Electron-Transfer Kinetics for Generation of Organoiron(IV) Porphyrins and the Iron(IV) Porphyrin π Radical Cations

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Abstract: Homogeneous electron-transfer kinetics for the oxidation of seven different iron(III) porphyrins using three different oxidants were examined in deaerated acetonitrile, and the resulting data were evaluated in light of the Marcus theory of electron transfer to determine reorganization energies of the rate-determining oxidation of iron(III) to iron(IV). The investigated compounds are represented as (P)Fe(R), where P = the dianion of 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraphenylporphyrin (OETPP) and R = C_6H_5, 3,5-$C_6F_2H_3$, 2,4,6-$C_6F_3H_2$, or C_6F_5 or P = the dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin (OEP) and R = C_6H_5, 2,4,6-$C_6F_3H_2$, or 2,3,5,6-C_6F_4H. The first one-electron transfer from (P)Fe(R) to [Ru(bpy)$_3$]$^{3+}$ (bpy = 2,2′-bipyridine) leads to an Fe(IV) σ-bonded complex, [(P)Fe^{IV}(R)]$^+$, and occurs at a rate which is much slower than the second one-electron transfer from [(P)Fe^{IV}(R)]$^+$ to [Ru(bpy)$_3$]$^{3+}$ to give [(P)Fe^{IV}(R)]$^{\bullet 2+}$. The one- or two-electron oxidation of each (OETPP)Fe(R) or (OEP)Fe(R) derivative was also attained by using [Fe(phen)$_3$]$^{3+}$ (phen = 1,10-phenanthroline) or [Fe(4,7-Me$_2$phen)$_3$]$^{3+}$ (Me$_2$phen = 4,7-dimethyl-1,10-phenanthroline) as an electron-transfer oxidant. The reorganization energies (kcal mol^{-1}) for the metal-centered oxidation of (P)-Fe^{III}(R) to [(P)Fe^{IV}(R)]$^+$ increase in the order (OEP)Fe(R) (83 ± 4) ≪ (OETPP)Fe(C$_6$F$_5$) (99 ± 2) < (OETPP)-Fe(2,4,6-C$_6$F$_3$H$_2$) (107 ± 2) < (OETPP)Fe(3,5-C$_6$F$_2$H$_3$) (109 ± 3) < (OETPP)Fe(C$_6$H$_5$) (113 ± 3). Each value is significantly larger than the reorganization energies determined for the porphyrin-centered oxidations involving the same two series of compounds, i.e., the second electron transfer of (P)Fe(R). In each case, the first metal-centered oxidation is the rate-determining step for generation of the iron(IV) porphyrin π radical cation. Coordination of pyridine to (OETPP)Fe(C$_6$F$_5$) as a sixth axial ligand enhances significantly the rate of electron-transfer oxidation.

Iron(IV) porphyrin π radical cations play an essential role in a number of oxidative catalytic processes including biological systems.[2–7] Although high-valent iron porphyrins are usually extremely reactive and thus difficult to characterize,[8] the one- and two-electron oxidations of σ-bonded iron porphyrins such

as (P)Fe(R), where P is a given porphyrin dianion, will lead first to an iron(IV) porphyrin and then to an iron(IV) porphyrin π radical cation, both of which have a stability that depends in large part upon the nature of the σ-bonded axial ligand (R) and the porphyrin macrocycle (P).[9,10] For example, the one-electron oxidation of (OETPP)Fe(C$_6$H$_5$) which has a saddle-shaped nonplanar porphyrin macrocycle (OETPP = the dianion of 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraphenylporphyrin) leads to a relatively stable iron(IV) compound, [(OETPP)-Fe^{IV}(C$_6$H$_5$)]$^+$.[11,12] In this regard, some octaalkyltetraphenylporphyrins, which are nonplanar as a result of steric crowding of the peripheral substituents, have been used as model compounds to investigate the consequences of nonplanar conformational distortions.[13–15] The further one-electron oxidation of [(OETPP)-

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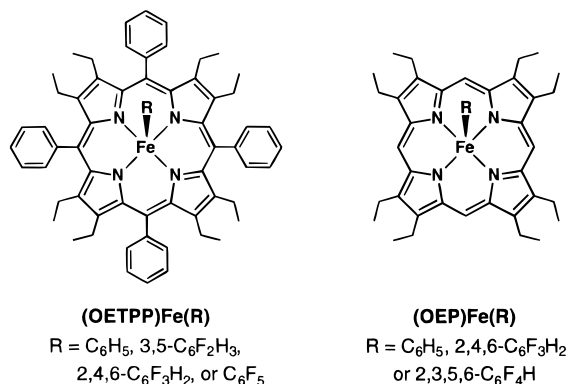
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Chart 1

