 15 mM (Figure S5 in Supporting Information). Similarly, the k_f values of other styrene derivatives were also proportional to concentrations of styrene derivatives (Figure S6 in Supporting Information). The observed second-order rate constants (k_{obs}) of epoxidation of styrene derivatives by $[(N4Py)Fe^{IV}(O)]^{2+}$ were determined from the slope in the plot of k_f versus concentration of styrene derivatives with HOTf (10 mM) in MeCN at 298 K; k_{obs} values are listed in Table 1.

The k_{obs} value of styrene oxidation by $[(N4Py)Fe^{IV}(O)]^{2+}$ increased parabolically with increasing [HOTf] as given by eq 1 (see also Figure 2a),

$$k_{obs} = k_0 + [HOTf](k_1 + k_2[HOTf]) \qquad (1)$$

where k_0, k_1, and k_2 are rate constants corresponding to zero-, first-, and second-order dependence on [HOTf], respectively. Similar dependence of k_f on [HOTf] was observed for other styrene derivatives (Figures 2b−d). Because k_0 is negligible, eq 1 is rewritten by eq 2, which exhibits a linear correlation between k_{obs}/[HOTf] and [HOTf] through the origin as shown in Figure 3.

$$k_{obs}/[HOTf] = k_1 + k_2[HOTf] \qquad (2)$$

Such a second-order dependence of k_{obs} on [HOTf] was reported to occur via proton-coupled electron transfer (PCET) from various electron donors to the diprotonated species ($[(N4Py)Fe^{IV}(OH_2)]^{4+}$).[24]

Driving Force Dependence on Rate Constants. The PCET reactivity of $[(N4Py)Fe^{IV}(O)]^{2+}$ in styrene epoxidation is compared with that in outer-sphere electron transfer reactions in light of the Marcus theory of adiabatic intermolecular electron transfer.[25,33] The driving force ($-\Delta G_{et}$) of PCET is obtained from the difference between the one-electron oxidation potentials (E_{ox}) of electron donors and the one-electron reduction potential (E_{red}) of $[(N4Py)Fe^{IV}(O)]^{2+}$ in the presence of HOTf (eq 3)

$$-\Delta G_{et} = e(E_{red} - E_{ox}) \qquad (3)$$

Table 1. One-Electron Oxidation Potentials of Styrene Derivatives, Formation Constants (K) of Complexes between Styrene Derivatives and $[(N4Py)Fe^{IV}(O)]^{2+}$, and Second-Order Rate Constants (k_{obs}) in Oxidation of Styrene Derivatives by $[(N4Py)Fe^{IV}(O)]^{2+}$ in the Presence of HOTf (10 mM) in MeCN at 298 K

no.	styrene derivative	E_{ox}[a] (V vs SCE)	K, M^{-1}	k_{obs}, M^{-1} s^{-1}
1	*trans*-stilbene	1.41	$(1.5 \pm 0.5) \times 10^2$	$(4.0 \pm 0.2) \times 10^2$
2	1,1-diphenylethene	1.73	$(9.5 \pm 0.5) \times 10$	$(1.5 \pm 0.2) \times 10$
3	α-methylstyrene	1.82	$(9.8 \pm 0.5) \times 10$	3.3 ± 0.3
4	3-methylstyrene	1.86	$(6.7 \pm 0.4) \times 10$	$(5.0 \pm 0.3) \times 10^{-1}$
5	styrene	1.88	$(3.8 \pm 1.0) \times 10$	$(4.3 \pm 0.3) \times 10^{-2}$

[a] One-electron oxidation potentials were determined by the second-harmonic alternating current voltammetry (SHACV) measurements at scan rate of 4 mV s^{-1} using a Pt working electrode (see Figure S7 in Supporting Information).

