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A New Active Intermediate in Monooxygenations Catalyzed by Iron Porphyrin Complexes

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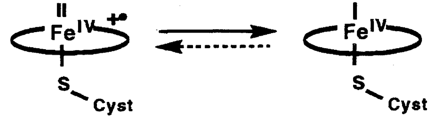
A new type of high-valent oxoiron porphyrin (**3b**) has been prepared by the reaction of $\mathrm{Fe^{III}}$(tdcpp) (**1b**) [tdcpp: 5, 10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin] with an oxidant such as *p*-nitroperbenzoic acid and pentafluoroiodosylbenzene at −90 °C in $\mathrm{CH_2Cl_2}$ *in the presence of a small amount of methanol.* The UV-vis spectrum of **3b** ($\lambda_{\max}$ at 418 and around 550 nm) is similar to that of $\mathrm{O{=}Fe^{IV}}$(tdcpp) (**4b**, $\lambda_{\max}$ 419, 543 nm). However, titration of **3b** by iodide ion indicates that the oxidation state of **3b** is two-electron oxidized from the iron(III) state. Further, **3b** catalyzes oxygenation of olefins such as styrene even at −90 °C. Possible formulation of **3b** as a π-cation radical is readily ruled out by deuterium NMR observation. The solution magnetic susceptibility ($\mu_{\mathrm{eff}} = 4.0\pm0.2\ \mu_{\mathrm{B}}$) of **3b** indicates that **3b** has three unpaired electrons. These results indicate the formal description of **3b** as being a high spin complex of either an O=Fe(V) porphyrin or ·O–Fe(IV) porphyrin. The same oxidation of **1b** *in the absence of methanol* gave $\mathrm{O{=}Fe^{IV}}$(tdcpp) π-cation radical (**2b**). We think the ligation of methanol causes the destabilization of iron d orbitals and eventually turns upside down the energy levels between the iron d_{xz}, d_{yz} orbitals and the porphyrin HOMO orbital (a_{2u}) since the a_{2u} orbital is stabilized by the introduction of electron-withdrawing groups on the porphyrin ring.

Synthetic iron porphyrin complexes in high oxidation states have served as models for the active species of peroxidase, catalase, and cytochrome P-450. Among them, two-electron oxidized iron porphyrin complexes have been extensively studied to understand the biological use and manipulation of reactive intermediates. For example, oxoiron(IV) porphyrin π-cation radicals,[1] iron(III) porphyrin *N*-oxides,[2] and iron(III) porphyrin dications,[3] which are formally two-electron oxidized from the iron(III) state, are now known. Especially, the oxoiron(IV) porphyrin π-cation radicals are closely related to compound **I** of peroxidases[4] and catalases.[5] The formation of compound **I** in the catalytic cycles of these heme enzymes is supported on the basis of electronic,[6] EPR,[7] NMR,[8] ENDOR,[4f,4g] resonance Raman,[9] and Mössbauer spectral measurements.[10]

The active species responsible for the oxidative metabolism of foreign compounds by P-450 has been considered to be similar to compound **I** of peroxidases,[11] since many types of monooxygenation by P-450 have been mimicked by oxoiron(IV) porphyrin π-cation radicals of synthetic iron porphyrin complexes.[12] Unfortunately, no higher valent intermediates in the catalytic cycle of P-450 have been characterized. Very recently, Egawa et al. have reported the observation of compound **I** as a transient intermediate by rapid scan absorption spectrometry in the reaction of *m*-chloroperbenzoic acid (*m*CPBA) with $\text{P-450}_{\text{cam}}$,[13] however, the observed spectrum is a mixture of several species and a spectrum obtained by the subtraction of undesired species is still controversial. Thus, efforts to identify the active species of P-450 are quite important. Especially, an oxoiron(V) porphyrin complex is an attractive candidate for the active species in the P-450 reactions. In 1989, Champion proposed favorable formulation of an iron(IV) porphyrin oxy radical (one extreme resonance structure of oxoiron(V) porphyrin) over compound **I** due to the strong electron donating ability of the thiolate ligand and non-polar environment of the heme pocket of P-450 (Eq. 1).[14]



(1)

Very recently, we have reported the transformation of $\mathrm{O{=}Fe^{IV}(tdcpp)^{+\bullet}}$ (**2b**, tdcpp: 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin) to an alternative intermediate, most likely, $\mathrm{O{=}Fe^{V}}$(tdcpp) (**3b**), which has a similar UV-vis spectrum to that of oxoiron(IV) porphyrin complexes (compound II), by *introducing MeOH* as a sixth ligand.[15] However, Jayaraj et al. also reported the oxidation of $\mathrm{Fe^{III}}$(tdcpp) in the presence of MeOH to give $\mathrm{O{=}Fe^{IV}(tdcpp)^{+\bullet}}$ under similar conditions.[16] Thus, we provide experimental evidence for the rationalization of these different observations. In addition, we have prepared **3b** by the reaction of [$\mathrm{Fe^{III}}$(tdcpp)] ($\mathrm{ClO_4}$) and pentafluoroiodosylbenzene under mild conditions. Two

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independent preparations of **3b** allows us to examine in more detail the reactivities of **3b** under various conditions. More importantly, we have shown herein the manipulation of the electronic structure of the two electron oxidized oxoiron porphyrin complexes, **2** and **3**, by introducing a series of electron-withdrawing substituents on the porphyrin ring.

Experimental

Materials. Dichloromethane was refluxed over CaH_2 and distilled under Ar just before use. H_2tdcpp, H_2tcmpp [tcmpp: 5,10,15,20-tetrakis(2-chloro-6-methylphenyl)porphyrin], H_2tcfpp [tcfpp: 5,10,15,20-tetrakis(2-chloro-6-fluorophenyl)porphyrin], and H_2ttcpp [ttcpp: 5,10,15,20-tetrakis(2,3,6-trichlorophenyl)-porphyrin] were prepared by the methods reported.[17] Pyrrole-deuterated H_2tdcpp was prepared as described previously.[18] *Meso*-substituents-deuterated H_2tdcpp was prepared by treating H_2tdcpp with concentrated $^2H_2SO_4$ at room temperature.[19] Iron was inserted into H_2tdcpp to form [Fe^{III}(tdcpp)](Cl) by a standard method.[20] [Fe^{III}(tdcpp)](OH) was prepared by passing a dichloromethane solution of [Fe^{III}(tdcpp)](Cl) through an alumina column. Addition of 1 equiv of *m*-chlorobenzoic acid (*m*CBA) to [Fe^{III}(tdcpp)](OH) gave [Fe^{III}(tdcpp)](*m*CB) (**1b**-*m*CB) (*m*CB: *m*-chlorobenzoate). [Fe^{III}(tdcpp)](ClO_4) (**1b**-ClO_4) was prepared as described earlier.[21] Pentafluoroiodosylbenzene (C_6F_5IO)[22] and *p*-nitroperbenzoic acid (*p*NPBA)[23] were prepared and purified by procedures from the literature. *m*-Chloroperbenzoic acid (*m*CPBA) was purchased from Wako Chemicals and purified as described before.[23] Silver perchlorate and tetrabutylammonium iodide (TBAI) were purchased from Aldrich and Wako, respectively. TBAI was purified by recrystallization from dichloromethane/hexane and dried in vacuo. Norbornylene, styrene, *p*-chlorostyrene, *p*-methylstyrene, and α-methylstyrene were purchased from Aldrich and used without further purification.

Physical Measurements. Absorption spectra were recorded on a Hitachi 330 spectrometer. Low-temperature absorption spectra were obtained using a DN 1704 variable-temperature liquid nitrogen cryostat (Oxford Instruments). Proton NMR and deuterium NMR spectra were recorded on a GE Omega-500 spectrometer and Nicolet NT-300 spectrometer. Chemical shifts were referenced to tetramethylsilane (TMS), and downfield shifts were given a positive sign. GLC analyses were done on a Shimadzu GC-14A fitted with a Shimadzu CBP1 (25 m) capillary column. Electrochemical measurements were done with a three-electrode potentiostatic system. The working electrode was a Ag/$AgNO_3$ saturated calomel electrode (SCE) separated from the bulk solution by fine glass frits. A cyclic voltammogram was obtained on a BAS CV-50W.