(OETPP)Fe(R)
R = C_6H_5, 3,5-C_6F_2H_3,
2,4,6-C_6F_3H_2, or C_6F_5

(OEP)Fe(R)
R = C_6H_5, 2,4,6-C_6F_3H_2
or 2,3,5,6-C_6F_4H

$Fe^{IV}(C_6H_5)]^+$ leads to an Fe(IV) porphyrin π radical cation, formally an Fe(V) compound, and this is followed by migration of the σ-bonded C_6H_5 ligand to a nitrogen of the porphyrin ring to give $[(N\text{-}C_6H_5OETPP)Fe^{III}]^{2+}$.[11,12] A migration of the σ-bonded axial ligand from singly oxidized iron porphyrins with planar macrocycles such as $(OEP)Fe(C_6H_5)$ or $(TPP)Fe(C_6H_5)$ (OEP = the dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin and TPP = the dianion of 5,10,15,20-tetraphenylporphyrin) has long been known to occur, and the resulting migration product can be further oxidized at the metal center to give $[(N\text{-}C_6H_5OEP)Fe^{III}]^{2+}$ and $[(N\text{-}C_6H_5TPP)Fe^{III}]^{2+}$ in the presence of excess oxidizing agent or under the application of an applied oxidizing potential.[16] Reversible oxidations have been obtained for both (OETPP)-Fe(R) and (OEP)Fe(R) by cyclic voltammetry at moderate scan rates,[11,12] but there has so far been no report in the literature on the kinetics of electron-transfer reactions for generation of iron-(IV) porphyrins or iron(IV) porphyrin π radical cations prior to the migration step which occurs on a much longer time scale than the electron transfer.

This study reports the first kinetic data for the electron-transfer oxidation of (P)Fe(R) derivatives, where P = OETPP and R = C_6H_5, 3,5-C_6F_2H_3, 2,4,6-C_6F_3H_2, or C_6F_5 or P = OEP and R = C_6H_5, 2,4,6-C_6F_3H_2, or 2,3,5,6-C_6F_4H (see Chart 1). In addition, plots of logarithms of rate constants for electron transfer vs the free energy change of electron transfer lead to the first evaluation of reorganization energies (λ) for formation of iron(IV) porphyrins and iron(IV) porphyrin π radical cations in light of the Marcus theory of electron transfer.[17] A comparison of the reorganization energies between (OETPP)Fe(R) and (OEP)Fe-(R) provides an excellent opportunity to understand the effects of nonplanar conformational distortion on the intrinsic barrier for the electron-transfer reactions.

Experimental Section

Materials. Free-base (OETPP)H_2 was prepared from benzaldehyde and 3,4-diethylpyrrole in the presence of BF_3·OEt_2, followed by oxidation of a resulting porphyrinogen with 2,3-dichloro-5,6-dicyano-

1,4-benzoquinone as described in the literature.[18] Iron was inserted using ferrous chloride tetrahydrate in deoxygenated dimethylformamide, and the formation of (OETPP)FeCl was confirmed by ^{1}H NMR as described elsewhere.[14] The (OETPP)Fe(R) complexes (R = C_6H_5, 3,5-C_6F_2H_3, 2,4,6-C_6F_3H_2, C_6F_5) were prepared by reacting an aryl Grignard reagent with (OETPP)FeCl according to literature procedures.[11,19] The synthesis of (OEP)Fe(R), where R = C_6H_5, 2,4,6-C_6F_3H_2, and 2,3,5,6-C_6F_4H, was carried out by reacting the corresponding aryl Grignard reagent with (OEP)FeCl according to literature procedures.[10,16a,20,21] Tris(2,2'-bipyridine)ruthenium dichloride hexahydrate, [Ru(bpy)_3]Cl_2·6H_2O, was obtained commercially from Aldrich. The oxidation of [Ru(bpy)_3]Cl_2 with lead dioxide in aqueous H_2SO_4 gives $[Ru(bpy)_3]^{3+}$, which was isolated as the PF_6 salt, [Ru(bpy)_3](PF_6)_3.[22] Tris(1,10-phenanthroline)-iron(II) and tris(4,7-dimethyl-1,10-phenanthroline)iron(II) complexes were prepared by adding 3 equiv of the corresponding ligand to an aqueous solution of ferrous sulfate.[23] Tris(1,10-phenanthroline)iron-(III) perchlorate, [Fe(phen)_3](ClO_4)_3, and tris(4,7-dimethyl-1,10-phenan-throline)iron(III) hexafluorophosphate, [Fe(4,7-Me_2phen)_3](PF_6)_3, were prepared by oxidizing the corresponding iron(II) complexes with ceric ammonium sulfate or lead dioxide in aqueous H_2SO_4 followed by the addition of NaClO_4 or KPF_6.[23,24] Acetonitrile (MeCN) and benzonitrile (PhCN) were purchased from Wako Pure Chemical Ind., Ltd., and purified by successive distillation over CaH_2 and P_2O_5, respectively, according to standard procedures.[25] Pyridine (py) was obtained commercially and purified using standard methods.[25] Tetra-n-butylammonium perchlorate (TBAP) was purchased from Sigma Chemical Co., recrystallized from ethyl alcohol, and dried under vacuum at 40 °C for at least 1 week prior to use.

Spectral and Kinetic Measurements. Typically, a 10 μL aliquot of [Ru(bpy)_3](PF_6)_3 (3.0×10^{-3} M) in MeCN was added to a quartz cuvette (10 mm i.d.) which contained (OETPP)Fe(C_6H_5) (5.0×10^{-6} M) in deaerated MeCN (3.0 mL). This led to an electron transfer from (OETPP)Fe(C_6H_5) to [Ru(bpy)_3](PF_6)_3. UV–vis spectral changes associated with this electron transfer were monitored using a Shimadzu UV-2200 spectrophotometer, a Hewlett-Packard 8452A diode array spectrophotometer, or a Hewlett-Packard 8453 diode array spectrophotometer. The same procedure was used for spectral measurements for other σ-bonded iron porphyrins. The coordination of pyridine as a sixth axial ligand to (OETPP)Fe(C_6F_5) in MeCN was monitored by measuring the UV–vis spectral changes as a function of the ligand concentration. All measurements were carried out in a dark cell compartment using deaerated solutions. It was confirmed that the monitoring light did not affect the thermal rates.