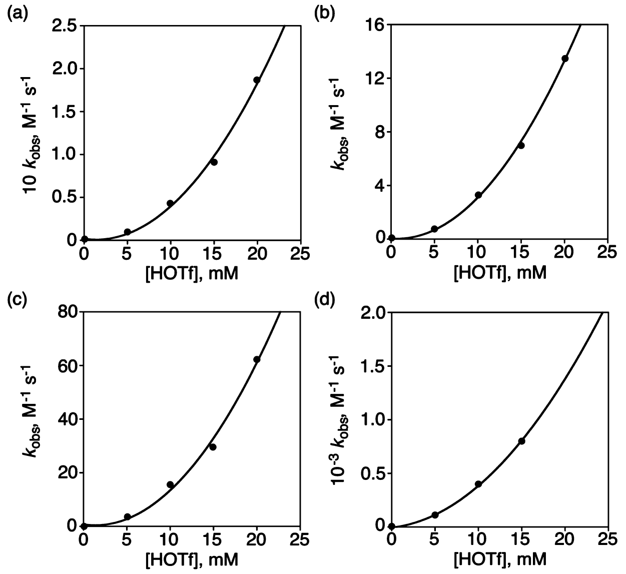


Figure 2. Plots of second-order rate constants (k_{obs}) vs concentrations of HOTf for oxidation of styrene derivatives [(a) styrene, (b) α-methylstyrene, (c) 1,1-diphenylethylene, and (d) *trans*-stilbene] by $[(N4Py)Fe^{IV}(O)]^{2+}$ (0.25 mM) in the presence of HOTf in MeCN at 298 K.

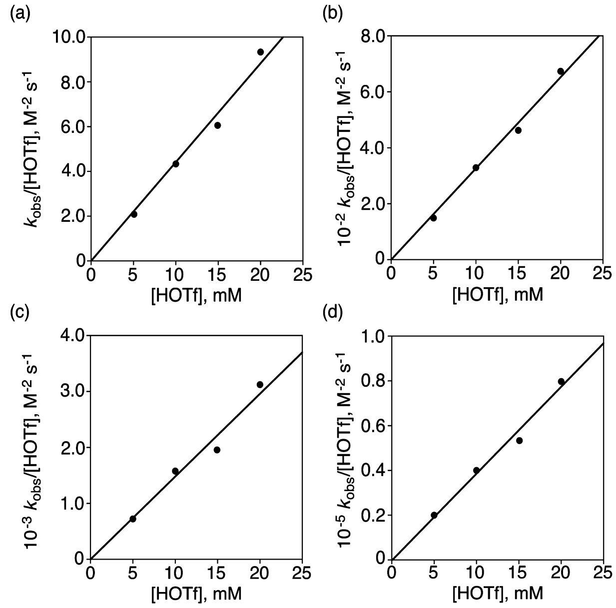


Figure 3. Plots of k_{obs}/[HOTf] vs [HOTf] for epoxidation of styrene derivatives [(a) styrene, (b) α-methylstyrene, (c) 1,1-dipheynylethene, and (d) *trans*-stilbene] by $[(N4Py)Fe^{IV}(O)]^{2+}$ (0.25 mM) in the presence of HOTf (10 mM) in MeCN at 298 K.

where e is the elementary charge. The E_{ox} values of styrene derivatives were determined by SHACV measurements (Figure S7 in Supporting Information).

The driving force dependence of log k_{et} of electron transfer from outer-sphere one-electron reductants (coordinatively saturated metal complexes) to $[(N4Py)Fe^{IV}(O)]^{2+}$ in the absence and presence of 10 mM of HOTf (reactions of 18–28 in Figure 4) is well-fitted by the Marcus equation of outer-sphere intermolecular electron transfer (eq 4),[24,25]

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

where Z is the frequency factor ($Z = k_BTK/h$ where k_B is the Boltzmann constant, T is absolute temperature, K is the formation constant of the precursor complex, and h is the Planck constant), using the same value of reorganization energy of electron transfer ($\lambda = 2.74$ eV).[23,25]

The Z value of outer-sphere intermolecular electron transfer reactions is normally taken as 1.0×10^{11} M^{-1} s^{-1}.[34−37] This indicates that the K value of outer-sphere electron transfer reactions is ca. 0.020 M^{-1}, because there is little interaction in the precursor complexes of outer-sphere one-electron reductants (coordinatively saturated metal complexes).