Preparation of 3b and 3b′. A dichloromethane solution of **1b**-*m*CB [2.2×10^{-5} M, 1 M = 1 mol dm^{-3}] in a UV cuvette was cooled to −90 °C. To the resulting solution was added 8 equiv of *m*CBA, 1.8 equiv of *p*NPBA (a small excess for complete oxidation), and *4 equiv of methanol*, to give a red species, **3b**. Complete formation of **3b** was confirmed by the UV-vis spectral changes at −90 °C. The reaction of 1.8 equiv of C_6F_5IO and **1b**-ClO_4 [1.0×10^{-4} M] in dichloromethane in the presence of 200 equiv of methanol at −90 °C also yielded a red species, **3b′**.

NMR sample of **3b** [3.0×10^{-3} M] and **3b′** [1.0×10^{-3} M] was prepared at −90 °C according to the stoichiometry described above.

Preparation of Oxoiron(IV) Porphyrin π-Cation Radicals (2). Oxoiron(IV) porphyrin π-cation radical (O=Fe^{IV}(tdcpp)$^{+\bullet}$, **2b**) was synthesized by the addition of 8 equiv of *m*CBA and 1.8 equiv of *p*NPBA to [Fe^{III}(tdcpp)](*m*CB) [2.2×10^{-5} M] *in dichloromethane* at −90 °C.[15] Other oxoiron(IV) porphyrin π-cation radicals (**2a—d**) were also prepared by the reaction of **1**-ClO_4 (**a—d**) [1.0×10^{-5} M] with 1.8 equiv of *m*CPBA in dichloromethane at −90 °C.[24] Characterization of the products was done on the basis of a less intense Soret band and broad absorption around 600—700 nm as well as a large upfield shift of the pyrrole β-protons of **2** on the NMR spectroscopy.

Preparation of Oxoiron(IV) Porphyrin (4b). As reported by Gold et al.,[25] [Fe^{III}(tdccp)](OH) [1.0×10^{-5} M] was oxidized by mixing with 4 equiv of *m*CPBA at −60 °C in dichloromethane solution containing 0.1% ethanol as a preservative. The formation of an oxoiron(IV) porphyrin complex (**4b**) was confirmed by comparison of its UV-vis spectrum (λ_{max} 419 and 543 nm) to that reported.[25]

Reaction of 2 and 3 with Olefins. In a typical run, a dichloromethane solution of **2** or **3** [ca. 2×10^{-5} M] was prepared by the addition of one equiv of the oxidants at −90 °C. Completion of the reaction was confirmed by monitoring spectral changes at −90 °C. Then, 500 equiv of norbornylene, 1000 equiv of styrene, or 1000 equiv of *p*-chlorostyrene at −90 °C was introduced to begin the oxygenation. The rate constant for each reaction was calculated on the basis of the time-dependent spectral changes.

To GLC samples, TBAI was added before injection to prevent thermal reactions of olefins with the remaining oxidizing species.

Results

p-Nitroperbenzoic acid (*p*NPBA) and pentafluoroiodosylbenzene (C_6F_5IO) have been used as convenient stoichiometric oxidants for the preparation of oxoiron(IV) porphyrin π-cation radicals (**2**). The rate for the formation of **2** is known to be dependent on the reaction conditions and the nature of the porphyrin ligands. For example, introduction of electron-withdrawing groups such as halogens on the porphyrin periphery decreases the rate, and the reaction can be accelerated by the addition of acid since the O–O bond cleavage in acylperoxo-iron(III) porphyrin complexes is catalyzed by acid.[2b,26] Thus, we have to use an excess of *m*-chlorobenzoic acid (*m*CBA) for the preparation of **2b** by the reaction of [Fe^{III}(tdcpp)](*m*CB) (**1b**-*m*CB) and *p*NPBA.[15] On the other hand, *m*-chloroperbenzoic acid (*m*CPBA) can be used when [Fe^{III}(tdcpp)](ClO_4) was used as a starting material.[24]

UV-vis Spectra of High Valent Intermediates. The reaction of **1b**-*m*CB with 1.8 equiv of *p*-nitroperbenzoic acid (*p*NPBA) in the presence of 8 equiv of *m*CBA was examined at −90 °C by UV-vis spectroscopy. The oxidation product was readily assigned to O=Fe^{IV}(tdcpp)$^{+\bullet}$ (**2b**) on the basis of its characteristic UV-vis spectrum (Fig. 1). As reported in our preliminary communication,[15] addition of 4 equiv of methanol to the dichloromethane solution of **2b** afforded a red species **3b**, the UV-vis spectrum (Fig. 1) of which is similar to those of oxoiron(IV) porphyrin complexes (**4**)[25] but very different from complexes of iron(III) porphyrin dications[3] and iron(III) porphyrin *N*-oxides.[2] **3b** can be directly prepared when the reaction of **1b**-*m*CB and *p*NPBA is done in the presence of a small amount of methanol. In most of the spectroscopic studies, including Fig. 1, we used a small excess of oxidants to complete the formation of **2b** and **3b**. **2b** and **3b** can also be prepared by the stoichiometric reactions

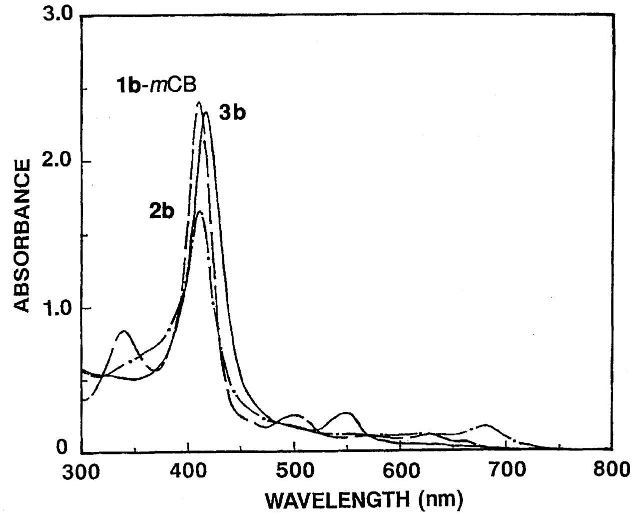
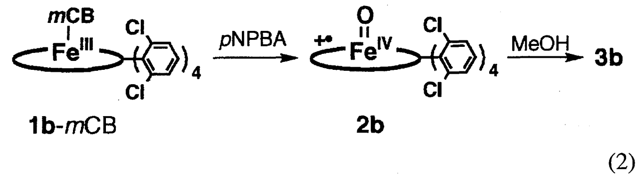


Fig. 1. UV-vis spectra of **1b**-*m*CB, **2b**, and **3b** [2.2×10^{-5} M] in dichloromethane at −90 °C. **2b** was obtained by the addition of 1.8 equiv of *p*NPBA to **1b**-*m*CB. **3b** was obtained by the addition of 4 equiv of methanol to **2b**.



(2)

of **1b** and *p*NPBA in 90% yield, which has been calculated from analysis of the spectrum.

In our previous report,[15] we have assigned **3b** as oxoiron(V) porphyrin on the basis of iodometric titration and EPR and NMR spectroscopic observations. The solution of **3b** contains additives such as *m*CBA and *p*NBA, which prevent us from examining the detailed structure of **3** and roles of methanol. Therefore, we have exploited other synthetic procedures of **3** under neutral conditions. Figure 2 shows time-dependent spectral changes upon the addition of pentafluoroiodosylbenzene (C_6F_5IO) to a dichloromethane solution (including 200 equiv of MeOH) of **1b**-ClO_4 at −90 °C. The UV-vis spectrum of the product (**3b′**) is essentially the same as that of **3b**, but the absorption maximum of **3b** at 546 nm is different from **3b′** by 14 nm (Table 1). Like the reaction of **3b** with olefins, addition of norbornylene to the solution of **3b′** in an UV cuvette at −90 °C caused the spectral changes to afford **1b** even at −90 °C, while independently prepared O=Fe^{IV}(tdcpp) (**4b**) did not react at all with olefins under similar conditions. That both **3b** and **3b′** react with olefins even at −90 °C to afford **1b** suggests that these complexes are two-electron-oxidized ones from **1b**.