Kinetic measurements of the electron transfer from (P)Fe(R) to the oxidants were carried out using a Union RA-103 stopped-flow spectrophotometer under deaerated conditions. Typically, deaerated MeCN solutions of (OETPP)Fe(C_6H_5) and [Ru(bpy)_3](PF_6)_3 were transferred to the spectrophotometric cell by means of a glass syringe which had earlier been purged with a stream of argon. Rates of electron transfer from (OETPP)Fe(C_6H_5) to [Ru(bpy)_3]$^{3+}$ in deaerated MeCN at 298 K were monitored by following a decrease in absorbance at 431 nm ($\epsilon = 1.04 \times 10^5$ M^{-1} cm^{-1}) due to (OETPP)Fe(C_6H_5) or an increase in absorbance at 287 nm ($\epsilon = 7.90 \times 10^4$ M^{-1} cm^{-1})[26] due to

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Table 1. Rate Constants (k_{et}, M^{-1} s^{-1}) and Free Energy Changes (ΔG^0_{et}, eV) for First One-Electron Oxidation of (P)Fe(R) with Various Oxidants in Deaerated MeCN at 298 K, Their Redox Potentials (E^1_{ox}, E^2_{ox}, and E^0_{red}, V vs SCE), and Reorganization Energies (λ_{11}, kcal mol^{-1}) for the Self-Exchange Reaction of (P)Fe(R)/[(P)Fe(R)]$^+$

(P)Fe(R)	E^1_{ox},[a] V	E^2_{ox},[a] V	oxidant	E^0_{red},[b] V	k_{et}, M^{-1} s^{-1} (ΔG^0_{et}, eV)	λ_{11}, kcal mol^{-1}
(OETPP)Fe(C$_6$H$_5$) (**1**)	0.27	1.06	[Ru(bpy)$_3$](PF$_6$)$_3$	1.24	2.0×10^7 (-0.97)	112
			[Fe(phen)$_3$](ClO$_4$)$_3$	1.07	7.7×10^5 (-0.80)	118
			[Fe(4,7-Me$_2$phen)$_3$](PF$_6$)$_3$	0.90	3.4×10^5 (-0.63)	110
(OETPP)Fe(3,5-C$_6$F$_2$H$_3$) (**2**)	0.39[c]	0.93[c]	[Ru(bpy)$_3$](PF$_6$)$_3$	1.24	7.8×10^6 (-0.85)	109
			[Fe(phen)$_3$](ClO$_4$)$_3$	1.07	4.5×10^5 (-0.68)	112
			[Fe(4,7-Me$_2$phen)$_3$](PF$_6$)$_3$	0.90	1.3×10^5 (-0.51)	106
(OETPP)Fe(2,4,6-C$_6$F$_3$H$_2$) (**3**)	0.48[c]	0.84[c]	[Ru(bpy)$_3$](PF$_6$)$_3$	1.24	2.2×10^6 (-0.76)	110
			[Fe(phen)$_3$](ClO$_4$)$_3$	1.07	5.7×10^5 (-0.59)	105
			[Fe(4,7-Me$_2$phen)$_3$](PF$_6$)$_3$	0.90	3.1×10^4 (-0.42)	106
(OETPP)Fe(C$_6$F$_5$) (**4**)	0.56	0.80	[Ru(bpy)$_3$](PF$_6$)$_3$	1.24	3.6×10^6 (-0.68)	102
			[Fe(phen)$_3$](ClO$_4$)$_3$	1.07	5.0×10^5 (-0.51)	99
			[Fe(4,7-Me$_2$phen)$_3$](PF$_6$)$_3$	0.90	6.7×10^5 (-0.34)	96
(OEP)Fe(C$_6$H$_5$) (**5**)	0.48	1.30	[Ru(bpy)$_3$](PF$_6$)$_3$	1.24	too fast (-0.76)	
			[Fe(phen)$_3$](ClO$_4$)$_3$	1.07	too fast (-0.59)	
			[Fe(4,7-Me$_2$phen)$_3$](PF$_6$)$_3$	0.90	4.7×10^4 (-0.42)	81
(OEP)Fe(2,4,6-C$_6$F$_3$H$_2$) (**6**)	0.76	1.19	[Ru(bpy)$_3$](PF$_6$)$_3$	1.24	3.3×10^6 (-0.48)	88
			[Fe(phen)$_3$](ClO$_4$)$_3$	1.07	1.1×10^6 (-0.31)	80
			[Fe(4,7-Me$_2$phen)$_3$](PF$_6$)$_3$	0.90	1.8×10^4 (-0.14)	86
(OEP)Fe(2,3,5,6-C$_6$F$_4$H) (**7**)	0.79	1.14	[Ru(bpy)$_3$](PF$_6$)$_3$	1.24	3.0×10^6 (-0.45)	86
			[Fe(phen)$_3$](ClO$_4$)$_3$	1.07	1.6×10^6 (-0.28)	76
			[Fe(4,7-Me$_2$phen)$_3$](PF$_6$)$_3$	0.90	1.3×10^4 (-0.11)	85

[a] Taken from refs 10 and 11 unless otherwise noted. [b] E^0_{red} values vs SCE in MeCN, 0.1 M TBAP; see Experimental Section. [c] Determined in this study; see Experimental Section.