The log k_{obs} values of epoxidation of styrene derivatives by $[(N4Py)Fe^{IV}(O)]^{2+}$ in the presence of 10 mM HOTf (reactions of 1–5) are significantly larger than the log k_{et} values of outer-sphere electron transfer reactions of $[(N4Py)Fe^{IV}(O)]^{2+}$ in the presence of 10 mM HOTf (see solid line in Figure 4). For example, the k_{obs} value of *trans*-stilbene (1) is 2 orders magnitude larger than the corresponding k_{et} value. The log k_{obs} values of oxygen atom transfer from thioanisoles to $[(N4Py)Fe^{IV}(O)]^{2+}$ (reactions of 6–10)[24] and hydrogen atom transfer from toluene derivatives to $[(N4Py)Fe^{IV}(O)]^{2+}$ (reactions of 11–17)[24] in the presence of 10 mM HOTf are also significantly larger than the Marcus line (solid line in Figure 4) for outer-sphere electron transfer reactions. Such deviation from the Marcus line may result from the difference in the K values of precursor complexes, because the stronger interaction of $[(N4Py)Fe^{IV}(OH_2)]^{4+}$ with organic substrates (styrene derivatives, thioanisoles, and toluene derivatives) is expected as compared with that of outer-sphere one-electron reductants (coordinatively saturated metal complexes).[24] This was confirmed by examining the dependence of the pseudo-first-order rate constants (k_f) on concentrations of styrene derivatives in the large concentration range (vide infra).

The dependence of k_f values of oxidation of styrene by $[(N4Py)Fe^{IV}(O)]^{2+}$ in the presence of HOTf (10 mM) on concentration of styrene exhibits a saturation behavior as shown in Figure 5. Such a saturation behavior is expressed by

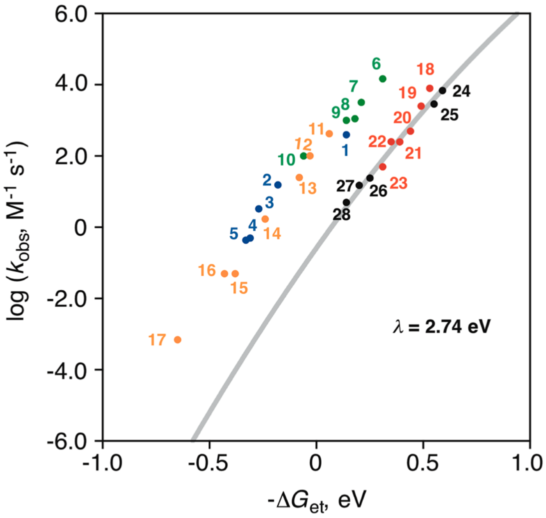


Figure 4. Driving force ($-\Delta G_{et}$) dependence of log k_{obs} for oxidation of styrene and toluene derivatives [(1) *trans*-stilbene, (2) 1,1-diphenylethene, (3) α-methylstyrene, (4) 3-methylstyrene, (5) styrene, (6) *p*-Me-thioanisole, (7) thioanisole, (8) *p*-Cl-thioanisole, (9) *p*-Br-thioanisole, (10) *p*-CN-thioanisole, (11) hexamethylbenzene, (12) 1,2,3,4,5-pentamethylbenzene, (13) 1,2,4,5-tetramethylbenzene, (14) 1,2,4-trimethylbenzene, (15) 1,4-dimethylbenzene, (16) 1,3,5-trimethylbenzene, and (17) toluene] by $[(N4Py)Fe^{IV}(O)]^{2+}$ and log k_{et} for PCET from various electron donors {coordinatively saturated metal complexes; (18) $[(Ph_2Phen)_3Fe^{II}]^{2+}$, (19) $[(bpy)_3Fe^{II}]^{2+}$, (20) $[(4,4'\text{-}Me_2Phen)_3Ru^{II}]^{2+}$, (21) $[(5,5'\text{-}Me_2Phen)_3Ru^{II}]^{2+}$, (22) $[(ClPhen)_3Fe^{II}]^{2+}$, and (23) $[(bpy)_3Ru^{II}]^{2+}$} to $[(N4Py)Fe^{IV}(O)]^{2+}$ in the presence of HOTf (10 mM) in MeCN at 298 K (see Table S1 in Supporting Information). The black circles show the driving force dependence of the rate constants (log k_{et}) of electron transfer from electron donors [(24) decamethylferrocene, (25) octamethylferrocene, (26) 1.1′-dimethylferrocene, (27) *n*-amylferrocene, and (28) ferrocene] to $[(N4Py)Fe^{IV}(O)]^{2+}$ in the absence of HOTf in MeCN at 298 K.[38]