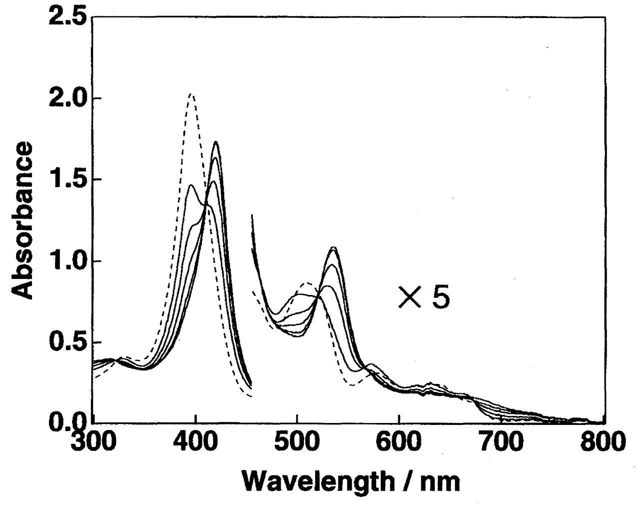
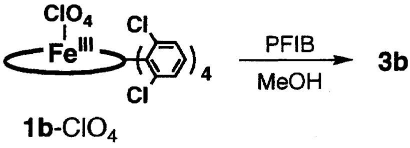


Fig. 2. UV-vis spectral changes upon the addition of 1.8 equiv of F_5-PhIO to [Fe^{III}(tdcpp)](ClO_4) (**1b**-ClO_4) [1.0×10^{-4} M] (- - -) in dichloromethane containing 200 equiv of methanol at −90 °C at 7-min intervals (first scan was immediate after the addition of F_5-PhIO).



(3)

To test these considerations, we have examined the oxidation state of **3b** and **3b′** as well as **2b** by iodometric titration.

Formal Oxidation State of 2b, 3b, and 3b′. Ten equiv of tetra-*n*-butylammonium iodide (TBAI) and *m*-chlorobenzoic acid (*m*CBA) were added at −90 °C to a dichloromethane solution of **2b** prepared by 1.8 equiv of *p*NPBA. The reaction was directly monitored by UV-vis spectroscopy as shown in Fig. 3a. The final spectrum is the superposition of iron(III) porphyrin complexes and I_3^-, which is generated by the oxidation of I^-. Figure 3a (*inset*) depicts a difference spectrum of the resulting solution and **1b**-*m*CB. The difference spectrum has an absorption maximum at 363 nm, showing the formation of I_3^-. The addition of 10 equiv of TBAI to the solution of **3b** prepared by 1.8 equiv of *p*NPBA gave a superimposed spectrum of **1b**-*m*CB and I_3^- (Fig. 3b) (*inset*)). The same amount of I_3^- was also observed for **3b′** prepared by 1.8 equiv of C_6F_5IO. The total amounts of I_3^- observed should include the amounts of I_3^- formed by the reaction of I^- with free oxidants, since we have used 1.8 equiv of the oxidant to complete the formation of **2b**, **3b**, and **3b′**. Therefore, the titration of 1.8 equiv of *p*NPBA by I^- was done and the same amount of I_3^- formation was observed. In this case, *p*NPBA is also reduced to *p*NBA by two electrons. The iodometric titration indicates that **2b**, **3b**, and **3b′** are in the same oxidation state, which is formally two-electron oxidized from the iron(III) state. Thus, we con-

Table 1. UV-vis and Proton NMR Spectral Data of **3b**, **3b′**, and **2b**

	UV-vis spectra	Chemical shift (ppm from TMS)	
Porphyrin	nm	Pyrrole-H	*meta*-H
3b[a]	418, 546	−35.1	8.0
3b′	418, 532	−22.9	8.8
2b[a]	409, 681	−46.2	44.0

a) Yamaguchi et al., *J. Chem. Soc., Chem. Commun.*, **1992**, 1721—1723.

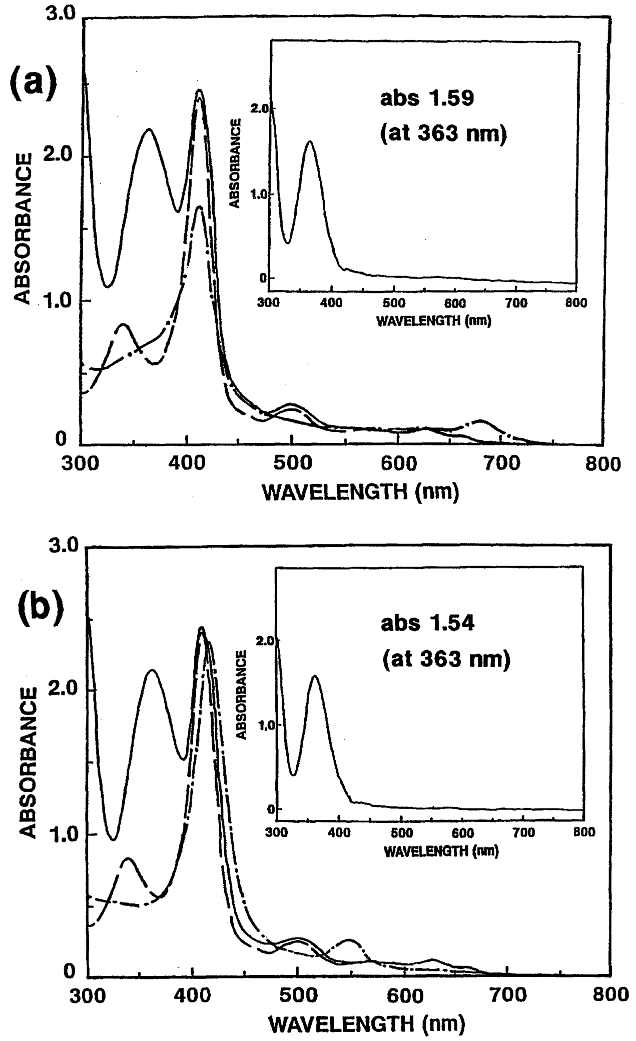


Fig. 3. (a) UV-vis spectra of **1b**-*m*CB (- - -), **2b**(– • • –), and **1b**-*m*CB and I_3^- (——), which was obtained by the addition of 10 equiv of TBAI to **2b**. (*inset*) UV-vis spectrum of I_3^-, which was given by subtracting the spectrum of **1b**-*m*CB from that of **1b**+I_3^-. (b) UV-vis spectra of **1b** (- - -), and **3b** (– • • –), and **1b**+I_3^- (——), which was obtained by the addition of 10 equiv of TBAI to **3b**. (*inset*) UV-vis spectrum of I_3^-, which was given by subtracting the spectrum of **1b** from that of **1b**+I_3^-.

cluded that **3b** and **3b′** are essentially the same species and a small shift of the Q band in **3b′** from **3b** could be induced by different reaction conditions (see Discussion).

The magnetic susceptibility of **3b** measured by the Evans method[27] was 4.0±0.2μ_B, which fits the spin-only value expected for an $S=3/2$ system. These results also suggest **3b** to be isoelectronic to the oxoiron(IV) porphyrin π-cation radical.

NMR Spectra of 2b, 3b, and 3b′. The reaction of pyrrole-d_8-**1b**-*m*CB with 1.8 equiv of *p*NPBA in the presence of 8 equiv of *m*CBA was also examined at −95 °C. Upon addition of *p*NPBA to a dichloromethane solution of pyrrole-d_8-**1b**-*m*CB, the pyrrole *β*-deuterium resonance of pyrrole-d_8-**1b**-*m*CB at 130 ppm (signal i, Fig. 4a) shifted to −46.2 ppm (signal ii, Fig. 4b) due to the formation of **2b**.[1,15,28] Addition of methanol to the solution of **2b** at −95 °C caused the solution to change color from green to red with the replacement of the pyrrole *β*-deuterium resonance by a new resonance of **3b** at −35.1 ppm (signal iii, Fig. 4c), which is in the region associated with the unpaired electron occupation in d_{xy}, d_{xz}, and d_{yz} orbitals.[29] The signal iii shows Curie law behavior from −95 to −40 °C, which could be accounted for by **3b** being a single spin state. During the deuterium NMR measurements, we have found reversible appearance of signal ii upon raising the temperature (Fig. 4, c—f). The temperature-dependent interconversion between **2b** and **3b** is a further demonstration of **3b** being in the same oxidation state as **2b**. Upon warming the solution to −65 °C, **3b** was reduced to **1b**-*m*CB (signal iv, Fig. 4f) in several hours.