[Ru(bpy)$_3$]$^{2+}$. The rate constants of electron transfer (k_{et}) were determined either by the second-order plots for the electron-transfer reactions of (P)Fe(R) with 2 equiv of oxidant or by the pseudo-first-order plots for the electron-transfer reactions in the presence of a large excess oxidant. In each case, it was confirmed that the k_{et} values derived from at least 5 independent measurements agreed within an experimental error of ±5%. Second- or pseudo-first-order rate constants were determined by a least-squares curve fit using a Macintosh microcomputer. The second-order plots of $(A_\infty - A)^{-1}$ vs time and the first-order plots of $\ln(A_\infty - A)$ vs time (A_∞ and A are the final absorbance and the absorbance at the reaction time, respectively) were linear for 3 or more half-lives with the correlation coefficient $\varrho > 0.999$.

Cyclic Voltammetry. The E^0_{red} values of oxidants in MeCN containing 0.1 M TBAP as supporting electrolyte were determined at room temperature by cyclic voltammetry under deaerated conditions using a three-electrode system and a BAS 100B electrochemical analyzer. The E^0_{ox} values of (OETPP)Fe(3,5-C$_6$F$_2$H$_3$) and (OETPP)-Fe(2,4,6-C$_6$F$_3$H$_2$) were determined in PhCN instead of MeCN because of a solubility problem as previously reported for other (P)Fe(R) derivatives.[11] The working and counter electrodes were platinum while Ag/AgNO$_3$ (0.01M) was used as the reference electrode. All potentials are reported as V vs SCE. The $E_{1/2}$ value of ferrocene used as a standard is 0.37 V vs SCE in PhCN or MeCN under our solution conditions.[27]

Results and Discussion

Rates of Electron-Transfer Oxidation of (P)Fe(R). Three oxidants which are strong enough to oxidize (P)Fe^{III}(R) to [(P)-Fe^{IV}(R)]$^+$ or to [(P)Fe^{IV}(R)]$^{•2+}$ were selected for use in acetonitrile (MeCN). The one-electron reduction potentials for the utilized oxidizing agents were determined in this study and are as follows: E^0_{red} = 1.24 V vs SCE for [Ru(bpy)$_3$](PF$_6$)$_3$ (bpy = 2,2′-bipyridine); E^0_{red} = 1.07 V vs SCE for [Fe(phen)$_3$]-(ClO$_4$)$_3$ (phen = 1,10-phenanthroline); E^0_{red} = 0.90 V vs SCE for [Fe(4,7-Me$_2$phen)$_3$](PF$_6$)$_3$ (4,7-Me$_2$phen = 4,7-dimethyl-1,-10-phenanthroline). The first of the three oxidants has an E^0_{red} which is more positive than the second oxidation potentials of each (P)Fe(R) complex except for (OEP)Fe(C$_6$H$_5$) (Table 1),[10,11]

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and the two-electron oxidation of all but one investigated (P)-Fe(R) derivative with [Ru(bpy)$_3$]$^{3+}$ is therefore energetically feasible.

A stopped-flow technique was used to determine the electron-transfer rates. The electron-transfer reaction between (P)Fe(R) (1.0×10^{-5} M) and 2 equiv of [Ru(bpy)$_3$]$^{3+}$ (2.0×10^{-5} M) in MeCN at 298 K was followed by UV–visible spectrophotometry and indicated an increase in absorbance at 287 nm due to the generated [Ru(bpy)$_3$]$^{2+}$ complex (Figure 1a). This is accompanied by a decrease in the Soret band (e.g., at 431 nm for (OETPP)Fe(C$_6$H$_5$)) due to loss of the (P)Fe(R) reactant (Figure 1b). Changes in absorbance due to [Ru(bpy)$_3$]$^{2+}$ formation and consumption of (P)Fe(R) both obey second-order kinetics, thus indicating that the two-electron oxidation of (P)-Fe(R) by [Ru(bpy)$_3$]$^{3+}$ occurs via an initial rate-determining electron transfer (Scheme 1). In such a case, the first electron transfer from (P)Fe(R) to [Ru(bpy)$_3$]$^{3+}$ is much slower than the second one-electron transfer between [(P)Fe^{IV}(R)]$^+$ and [Ru-(bpy)$_3$]$^{3+}$, although this second step is energetically less favorable. The first electron transfer is known to occur at the metal center and the second at the porphyrin ring to give [(P)-Fe^{IV}(R)]$^+$ and [(P)Fe^{IV}(R)]$^{•2+}$, respectively.[10,11] Thus, the metal-centered oxidation is kinetically harder than the macrocycle oxidation.

The one- or two-electron oxidation of each (OETPP)Fe(R) and (OEP)Fe(R) derivative was also attained by using [Fe-(phen)$_3$]$^{3+}$ or [Fe(4,7-Me$_2$phen)$_3$]$^{3+}$ as an electron-transfer oxidant.[28] The observed second-order rate constants for the first rate-determining electron transfer with all three oxidants are listed in Table 1, which includes the first and second oxidation potentials of (OETPP)Fe(R) and (OEP)Fe(R) as well as the one-electron reduction potentials of the three oxidants (see Experimental Section).