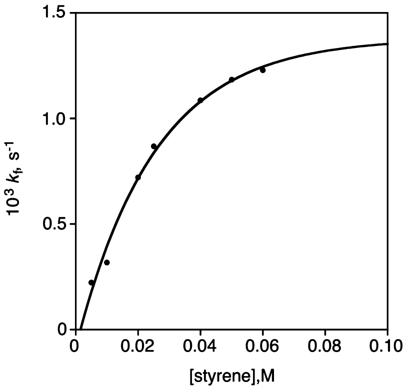


Figure 5. Plot of first-order rate constant (k_f) vs concentration of styrene in the reaction of $[(N4Py)Fe^{IV}(O)]^{2+}$ (0.25 mM) with styrene in the presence of 10 mM of HOTf in MeCN at 298 K.

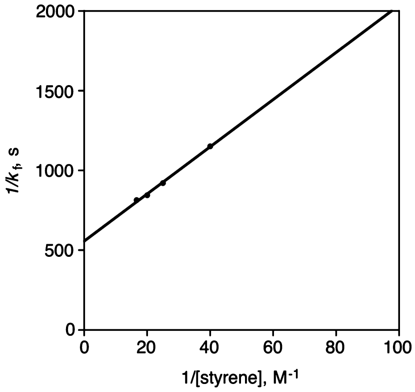


Figure 6. Plot of $1/k_f$ vs 1/[styrene] for oxidation of styrene by $[(N4Py)Fe^{IV}(O)]^{2+}$ in the presence of HOTf (10 mM) in MeCN at 298 K. The slope $[(k_{ET}K)^{-1}]$ and intercept $(k_{ET}{}^{-1})$ were determined to be 1.5 × 10 M s and 5.5 × 10^2 s, respectively.

eq 5, resulting from formation of the precursor complex with the formation constant K prior to electron transfer (k_{ET}) as reported previously.[24] The k_{ET} and K values are obtained from the intercept and slope of a linear plot of $k_f{}^{-1}$ versus $[S]^{-1}$ (eq 6) as shown in Figure 6 to be 1.8 × 10^{-3} s^{-1} and 37 M^{-1}, respectively. Similarly, the k_{ET} and K values were determined for oxidation of various styrene derivatives by $[(N4Py)Fe^{IV}(O)]^{2+}$ in the presence of HOTf (10 mM) in MeCN at 298 K (Figures S8 − S11 in Supporting Information) as listed in Table 1 together with the one-electron oxidation potentials of styrene derivatives (E_{ox}, see Figure S7 in Supporting Information).[39] Both the k_{ET} and K values increase with decreasing the E_{ox} values of styrene derivatives, because both electron transfer and charge transfer become thermodynamically more feasible.

$$k_f = k_{ET}K[S]/(1 + K[S]) \qquad (5)$$

$$k_f{}^{-1} = (k_{ET}K)^{-1}[S]^{-1} + k_{ET}{}^{-1} \qquad (6)$$

The first-order (unimolecular) rate constants (k_{ET}) of PCET from various electron donors to the diprotonated species ($[(N4Py)Fe^{IV}(O)^{2+}\text{-}(HOTf)_2]$) in the precursor complexes can be well-fitted as a function of the driving force of PCET by the Marcus equation of the adiabatic outer-sphere intramolecular electron transfer as given by eq 7.[24]

$$k_{ET} = (k_BT/h)\exp[-(\lambda/4)(1 + \Delta G_{et}/\lambda)^2/k_BT] \qquad (7)$$