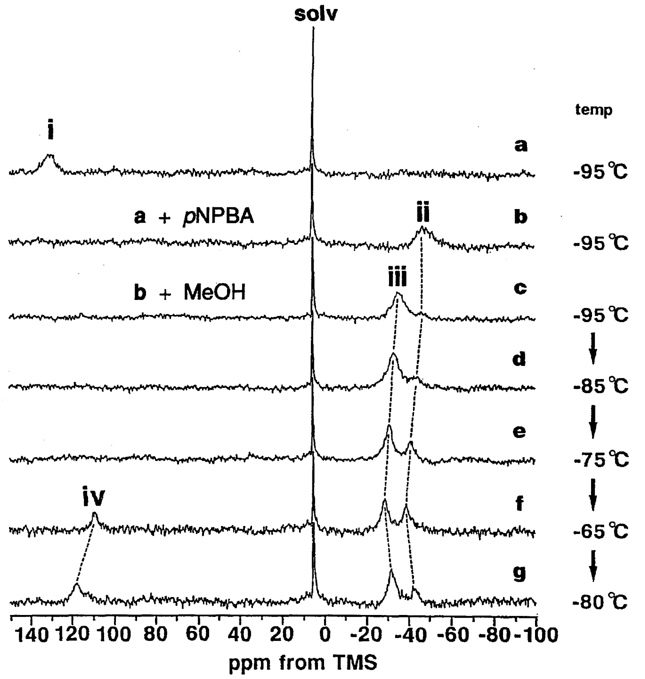


Fig. 4. Deuterium NMR spectra of (a) pyrrole-d_8-**1b**-*m*CB [3.0×10^{-3} M]; (b) **2b** prepared by the addition of 1.8 equiv of *p*NPBA to **1b**-*m*CB; (c) **3b** formed by the addition of 2 equiv of **2b** in dichloromethane at −95 °C; (d)—(f) temperature dependence of deuterium NMR spectra of solution (c) at −85 °C, −75 °C, and −65 °C; (g) a NMR spectrum of solution (f) at −80 °C.

Figure 5 shows the deuterium NMR spectra of pyrrole-d_8-*meta*-d_8-**1b**-ClO$_4$ and its oxidized product (**3b′**). Upon addition of C_6F_5IO to a dichloromethane solution of pyrrole-d_8-*meta*-d_8-**1b**-ClO$_4$, the pyrrole *β*-deuterium and *meta*-deuterium resonances of **3b′** appeared at −22.9 and 8.8 ppm from TMS at −90 °C, respectively. The signals were assigned based upon the result of the oxidation of pyrrole-d_8-**1b**-ClO$_4$. The appearance of the *meta*-deuterium resonance in the diamagnetic region readily eliminates the possible formulation of **3b′** as a porphyrin π cation radical[29] (see Discussion). The signals at ca. 110 ppm and ca. −50 ppm could be assigned to the pyrrole *β*-deuterium of decomposed products of **3b′**, iron(III) and iron(IV) species, respectively, since the intensity of these signals gradually increased during NMR

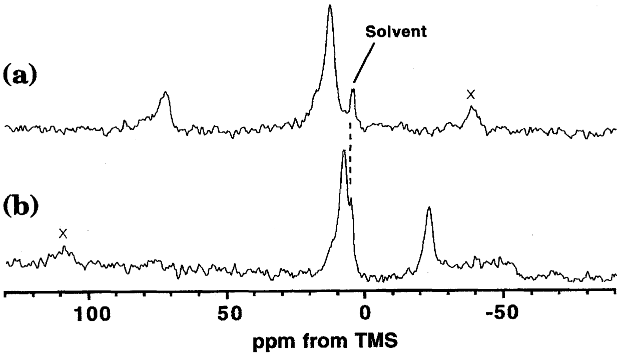


Fig. 5. Deuterium NMR spectra of (a) pyrrole-d_8-*meta*-d_8-**1b**-ClO_4 [1.0×10^{-3} M] and (b) **3b′** formed by the addition of 1.8 equiv of F_5-PhIO in dichloromethane containing 200 equiv of methanol at −90 °C. In (a), the signal at ca. 40 ppm is assigned to pyrrole β-^{2}H of iron(III) low spin species.

Table 2. Comparison of k_2 (10^{-2} M^{-1} s^{-1}) for Reaction of **2b**, **3b**, and **3b′** with Olefins in Dichloromethane at −90 °C

Olefin	**2b**[a)]	**3b**[a)]	**3b′**
Norbornylene	120	13	3.3
Styrene	120	11	2.9
p-Chlorostyrene	22	2.3	0.62

a) Yagaguchi et al., *J. Chem. Soc., Chem. Commun.*, **1992**, 1721—1723.

measurement. Finally, the disappearance of the signal at ca. −50 ppm with a concomitant increase of the signal at ca. 110 ppm was observed. Further, addition of olefin to the solution of **3b′** at −90 °C caused the pyrrole β-deuterium resonance shift to 108 ppm, which is typical for pyrrole β-protons of high spin iron(III) porphyrin complexes.[29)] NMR spectral data of **2b**, **3b**, and **3b′** are summarized in Table 1. As observed in the UV-vis spectra of **3b** and **3b′**, the chemical shifts of the pyrrole β-protons of **3b** and **3b′** are also different. These would be attributable to the different reaction conditions (see Discussion).

Upon the addition of a small amount of methanol-d_4 to a dichloromethane solution of pyrrole-d_8-**2b**, an additional deuterium NMR signal at 25.6 ppm was observed at −95 °C, together with free methanol signals at 3.4 (CD_3) and 4.8 (OD) ppm and the pyrrole deuterium signal for **3b** at −35.1 ppm. Disappearance of the signal at 25.6 ppm by replacement of methanol-d_4 by methanol allows us to assign it to methyl deuterium of methanol (or methoxide) ligated to **3b**. On the basis of these observations, we assigned **3b** and **3b′** as O=Fe(V) (or •O–Fe(IV)) porphyrin complexes having methanol or methoxide as a 6th ligand.

Reactivity of 3b with Olefins. Reactions of olefins with **2b** or **3b** were studied by following the time-dependent UV-vis spectral changes of **2b** or **3b**. In these cases, **2b** and **3b** were prepared by the use of *one equiv* of oxidant to avoid reproduction of **2b** and **3b** by the reaction of an excess of oxidant. Upon addition of 500 equiv of norbornylene at −90 °C, disappearance of **2b** (or **3b**) was found to be first order both in [olefin] and in [**2b** (or **3b**)] (Eq. 4). The same reactions with 1000 equiv of styrene and *p*-chlorostyrene were also examined. The rate constants obtained are listed in Table 2. In all cases, **3b** was less reactive than **2b**.

$$d[\mathbf{1b}]/dt = k_2[\text{olefin}][\mathbf{2b}\ (\text{or } \mathbf{3b})] = k_{\text{obs}}[\mathbf{2b}\ (\text{or } \mathbf{3b})]. \qquad (4)$$

Competitive oxygenation of norbornylene and α-methylstyrene by **2b** or **3b** was also done to examine the steric effects of substrates on the oxidation. Oxidation of a mixture of norbornylene and α-methylstyrene (1 : 1, 20 equiv with respect to the porphyrin) took place at −90 °C for 30 min. The oxidized products were measured by GC. The total yields of norbornylene oxide and α-methylstyrene oxide based on **2b** and **3b** were 72 and 53%, respectively. Both **2b** and **3b** preferably oxygenated norbornylene over α-methylstyrene with the selectivity (norbornylene oxide : α-methylstyrene oxide) of 100 : 30 and 100 : 35 by **2b** and **3b**, respectively.

Effects of Electron-Withdrawing Substituents Bound to the Porphyrin Ring on the Formation of 3′. Groves et al. showed for the first time that the oxidation of Fe^{III}(tmp) by *m*CPBA in dichloromethane/methanol affords the corresponding oxoiron(IV) porphyrin π-cation radical.[1)] In this study, **3b** was formed by the oxidation of Fe^{III}(tdcpp) (**1b**) *in the presence of methanol*. In our preliminary report, we have assigned **3b** as O=Fe^V(tdcpp) due to its relatively lower HOMO of the porphyrin ring over the HOMO of a methanol-coordinated heme iron, since the introduction of electron-withdrawing chlorides on the porphyrin periphery.[15)] If our assumption is correct, we could control the electronic structure of two-electron oxidized oxoiron porphyrin complexes between **2** and **3** by changing the porphyrin substituents. Therefore, we have prepared a series of iron porphyrins having substituents at the *meso*-positions of the porphyrin ring (Fig. 6). Figure 7 shows the UV-vis spectra of the oxidation products of **1**-ClO_4 (**a**—**d**) by C_6F_5IO in dichloromethane containing *200 equiv of methanol* at −90 °C. Apparently the spectra of **3c′** and **3d′** are essentially the same as that of **3b′**. By contrast, the UV-vis spectrum obtained by the reaction of **1a**-ClO_4 and C_6F_5IO is quite unusual. A less intense Soret band at ca. 395 nm and broad absorption around 600—700 nm are the indications of oxoiron(IV) porphyrin π-cation radical (**2a**) formation, and a red-shifted Soret band at 420

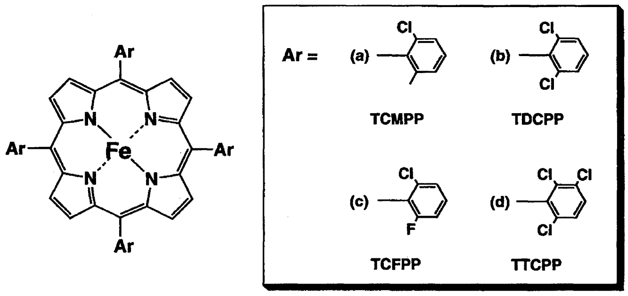


Fig. 6. Structure of the porphyrin core of various substituted iron porphyrin complexes (**a**—**d**) employed in this study. Axial ligands have been omitted for simplicity.