Reorganization Energies for Electron-Transfer Oxidation of (P)Fe(R). Reorganization energies for the self-exchange

(28) The singly oxidized Fe(IV) porphyrin was generated in all cases and this was followed by a second electron transfer when the difference in potential between the porphyrin oxidation and the oxidant reduction is energetically feasible, i.e., $\Delta G^0_{et} < 0$.
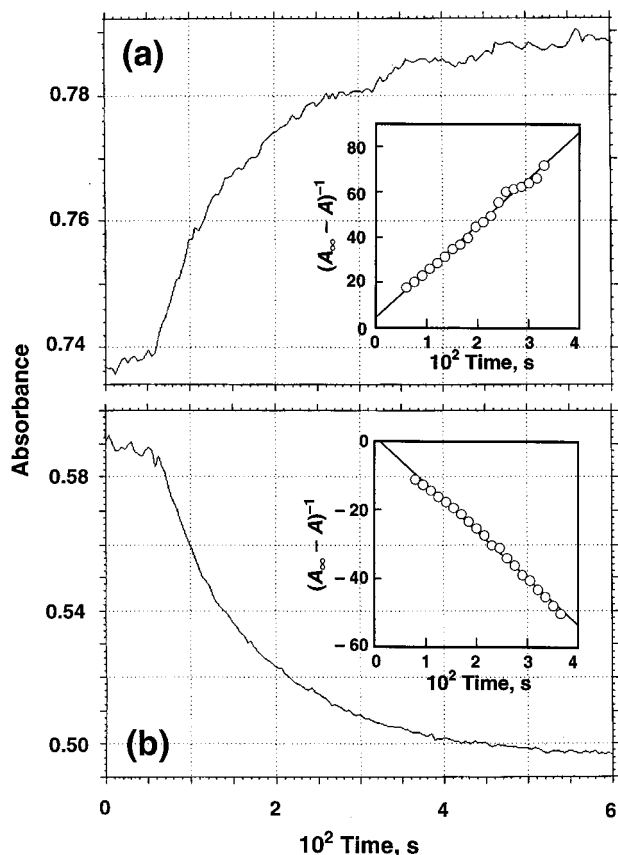
Figure 1. Time course of the absorption change (a) at 287 nm due to formation of $[Ru(bpy)_3]^{2+}$ and (b) at 431 nm due to decay of (OETPP)-Fe(C_6H_5) in the electron-transfer reaction from (OETPP)Fe(C_6H_5) (1.0×10^{-5} M) to $[Ru(bpy)_3]^{3+}$ (2.0×10^{-5} M) in MeCN at 298 K. Inset: second-order plot.

Scheme 1
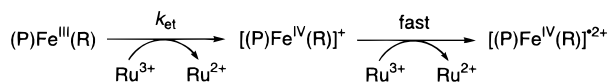
reaction of (P)Fe(R)/[(P)Fe(R)]$^+$ (λ_{11}) are shown in Table 1 and were determined by eq 1, which is readily derived from the Marcus equation,[17] where $\Delta G^{\ddagger}$ is the activation free energy and λ_{22} is the reorganization energy for the self-exchange reaction of oxidant/(oxidant)$^-$.

$$\lambda_{11} = 2(2\Delta G^{\ddagger} - \Delta G^0_{et} + 2[\Delta G^{\ddagger}(\Delta G^{\ddagger} - \Delta G^0_{et})]^{1/2}) - \lambda_{22} \tag{1}$$

The λ_{22} value for the oxidants used in this study can be neglected.[29] The $\Delta G^{\ddagger}$ values are obtained from the observed rate constant of electron transfer (k_{et}) and the diffusion rate constant (k_{diff}) using eq 2, where Z is the collision frequency taken as 1×10^{11} M^{-1} s^{-1}, the k_{diff} value in MeCN is 2.0×10^{10} M^{-1} s^{-1}, and the other notations are conventional.

$$\Delta G^{\ddagger} = 2.3RT \log[Z(k_{et}^{-1} - k_{diff}^{-1})] \tag{2}$$

Significant differences are observed in the reorganization energies depending on the type of porphyrin macrocycle and the σ-bonded axial ligand, and the λ_{11} values (in kcal mol^{-1})

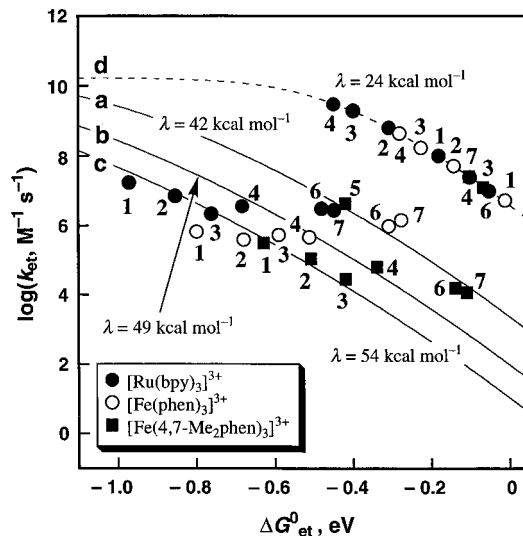(29) Fukuzumi, S.; Wong, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 2, 2928.