The driving force dependence of k_{ET} of oxidation of styrene derivatives by $[(N4Py)Fe^{IV}(O)]^{2+}$ in the presence of 10 mM HOTf in MeCN at 298 K is remarkably unified with that of k_{ET} of PCET from various electron donors to $[(N4Py)Fe^{IV}(O)]^{2+}$ using the same value of reorganization energy of electron transfer (λ = 2.74 eV) as shown in Figure 7.[23,24]

The unified driving force dependence of k_{ET} in Figure 7 strongly indicates that the rate-determining step in the epoxidation of styrene derivatives by $[(N4Py)Fe^{IV}(O)^{2+}\text{-}(HOTf)_2]$ in the presence of HOTf (10 mM) in MeCN is definitely PCET from styrene derivatives to the diprotonated species ($[(N4Py)Fe^{IV}(O)^{2+}\text{-}(HOTf)_2]$) as shown in Scheme 2, which has been proposed for oxidation of toluene and thioanisole derivatives by $[(N4Py)Fe^{IV}(O)^{2+}\text{-}(HOTf)_2]$.[23,24] The formation constants of precursor complexes of $[(N4Py)Fe^{IV}(OH_2)]^{4+}$ with styrene derivatives prior to electron transfer in Table 1 are similar to those reported for toluene and thioanisole derivatives.[24] The rate-determining PCET may be followed by rapid $O^{\bullet-}$ transfer from $[(N4Py)Fe^{III}(OH_2)]^{3+}$ to styrene radical cation to produce $[(N4Py)Fe^{II}]^{2+}$ and styrene epoxide by releasing two protons (Scheme 2). Because the corresponding epoxide was obtained without radical coupling products, the produced radical in Scheme 2 is caged to react with $[(N4Py)Fe^{III}(OH_2)]^{3+}$ in the cage. $[(N4Py)Fe^{II}]^{2+}$ must be rapidly oxidized by $[(N4Py)Fe^{IV}(O)]^{2+}$ with two protons to produce 2 equiv of $[(N4Py)Fe^{III}]^{3+}$ and H_2O, because the one-

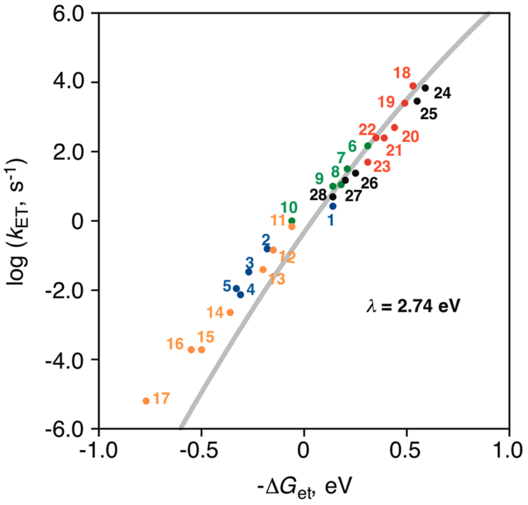
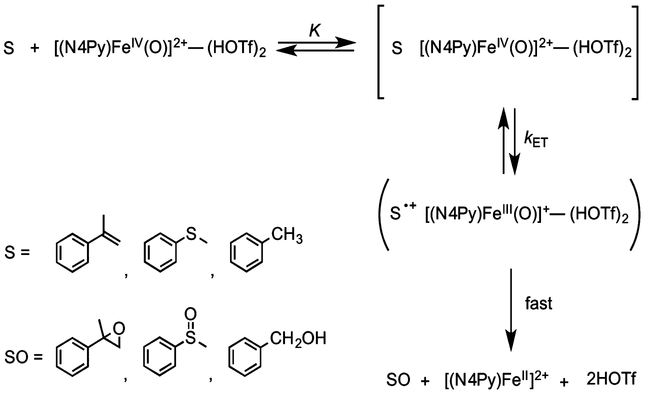