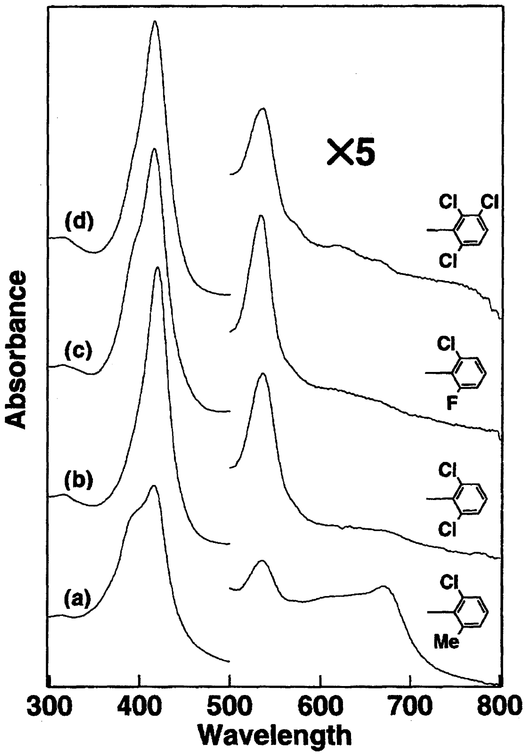


Fig. 7. UV-vis spectra of (a) **2a**/**3a′**, (b) **3b′**, (c) **3c′**, and (d) **3d′** in dichloromethane containing 200 equiv of methanol at −90 °C.

nm and a Q band around 540 nm are the spectrum expected for oxoiron(V) porphyrin (**3a′**). Thus, we conclude that the oxidation of **1a**-ClO_4 by C_6F_5IO gave a mixture of two oxidation products, **2a** and **3a′**. This assignment was further supported by the interconversion of two oxidation products upon temperature changes (Fig. 8).

Figure 9 shows ^{1}H NMR spectra of the oxidation products of **1**(**a**—**d**)-ClO_4 prepared by C_6F_5IO in dichloromethane-d_2 containing 200 equiv of methanol-d_4 at −90 °C. The oxidation products of **1** gave well-resolved hyperfine-shifted proton NMR spectra that are different from those of the parent iron(III) porphyrins. Signals were assigned based on the selective deuteration. Appearance of the resonances of the pyrrole β-protons and *meta*-protons of **3c′** and **3d′** around −21 and 9 ppm, respectively, suggests that **3c′** and **3d′** are assignable to oxoiron(V) porphyrin complexes, not oxoiron(IV) porphyrin π-cation radicals. Under these NMR conditions, formation of a small amount of **2b** and **2c** was observed (pyrrole β- and *meta*-proton resonances: −67 and 35 ppm for **2b** and −80 and 24 ppm for **2c**[24]). Though the increase of electron-withdrawing ability of the porphyrin substituents has been shown to cause an upfield shift of the pyrrole β-proton and *meta*-proton signals of oxoiron(IV) porphyrin π-cation radicals,[24] the chemical shifts of the pyrrole β-protons and *meta*-protons of **3b′**—**d′**, are almost the same regardless of the electron-withdrawing ability of the porphyrin substituent.

On the other hand, observation of two pyrrole β-proton resonances at −44[24] and −21 ppm (Fig. 9a) upon the oxidation of **1a** indicates the formation of two products, **2a** (major product) and **3a′** (minor product), consistent with the UV-vis spectroscopic study. In a separate experiment, **2a** prepared *in the absence of methanol* gave the pyrrole β-proton resonance at −62 ppm.[24] Upon the addition of methanol, the signal at −62 ppm became less intense with concomitant appearance of signals at −44 ppm. Thus, the resonance at −44 ppm could have appeared as a major component due to an interaction of **2a** with methanol.

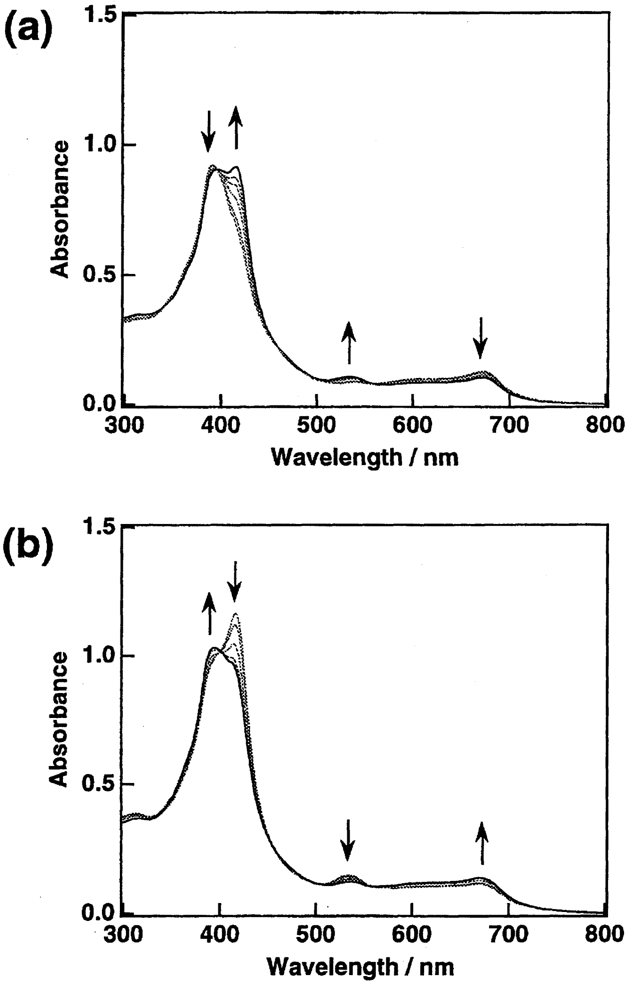


Fig. 8. UV-vis spectral changes of **2a**/**3a′** for (a) lowering temperature from −80 to −100 °C and (b) raising temperature from −95 to −85 °C.

In our previous report, we attributed the coordination of MeOH (or MeO^-) to **2b** to afford **3b**.[15] If this is the case, observation of **2a** and **3a′** even in the presence of methanol could be rationalized by the equilibrium between the methanol-bound oxoiron(V) porphyrin and the methanol-unbound oxoiron(IV) porphyrin π-cation radical. However, as shown in Fig. 9a, we have observed two different resonances assignable to pyrrole β-protons of **2a** in the presence of methanol. Moreover, the resonance at −62 ppm was also observed for **2a** in the absence of methanol as described above. These results do not fit to a simple binding mechanism like methanol-bound oxoiron(V) porphyrin and methanol-unbound oxoiron(IV) porphyrin$^{+\bullet}$.