Figure 2. Dependence of log k_{et} on ΔG^0_{et} for the rate-determining first one-electron oxidation of (P)Fe(R) with three different oxidants in MeCN at 298 K (see Scheme 1). The identity of compounds (**1**−**7**) is given in Table 1, and the fit of the curves based on the Marcus theory of electron transfer (eqs 2 and 3) is shown by the solid lines (a) (OEP)Fe(R)/[(OEP)Fe(R)]$^+$ (R = C_6H_5, 2,4,6-$C_6F_3H_2$, 2,3,5,6-C_6F_4H), (b) (OETPP)Fe(C_6F_5)/[(OETPP)Fe(C_6F_5)]$^+$, and (c) (OETPP)Fe(R)/[(OETPP)Fe(R)]$^+$ (R = C_6H_5, 3,5-$C_6F_2H_3$, 2,4,6-$C_6F_3H_2$). The broken line (d) shows the calculated dependence of log k_{et} on ΔG^0_{et} for the second electron transfer; see text.

increase in the following order: (OEP)Fe(R) (83 ± 4) $\ll$ (OETPP)Fe(C_6F_5) (99 ± 2) < (OETPP)Fe(2,4,6-$C_6F_3H_2$) (107 ± 2) < (OETPP)Fe(3,5-$C_6F_2H_3$) (109 ± 3) < (OETPP)Fe(C_6H_5) (113 ± 3). Thus, the electron-transfer rate at the same free energy change of electron transfer (ΔG^0_{et}) should also decrease in this order. This is clearly shown in Figure 2, where the log k_{et} values are plotted against ΔG^0_{et} for electron transfer from (P)Fe(R) to the oxidants in MeCN at 298 K. The fit of the curves in light of the Marcus theory of adiabatic outer-sphere electron transfer (eqs 2 and 3)[17] using the reorganization energies for

$$\Delta G^{\ddagger} = (\lambda/4)(1 + \Delta G^0_{et}/\lambda)^2 \tag{3}$$

$$\lambda = (\lambda_{11} + \lambda_{22})/2 \tag{4}$$

the cross reactions between (P)Fe(R) and the oxidants (λ), which is given by eq 4, is shown in Figure 2 which indicates that the rate variations at the same ΔG^0_{et} value arise from a difference in the λ value and not from the nonadiabaticity.

The λ values are equal to 54, 49, and 42 kcal mol^{-1} respectively for the electron-transfer oxidation of (OETPP)Fe^{III}-(R) to [(OETPP)Fe^{IV}(R)]$^+$ (R = C_6H_5, 3,5-$C_6F_2H_3$, and 2,4,6-$C_6F_3H_2$), (OETPP)Fe^{III}(C_6F_5) to [(OETPP)Fe^{IV}(C_6F_5)]$^+$, and (OEP)Fe^{III}(R) to [(OEP)Fe^{IV}(R)]$^+$.[30] Each value is significantly larger than reorganization energies (ca. 24 kcal mol^{-1} in MeCN) for the ligand-centered oxidation of free-base porphyrins.[31]

Rate constants for the second electron transfer from [(P)Fe-(R)]$^+$ to the oxidants to produce [(P)Fe^{IV}(R)]$^{•2+}$ were also calculated using the λ value (24 kcal mol^{-1}) for the ligand-centered oxidation[32] and the ΔG^0_{et} values based on eqs 2 and

(30) Since the λ_{22} value for the oxidants used in this study can be neglected (see ref 29), the λ value corresponds approximately to $\lambda_{11}/2$.

(31) Marguet, S.; Hapiot, P.; Neta, P. *J. Phys. Chem.* **1994**, *98*, 7136.

(32) The reported λ value (24 kcal mol^{-1}) which is mainly the solvent reorganization energy for the electron-transfer oxidation of free-base porphyrins (see ref 31) is used for the electron-transfer oxidation of both [(OETPP)Fe(R)]$^+$ and [(OEP)Fe(R)]$^+$.

3. The calculated dependence of log k_{et} on ΔG^0_{et} for the second electron transfer is shown by the broken line in Figure 2. A comparison of the k_{et} values between the first and second electron transfers clearly indicates that the second electron transfer from the porphyrin ligand to produce $[(P)Fe^{IV}(R)]^{\bullet 2+}$ is much faster than the first electron transfer to produce $[(P)Fe^{IV}(R)]^+$ due to a much smaller reorganization energy required for the ligand-centered oxidation as compared to the metal-centered oxidation. Thus, the first electron transfer from iron(III) to give iron(IV) is the rate-determining step for the generation of the iron(IV) porphyrin π radical cation, $[(P)Fe^{IV}(R)]^{\bullet 2+}$.