Figure 7. Driving force ($-\Delta G_{et}$) dependence of log k_{obs} for oxidation of styrene and toluene derivatives [(1) *trans*-stilbene, (2) 1,1-diphenylethene, (3) α-methylstyrene, (4) 3-methylstyrene, (5) styrene, (6) *p*-Me-thioanisole, (7) thioanisole, (8) *p*-Cl-thioanisole, (9) *p*-Br-thioanisole, (10) *p*-CN-thioanisole, (11) hexamethylbenzene, (12) 1,2,3,4,5-pentamethylbenzene, (13) 1,2,4,5-tetramethylbenzene, (14) 1,2,4-trimethylbenzene, (15) 1,4-dimethylbenzene, (16) 1,3,5-trimethylbenzene, and (17) toluene] by $[(\mathrm{N4Py})\mathrm{Fe}^{\mathrm{IV}}(\mathrm{O})]^{2+}$ and log k_{ET} for PCET from various electron donors {coordinatively saturated metal complexes; (18) $[(\mathrm{Ph_2Phen})_3\mathrm{Fe}^{\mathrm{II}}]^{2+}$, (19) $[(\mathrm{bpy})_3\mathrm{Fe}^{\mathrm{II}}]^{2+}$, (20) $[(4,4'\text{-}\mathrm{Me_2Phen})_3\mathrm{Ru}^{\mathrm{II}}]^{2+}$, (21) $[(5,5'\text{-}\mathrm{Me_2Phen})_3\mathrm{Ru}^{\mathrm{II}}]^{2+}$, (22) $[(\mathrm{ClPhen})_3\mathrm{Fe}^{\mathrm{II}}]^{2+}$, and (23) $[(\mathrm{bpy})_3\mathrm{Ru}^{\mathrm{II}}]^{2+}$} to $[(\mathrm{N4Py})\mathrm{Fe}^{\mathrm{IV}}(\mathrm{O})]^{2+}$ in the presence of HOTf (10 mM) in MeCN at 298 K (Tables S1 and S2 in Supporting Information). The black circles show the driving force dependence of the rate constants (log k_{et}'s) of electron transfer from electron donors [(24) decamethylferrocene, (25) octamethylferrocene, (26) 1.1′-dimethylferrocene, (27) *n*-amylferrocene, and (28) ferrocene] to $[(\mathrm{N4Py})\mathrm{Fe}^{\mathrm{IV}}(\mathrm{O})]^{2+}$ in the absence of HOTf in MeCN at 298 K.[38] The pink and purple rectangles show the driving force ($-\Delta G_{et}$) dependence of log k_{obs} for oxidation of (29) styrene oxide and (30) cyclohexene by $[(\mathrm{N4Py})\mathrm{Fe}^{\mathrm{IV}}(\mathrm{O})]^{2+}$ in the presence of HOTf (10 mM) in MeCN at 298 K.

Scheme 2. Unified Mechanism of HOTf-Promoted Oxidation of Styrene, Thioanisole, and Toluene derivatives by $[(\mathrm{N4Py})\mathrm{Fe}^{\mathrm{IV}}(\mathrm{O})]^{2+}$



electron reduction potential of $[(\mathrm{N4Py})\mathrm{Fe}^{\mathrm{IV}}(\mathrm{O})]^{2+}$ in the presence of 10 mM HOTf (E_{red} = 1.55 V vs SCE) is much more positive than the one-electron oxidation potential of $[(\mathrm{N4Py})\mathrm{Fe}^{\mathrm{II}}]^{2+}$ (E_{ox} = 1.00 V vs SCE).[24] The styrene oxide may be further oxidized by $[(\mathrm{N4Py})\mathrm{Fe}^{\mathrm{IV}}(\mathrm{O})]^{2+}$ in the presence of HOTf to produce benzaldehyde, which was confirmed by starting the reaction using styrene oxide instead of styrene (Figure S12 in Supporting Information). Because the E_{ox} value of styrene oxide (1.75 V vs SCE, Figure S13 in Supporting Information) is lower than the E_{ox} value of styrene, the oxidation of styrene oxide by $[(\mathrm{N4Py})\mathrm{Fe}^{\mathrm{IV}}(\mathrm{O})]^{2+}$ in the presence of HOTf may also proceed via the rate-determining PCET pathway (pink circle in Figure 7; Figure S14 in Supporting Information).[40]

When styrene (E_{ox} = 1.88 V vs SCE) was replaced by cyclohexene (E_{ox} = 2.30 V vs SCE, Figure S15 in Supporting Information), no acceleration of the rate of oxidation of cyclohexene by $[(\mathrm{N4Py})\mathrm{Fe}^{\mathrm{IV}}(\mathrm{O})]^{2+}$ was observed by the presence of HOTf in MeCN at 298 K as shown in Figure 8.