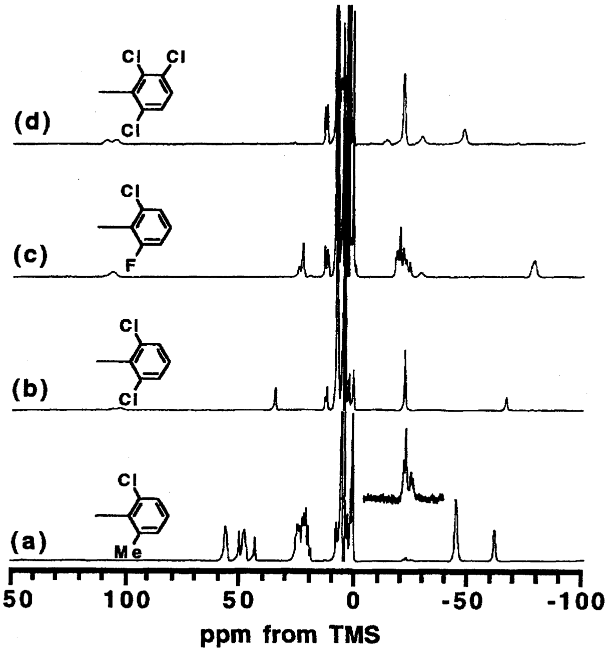


Fig. 9. Proton NMR spectra of (a) **2a**/**3a′**, (b) **3b′**, (c) **3c′**, and (d) **3d′** in dichloromethane-d_2 containing 200 equiv of methanol-d_4 at −90 °C. In (a), the signals at ca. 50 and ca. 20 ppm are assigned to the *meta*-H and *ortho*-methyl H of **2a′**, respectively.[22] In (b), (c), and (d), the signals of the pyrrole β-H and *meta*-H for iron(III) porphyrins can be seen at ca. 110 and ca. 10 ppm, respectively. The signals in high field region in (d) except −21 ppm are now not assigned.

To understand the details of the roles of methanol in the transformation of **2** to **3**, NMR spectra of **2a** and **3a′** in the presence of methanol-d_4 were examined.[30] Figure 10a depicts the deuterium NMR spectrum of a mixture of **2a** and **3a′** in the presence of methanol-d_4. Appearance of the paramagnetically shifted resonance at 20 ppm allows us to assign it to be the methyl deuterium of methanol (or methoxide) ligated to the paramagnetic complex, **3a′**. We have applied the same systems to $\mathrm{O{=}Fe^{IV}(tmp)^{+\bullet}}$ prepared by C_6F_5IO, since $\mathrm{O{=}Fe^{IV}(tmp)^{+\bullet}}$ is known to form even in the presence of methanol.[1] A resonance at 17.2 ppm in Fig. 10b is readily assigned to the methyl signal of methanol bound to $\mathrm{O{=}Fe^{IV}(tmp)^{+\bullet}}$ as an axial ligand. The coordination of methanol to $\mathrm{O{=}Fe^{IV}(tmp)^{+\bullet}}$ without changing its electronic structure is indicative of similar binding of methanol to **2a**, consistent with our tentative assignment of the −44 ppm resonance to **2a** interacting with methanol. These observations can be rationalized by Eq. 5, expressing how the coordination of methoxide anion (MeO^-) only causes the transformation of **2a** to **3a′** and **2a** can be observed as methanol ligated and unligated forms. Considering that the resonance of the methyl group of MeO^- bound to **3b** appears at 25.6 ppm,[15] the resonance at 20 ppm in Fig. 10a is interpreted as the superposed resonance of methanol derivative bound to **2a** and **3a′** under chemical equilibrium.

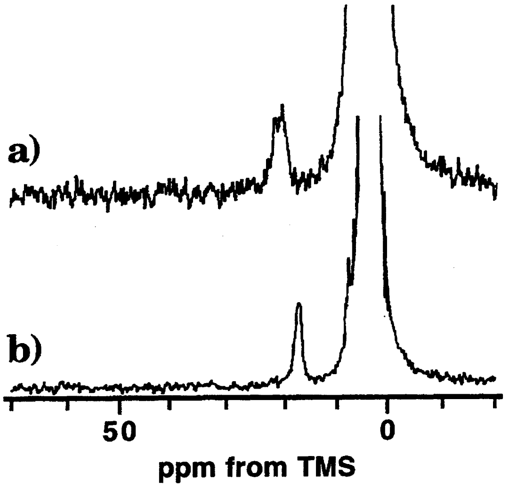
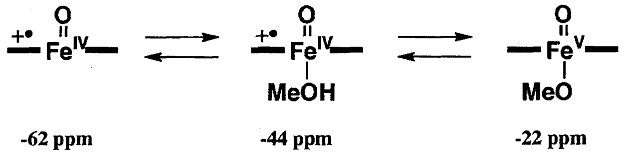


Fig. 10. Deuterium NMR spectra of (a) **2a**/**3a′** in the presence of methanol-d_4, and (b) $\mathrm{O{=}Fe^{IV}(tmp)^{+\bullet}}$ in the presence of methanol-d_4 at −90 °C.



(5)

Effects of Electron-Withdrawing Substituents on the Reactivity of 3′. The effects of electron-withdrawing substituents bound to the *meso*-phenyl groups of the porphyrin ring on the reactivity of oxoiron(IV) porphyrin π-cation radical complexes have been studied using various *meso*-substituted porphyrins.[24] The results indicate that the reactivity of the oxoiron(IV) porphyrin π-cation radicals is dependent on their oxidation potentials. Therefore, we have examined the substituent effects on the oxygenation of styrene by **3′** formed by the addition of one equiv of C_6F_5IO. As mentioned earlier, the use of one equiv of the oxidant to prepare **3′** prevents reproduction of active species during the oxygenation. At the same time, we have also examined the oxygenation by oxoiron(IV) porphyrin π-cation radicals (**2a**—**d**), which were synthesized by the reaction of **1**-ClO_4 with one equiv of oxidant *in the absence of methanol.*

On the other hand, the first oxidation potentials of **1a**—**d** were measured by cyclic voltammograms in dichloromethane containing 0.1 M TBAP. Reversible oxidation peaks for **1a**—**d** were observed in the range from 1.0 to 1.5 V vs. SCE. The half-wave oxidation potentials of **1a**—**d** along with the rate constants of the styrene oxygenation by **2** and **3′** are summarized in Table 3.

Discussion

Electronic Structure of New Active Intermediates, 3 and 3′. Iron(III) porphyrin *N*-oxides, iron(III) porphyrin dications, and oxoiron(IV) porphyrin π-cation radicals have been reported as high-valent iron porphyrins formally two-electron oxidized from the iron(III) state. In this study we have described the formation of new two-electron oxidized oxoiron porphyrins, **3** and **3′**, by the chemical oxidation of iron(III) porphyrins in the presence of methanol under acidic

Table 3. E_{ox} of Chloro Iron(III) Porphyrins and k_2 for Styrene Oxidation by High-Valent Oxo-Iron Porphyrins

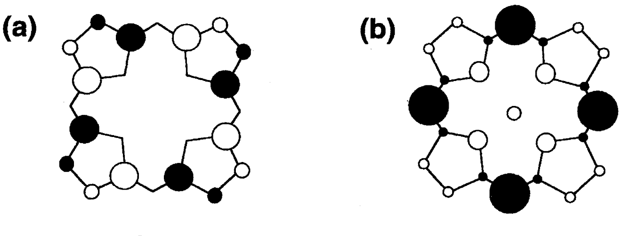
	E_{ox}.	k_2 (10^{-2} M^{-1} s^{-1})	
Porphyrin	V	3′	2
tcmpp (**a**)	1.29[a)]	—	—
tdcpp (**b**)	1.35[a)]	2.9	550
tcfpp (**c**)	1.39	4.4	800
ttcpp (**d**)	1.44	4.7	1300

a) Fujii, *J. Am. Chem. Soc.*, **115**, 4641—4648 (1993).

and neutral conditions. The formulation of **3** is supported by iodometric titration, UV-vis and NMR spectroscopic measurements, thermal interconversion between **2** and **3**, and ability for oxygenation at −90 °C.

The UV-vis spectra of **3b** and **3b′** (Figs. 1 and 2, λ_{max} 418 and 546, and 418 and 532 nm, respectively) are different from those of iron(III) porphyrin *N*-oxides (λ_{max} 441 and 547 nm in toluene for Fe^{III}(tmp) *N*-oxide), iron(III) porphyrin dications (λ_{max} 412 nm in toluene for Fe^{III}(tmp) dication), and also different from both of a_{2u} oxoiron(IV) porphyrin π-cation radicals (λ_{max} 409 and 681 nm in dichloromethane for $O{=}Fe^{IV}(tdcpp)^{+\bullet}$ (**2b**)) and a_{1u} type complexes.[24)] Though the spectrum of oxoiron(IV) porphyrin (**4b**) (λ_{max} 419 and 543 nm in dichloromethane) is rather similar to those of **3b** and **3b′**, oxygenation activity at −90 °C, thermal stability, and oxidizing equivalents measured by iodometric titration readily discriminate **3b** and **3b′** from **4b**. Especially, **4b** is observable even at 0 °C and does not react with olefins at low temperature. Further, the magnetic moment ($\mu_{eff} = 4.0\,\mu_B$) of **3b** provides evidence for the presence of three unpaired electrons in **3b**. These results indicate that **3b** and **3b′** are two-electron oxidized complexes from the resting state and may not be the π-cation radicals, such as **2b**.