The crystallographic results obtained for the metal complexes of OETPP have shown that the size of metal ion alters the degree of planarity of the porphyrin macrocycle, with a smaller metal ion favoring a more nonplanar conformation.[14] The metal ion is placed inside the curved surface of the nonplanar porphyrin macrocycle. Such a distorted conformation results in an appreciably shorter metal–N distance than that of a planar metal porphyrin.[14,33,34] Thus, the stronger binding of metal ion with the nonplanar porphyrin upon the oxidation of metal ion may give rise to a larger inner-shell reorganization energy and hence to the slower electron-transfer rate as compared with that of a planar metal porphyrin as experimentally observed in this study. The E^0_{ox} value of (OETPP)Fe(R) (e.g., 0.27 V for R = C_6H_5) is more negative than that of (OEP)Fe(R) (0.48 V for R = C_6H_5) despite the electron-withdrawing effect of extra phenyl groups in OETPP (Table 1), and this is also ascribed to the stronger Fe(IV)–N binding which decreases the HOMO level because of the nonplanar conformation of the OETPP ligand as compared with the planar OEP ligand.

As seen in Table 1 the reorganization energy is only slightly affected by the number of F atoms on the σ-bonded axial ligand R for all compounds in the (OETPP)Fe(R) and (OEP)Fe(R) series except for (OETPP)Fe(C_6F_5), which has a somewhat smaller λ_{11} value as compared with the less fluorinated phenyl σ-bonded Fe complexes of OETPP. Such a difference in the λ_{11} values cannot be ascribed to the difference in the spin state, since all known (OETPP)Fe(R) complexes are low spin.[35] The spin state of (OEP)Fe(R) is also not a key factor which determines the reorganization energy, since low-spin (OEP)-Fe(R) (R = C_6H_5) and the high-spin complexes (R = 2,4,6-$C_6F_3H_2$ and 2,3,5,6-C_6F_4H) have similar λ_{11} values (Table 1).

Although there have so far been no reports on the electron-transfer oxidation of Fe(III) porphyrins to Fe(IV) or Fe(IV) porphyrin π radical cations, the reorganization energy for reduction of iron oxo complexes of (TPFPP)Fe (TPFPP = tetrakis(pentafluorophenyl)porphyrin dianion) by N,N-dimethylanilines has recently been estimated as 47 kcal mol^{-1},[36] a value which is as large as the reorganization energy for the oxidation of (P)Fe^{III}(R) to $[(P)Fe^{IV}(R)]^+$ (42–54 kcal mol^{-1}) by our one-electron oxidants (Figure 2). The reactions of $[(TMP)Fe^{IV}-(=O)]^{\bullet+}$ (TMP = 5,10,15,20-tetramesitylporphyrin dianion) with N,N-dimethylanilines have been shown to proceed via electron
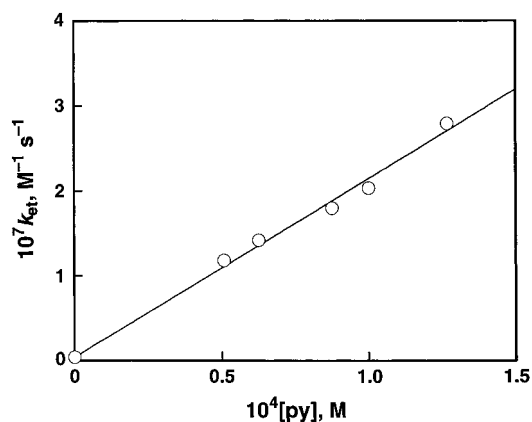

Figure 3. Plot of k_{et} vs [py] for the electron transfer from (OETPP)-Fe(C_6F_5) (4.3 × 10^{-6} M) to $[Fe(4,7-Me_2phen)_3]^{3+}$ (4.6 × 10^{-5} M) in the presence of pyridine (py) in MeCN at 298 K.

transfer, and the logarithm of the rate constants of electron-transfer is linearly correlated with the one-electron oxidation potentials of a series of p-substituted N,N-dimethylanilines.[37] The slope of the linear correlation also indicates a large reorganization energy associated with the electron-transfer reduction of the Fe(IV) to the Fe(III) porphyrin. Thus, the large reorganization energy determined for the electron-transfer oxidation of (P)Fe^{III}(R) to $[(P)Fe^{IV}(R)]^+$ (Figure 2) provides the first experimentally determined energetic basis for the electron transfer between Fe(III) and Fe(IV) porphyrins which plays an essential role in biological oxidations and also provides valuable insights into the mechanistic viability of electron transfer in iron porphyrin-catalyzed oxidation processes.

Effects of a Base on Electron-Transfer Oxidation of (OETPP)Fe(R). The addition of nitrogenous bases such as pyridine to five-coordinate iron porphyrins often results in substantial changes in the redox reactivities.[38,39] For this reason we have also examined the effects of a base on the electron-transfer oxidation of (OETPP)Fe(R). The addition of pyridine to the (OETPP)Fe(R)–oxidant system results in a significant increase in the rate of electron transfer from (OETPP)Fe(R) to the oxidant. Most electron-transfer rates of (OETPP)Fe(R) in the presence of pyridine were so rapid as to fall outside the stopped-flow range. Thus, the least reactive system in Table 1, i.e., the (OETPP)Fe(C_6F_5)/$[Fe(4,7-Me_2phen)_3]^{3+}$ system, was chosen to determine the effect of pyridine on the electron-transfer rate. The electron-transfer rate constant k_{et} increases linearly with increase in the pyridine concentration as shown in Figure 3.