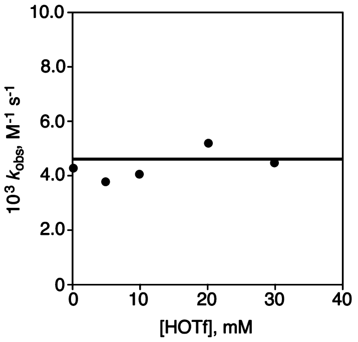


Figure 8. Plot of second-order rate constants (k_{obs}'s) for oxidation of cyclohexene by $[(\mathrm{N4Py})\mathrm{Fe}^{\mathrm{IV}}(\mathrm{O})]^{2+}$ (0.25 mM) in the presence of HOTf (10 mM) in MeCN at 298 K vs concentrations of HOTf.

In this case no epoxide was formed, and instead the allylic oxidation occurred as reported previously.[41] The k_f values of oxidation of cyclohexene by $[(\mathrm{N4Py})\mathrm{Fe}^{\mathrm{IV}}(\mathrm{O})]^{2+}$ in the presence of HOTf (10 mM) also show saturation behavior with very high concentration of cyclohexene (Figure S16 in Supporting Information). The K value was determined as 7 (±2), which is a quite small value compared with other styrene derivatives. Since the driving forces of PCET from styrene and cyclohexene to $[(\mathrm{N4Py})\mathrm{Fe}^{\mathrm{IV}}(\mathrm{O})]^{2+}$ in the presence of 10 mM HOTf are $-\Delta G_{et}$ = −0.30 and −0.75 eV, respectively, the energetic limit for the PCET pathway may be located around $-\Delta G_{et} > -0.30$ eV.[24] The allylic oxidation of cyclohexene by $[(\mathrm{N4Py})\mathrm{Fe}^{\mathrm{IV}}(\mathrm{O})]^{2+}$ may occur via hydrogen atom transfer as indicated by the large KIE value.[41] In sharp contrast to the PCERT pathway, the hydrogen atom transfer is retarded when $[(\mathrm{N4Py})\mathrm{Fe}^{\mathrm{IV}}(\mathrm{O})]^{2+}$ is protonated by HOTf because of the steric effect of HOTf.

■ CONCLUSION

We have shown that the protonation of $[(\mathrm{N4Py})\mathrm{Fe}^{\mathrm{IV}}(\mathrm{O})]^{2+}$ with HOTf increases the reactivity of the iron(IV)-oxo species that allows the occurrence of the epoxidation of styrene derivatives via PCET from styrene derivatives to $[(\mathrm{N4Py})\mathrm{Fe}^{\mathrm{IV}}(\mathrm{OH_2})]^{4+}$, as demonstrated in the case of C−H bond cleavage of toluene derivatives and sulfoxidation of thioanisole derivatives by $[(\mathrm{N4Py})\mathrm{Fe}^{\mathrm{IV}}(\mathrm{O})]^{2+}$ with HOTf. Such a drastic enhancement of the reactivity of $[(\mathrm{N4Py})\mathrm{Fe}^{\mathrm{IV}}(\mathrm{O})]^{2+}$ with HOTf via PCET pathways may open a new strategy for efficient oxidation of various substrates by high-valent metal-oxo complexes. Moreover, a unified PCET driving force dependence shown in Figure 7 makes it possible to evaluate PCET reactivity of high-valent metal-oxo complexes toward substrate oxidation quantitatively.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Tables S1−S2 and Figures S1−S16. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b00504.

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Notes

The authors declare no competing financial interest.

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