The resonance of *meta*-deuterium in **3b** was observed in a diamagnetic region (8.8 ppm). Thus, the assignment of **3b** as an a_{2u} radical species such as **2b** is clearly excluded, because a large downfield shift for the *meta*-deuterium should be observed for the a_{2u} radical species due to the large π-spin density on the *meso*-carbons in the a_{2u} radical orbital, as shown in Fig. 11b. While the signal in a diamagnetic region reminds us of the a_{1u} radical species having a node at the *meso*-carbons (Fig. 11a), the UV-vis spectrum of **3b** is inconsistent with a_{1u} oxoiron(IV) porphyrin π-cation radicals, as already mentioned.[24)] Similar considerations are also applicable to **3b′**. Furthermore, the pyrrole β-deuterium signals of **3b** at −35.1 ppm and **3b′** at −22.9 ppm are less paramagnetically shifted than that of **2b** (−46.2 ppm) and rather similar to **4b** (−33.1 ppm). These results also suggest that **3b** and **3b′** have a neutral porphyrin ring. Thus, the most likely description for **3b** is high spin complexes of either $O{=}Fe^{V}$(tdcpp) or $\cdot O{-}Fe^{IV}$(tdcpp). At this moment, we are not able to differentiate the $O{=}Fe^{V}$ complex from an $\cdot O{-}Fe^{IV}$ complex, thus we describe them as the $O{=}Fe^{V}$ complex for simplicity. To gain further insight, resonance Raman and Mössbauer measurements are planned.

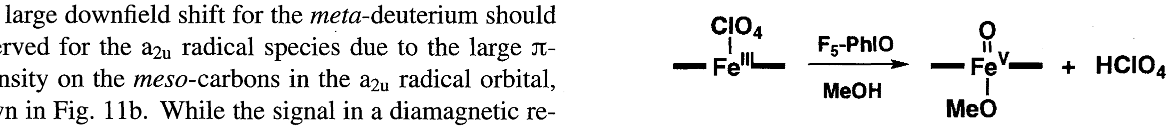


a_{1u} a_{2u}

Fig. 11. Electron spin distribution of porphyrin HOMO: (a) a_{1u}, (b) a_{2u}.

Figure 4 depicts temperature dependent interconversion between **2b** and **3b**. Favorable formation of **3b** at lower temperatures and observation of the paramagnetically shifted methyl deuterium of methanol at 25.6 ppm (data not shown) indicate that the ligation of methanol (or methoxide) to **2b** altered its electronic structure to **3b**.[30)] Though appreciable UV-vis spectral change was not observed upon the introduction of methanol to a dichloromethane solution of $O{=}Fe^{IV}(tmp)^{+\bullet}$, ligation of methanol has been confirmed by the appearance of the methyl resonance at 17.2 ppm. Therefore, formation of both **2a** and **3a′** in the same solution containing methanol may not be simply attributed to the exclusive ligation of methanol in **3a′**. Ligation of methanol both to **2a** and **3a′** but in a different manner as shown in Eq. 6 seems to be rather likely.

On the basis of these considerations, both **3b** and **3b′** can be formulated as oxoiron(V) high spin porphyrins with the methoxide ligand. So far, we could not explain why small differences in UV-vis and NMR spectra were observed for **3b** and **3b′**. These differences are also reflected in the oxygenation activities of **3b** and **3b′** (Table 2). One of the major differences between **3b** and **3b′** is that perchloric acid must be formed in the course of **3b′** formation (Eq. 6) while very weak *m*-chlorobenzoic acid is present in a solution of **3b**. Therefore, one may expect a hydrogen bond between the oxo-oxygen and/or methanol-oxygen of the axial ligand in **3b′** and perchloric acid, because such a small difference in the reaction conditions is known to cause spectral changes.[31)] Further investigation is needed on the effects of acid.



$$\overset{ClO_4}{—Fe^{III}—} \xrightarrow[MeOH]{F_5\text{-}PhIO} \underset{MeO}{\overset{O}{—Fe^{V}—}} + HClO_4 \qquad (6)$$

Recently, Jayaraj et al. reported the influence of *meso*-substituents on the electronic states of oxoiron(IV) porphyrin π-cation radicals.[16)] In the report, oxoiron(IV) porphyrin π-cation radicals were the sole oxidation products under conditions similar to ours, where iron(III) porphyrins with electron-withdrawing substituents were oxidized by peracid in the presence of methanol. Therefore, we have examined the same reactions using UV-vis spectroscopy. Figure 12(a) shows the spectrum of the oxidation product given under almost the same conditions as those reported by Jayaraj et al. ([[Fe^{III}(tdcpp)]($OCOCF_3$)]=1 mM; **4 equiv of *m*CPBA**; $CH_2Cl_2 : CD_3OD = 10:1$; −90 °C). Since the oxidation prod-

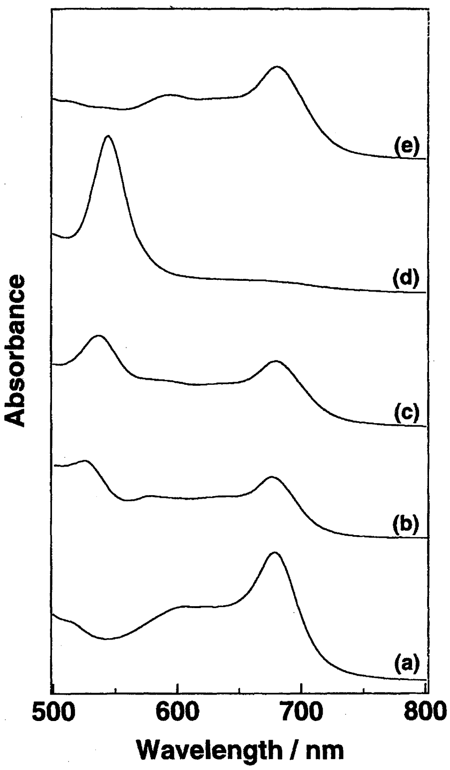


Fig. 12. UV-vis spectra of the oxidation products under various conditions: (a) [Fe^{III}(tdcpp)](trifluoroacetate) + 4 equiv of *m*CPBA in CH_2Cl_2/CD_3OD (10 : 1) at −90 °C, (b) + 1.5 equiv of *m*CPBA, (c) + 1.5 equiv of *m*CPBA in CH_2Cl_2 containing 100 equiv of CD_3OD at −90 °C, (d) [Fe^{III}(tdcpp)](OH) + 1.5 equiv of *m*CPBA in CH_2Cl_2 containing 100 equiv of CD_3OD at −90 °C, (e) (d) + 2 equiv of TFA.

uct has the same spectral characteristics reported by Jayaraj et al., the formation of oxoiron(IV) porphyrin π-cation radical (**2b**) is apparent. As described in the experimental section, we have prepared high-valent oxo species *with a small excess of oxidants (1—1.8 equiv)*. Therefore, we have also examined the reaction of Jayaraj et al. with **1.5 equiv of *m*CPBA** (Fig. 12(b)). In this case, the absorbance at 678 nm clearly decreased with concomitant appearance of absorption at ca. 520 nm. Then we did the oxidation *in the presence of only 100 equiv of CD_3OD* with 1.5 equiv of *m*CPBA (Fig. 12(c)). Surprisingly, new absorption was observed around 540 nm. The addition of 100 equiv of styrene to the solution caused the conversion of 540 nm species to iron(III) porphyrin as well as the oxoiron(IV) porphyrin π-cation radical at −90 °C. Judging from these results, we concluded that the 540 nm species was oxoiron(V) porphyrin (**3b**) and **3b** was not formed in the presence of a large amount of peracid. We attribute the suppression of the oxoiron(V) porphyrin formation to the coordination of peracid (acid) or methanol instead of methoxide, the coordination of which is crucial for the formation of oxoiron(V) porphyrin. As shown in Fig. 12(d), the oxidation of [Fe^{III}(tdcpp)](OH) by 1.5 equiv of *m*CPBA in CH_2Cl_2 containing 100 equiv of CD_3OD afforded **3b** as the sole product at −90 °C, since the resulting solution was almost neutral. Furthermore, the conversion of **3b** to oxoiron(IV) porphyrin π-cation radical (**2b**) was observed upon the addition of 2 equiv of trifluoroacetic acid (TFA) to the solution of (d) (Fig. 12(e)). These results are summarized in Table 4, and indicate that the formation of **2** and **3** (and **3′**) is very dependent on reaction conditions, especially the nature of the 6th ligand and acid.