The addition of pyridine to an MeCN solution of (OETPP)-Fe(C_6F_5) results in a significant change in the UV–vis spectrum. From these changes, the formation constant (K) for axial ligand binding of pyridine to (OETPP)Fe(C_6F_5) was determined as K = 62 M^{-1} in MeCN at 298 K. The acceleration of the rate of electron transfer by the presence of pyridine may be ascribed to the much faster electron-transfer rate constant for the six coordinate complex ($k_{et(6)}$), (OETPP)Fe(C_6F_5)(py), than that for the five coordinate complex ($k_{et(5)}$), (OETPP)Fe(C_6F_5) as shown

(33) Guilard, R.; Perié, K. P.; Barbe, J.-M.; Nurco, D. J.; Smith, K. M.; Van Caemelbecke, E.; Kadish, K. M. *Inorg. Chem.* **1998**, *37*, 973.

(34) VanAtta, R. B.; Strouse, C. E.; Hanson, L. K.; Valentine, J. S. *J. Am. Chem. Soc.* **1987**, *109*, 1425.

(35) The inductive effect of five F atoms on the σ-bonded axial ligand may result in an increase in the contribution of the porphyrin ligand-centered oxidation which decreases the reorganization energy of the electron-transfer oxidation.

(36) Baciocchi, E.; Lanzalunga, O.; Lapi, A.; Manduchi, L. *J. Am. Chem. Soc.* **1998**, *120*, 5783.

(37) Goto, Y.; Watanabe, Y.; Fukuzumi, S.; Jones, J. P.; Dinnocenzo, J. P. *J. Am. Chem. Soc.* **1998**, *120*, 10762.

(38) (a) Kadish, K. M. In *Iron Porphyrins, Part 2*; Lever, A. B. P., Gray, H. B., Eds.; Addison-Wesley: Reading, MA, 1982; pp 161–249. (b) Kadish, K. M.; Bottomley, L. A. *Inorg. Chem.* **1980**, *19*, 832. (c) Walker, F. A.; Barry, J. A.; Balke, V. L.; McDermott, G. A.; Wu, M. Z.; Linde, P. F. *Adv. Chem. Ser.* **1981**, *No. 201*, 377.

(39) Lançon, D.; Cocolios, P.; Guilard, R.; Kadish, K. M. *Organometallics* **1984**, *3*, 1164.

Scheme 2
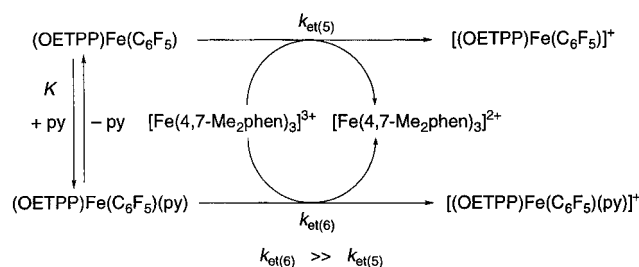
in Scheme 2. The observed rate constant of electron transfer in the presence of pyridine is then given by eq 5. Since $K[\text{py}] \ll$

$$k_{et} = (k_{et(5)} + k_{et(6)}K[\text{py}])/(1 + K[\text{py}]) \qquad (5)$$

1 for the pyridine concentrations as indicated in Figure 3, the slope of the linear plot of k_{et} vs the pyridine concentration in Figure 3 corresponds to the $k_{et(6)}K$ value. The $k_{et(6)}$ value is then determined from the $k_{et(6)}K$ value as 3.4×10^9 M^{-1} s^{-1}, which is close to the diffusion-limited value. The one-electron oxidation potential is expected to be shifted in a positive direction by the axial ligand coordination of pyridine, when the electron transfer oxidation becomes energetically more favorable. However, the observed positive shift in the oxidation potential in pyridine as compared to the observed potential in MeCN is only 0.09 V, which cannot account for the remarkable acceleration of the rate of electron transfer for the pyridine-coordinated complex as compared with the noncoordinated complex. Thus, the acceleration in the rate of electron transfer upon axial coordination of pyridine results from a significant decrease in

the reorganization energy associated with the electron-transfer oxidation of (OETPP)Fe(C$_6$F$_5$)(py). Although the acceleration effects of pyridine on rates of electron transfer for other (OETPP)Fe(R) complexes could not be determined quantitatively (because of the fast electron-transfer rates for (OETPP)-Fe(R)(py) which are beyond the detection limit of a stopped-flow technique), such a rate acceleration effect of pyridine indicates a significant decrease in the reorganization energy upon the axial ligand coordination of bases. The self-exchange rate constant for a six-coordinate iron(III) porphyrin complex, [(TMpyP)Fe(OH)(H$_2$O)]$^{4+}$ (TMpyP = tetrakis(4-*N*-methylpyridiniumyl)porphyrin dication), has been reported to be at least 3 orders of magnitude greater than that for a five-coordinate iron(III) complex, [(TMpyP)Fe(H$_2$O)]$^{5+}$ (1.2×10^6 M^{-1} s^{-1}).[40] The sixth axial coordination of a base may minimize the structural change associated with the electron transfer, since the six-coordinate iron atom may remain in the plane of the rather rigid porphyrin ligand irrespective of the oxidation state.[41]

(40) Pasternack, R. F.; Spiro, E. G. *J. Am. Chem. Soc.* **1978**, *100*, 968.

(41) Although the self-exchange rate of a six-coordinate low-spin iron porphyrin is suggested to be faster than the five-coordinate high-spin iron porphyrin,[40] the spin state is not a key factor to determine the reorganization energy in the present case.