Possible Mechanism for the Formation of Oxoiron(V) Porphyrins. On the basis of the various spectroscopic data for **3**, it is clear that this complex has three unpaired electrons on the iron-oxo unit (possibly only iron), not the porphyrin ring. We credit the electron-withdrawing substituents on the porphyrin ring and the axial ligand for the formation of **3** instead of **2**. Introduction of electron-withdrawing groups on the porphyrin ring is known to lower the porphyrin orbital energy. For instance, a higher oxidation potential of [Fe^{III}(tdcpp)]$^+$/[Fe^{III}(tdcpp)$^{+\bullet}$]$^{2+}$ (1.35 V) than that of [Fe^{III}(tmp)]$^+$/[Fe^{III}(tmp)$^{+\bullet}$]$^{2+}$ (1.11 V)[24] suggests that HOMO (a_{2u}) energy of the chloro substituted complex (Fe^{III}(tdcpp)) is 0.24 V lower than that of the methyl substituted complex (Fe^{III}(tmp)) as shown in Figs. 13a and 13b. Ligation of methoxide to **2b** raises the d_{xz} and d_{yz} orbitals as well as the d_{z^2} orbital. These effects eventually turn upside down the energy levels between the a_{2u} orbital and the d_{xz} and d_{yz} orbitals to form **3b** (Fig. 13c). The idea is supported by the result of the oxidation of **1**(**b**—**d**)-ClO_4 by C_6F_5IO in the presence of methanol. While the preferable formations of **3b′**—**d′** are observed, the oxidation of a less electron deficient complex (**1a**-ClO_4) afforded a mixture of **2a** (major) and **3a′** (minor). These results suggest that the electron-withdrawing substituents on the porphyrin ring play two roles in the formation of **3**. One is lowering the π energy level of the porphyrin ring, and the other is increasing methoxide

Table 4. Summary of Fig. 12

Symbol[a)]	Axial ligand of ferric complex	Quantity of added *m*CPBA	Reaction condition	Products (total 100%)	
				2b (%)	**3b** (%)
Ref. 16	$CF_3SO_3^-$	8 equiv	in CH_2Cl_2 : MeOH = 10 : 1 at −80 °C	100	
(a)	CF_3COO^-	4 equiv	in CH_2Cl_2 : MeOH = 10 : 1 at −90 °C	100	
(c)	CF_3COO^-	1.5 equiv	in CH_2Cl_2/100 equiv of MeOH at −90 °C[b)]	ca. 50[c)]	ca. 50[c)]
(d)	OH^-	1.5 equiv	in CH_2Cl_2/100 equiv of MeOH at −90 °C[b)]		100
(e)	—	—	(d) + 2 equiv of TFA	ca. 90[c)]	ca. 10[c)]

a) Symbols for the spectra in Fig. 13. b) CH_2Cl_2/100 equiv of MeOH approximately corresponds to CH_2Cl_2 : MeOH=300 : 1. c) These ratios were determined by the decomposition of each spectrum into **2b** (a) and **3b** (d).

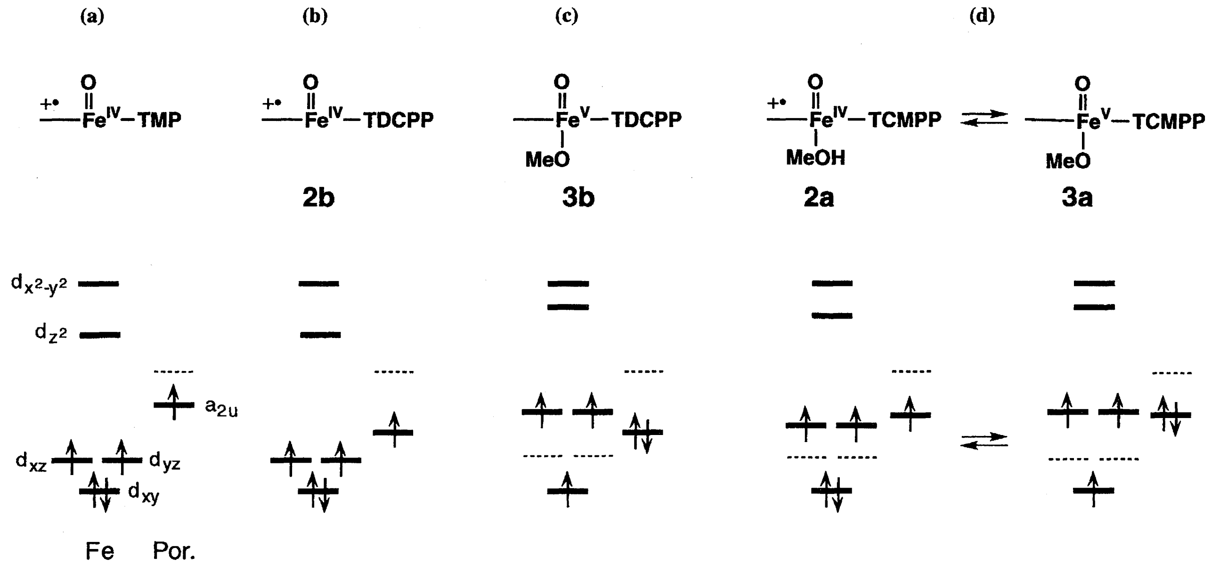
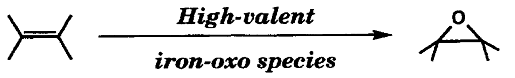


Fig. 13. Orbital energy diagram for high-valent iron porphyrins: (a) O=Fe^{IV}(tmp)$^{+\bullet}$, (b) **2b**, (c) **3b**, (d) **2a** and **3a**.

ligation rather than methanol to raise iron d orbitals. Once the energy level between the a_{2u} orbital of the porphyrin ring and the d_{xy} and d_{yz} orbitals of the iron turns upside down, transformation of **2** to **3** will be observed. In the case of **2a** and **3a′**, less electron-withdrawing ability of the substituents failed to complete the ligation of methoxide as shown in Fig. 13d. So far, this proposed mechanism explains all the results obtained in this study without contradiction.

Reactivity of Oxoiron(V) Porphyrins and Oxoiron(IV) Porphyrin π-Cation Radicals. It has been known that oxometalloporphyrin complexes are able to oxidize various substrates observed in P-450 catalyzed reactions such as oxygenation of olefins (Eq. 7).[32] Although kinetic studies of the oxygenation catalyzed by metalloporphyrins have been done by many groups, the direct comparison of reactivities between oxoiron(V) porphyrins (**3**) and oxoiron(IV) porphyrin π-cation radicals (**2**) has never been done except for our preliminary study. Preparation of **2** and **3** now allows us to examine the roles of porphyrin π-cation radicals in **2** in the olefin oxygenation.



(7)

Thus, we have measured the rate constants of the oxygenation reactions by stoichiometric oxidation of olefins by **2** and **3** at −90 °C (Tables 2 and 3). Interestingly, **3** is found to be less reactive than **2** in the oxygenation of olefins. That one electron oxidation of either the porphyrin ring or the central iron in an O=Fe^{IV} complex (**4**) has a different reactivity could be explained as follows: while the π-cation radical orbital (a_{2u}) in **2** interacts with the p_z orbital of the oxo ligand through an iron p_z orbital as well as the interactions between iron d_{xz} (d_{yz}) and p_x (p_y) of the oxo ligand, the iron d_{xy} orbitals of **3** do not interact with any of the oxo ligand orbitals.[24,33] This implies that the radical character of the oxo ligand in **3** is similar to that of **4**, but the lack of one electron from the d_{xy} orbital makes **3** less electron rich than **4**. Therefore, the reactivity of **3** is expected to be between **2** and **4**. The observations indicate that the presence of the porphyrin radical is crucial for the activation of the oxo ligand.

That **3**, with a higher oxidation potential porphyrin, is more reactive as shown in Table 3 indicates the mechanism for oxygenation reaction by **3** involves the electrophilic character as observed in the oxygenation by oxoiron(IV) porphyrin π-cation radicals. Thus, *p*-chlorostyrene is less reactive than styrene. Interestingly, the relative rates of olefin oxygenation by **2b** and **3b** are very close (Table 2). In addition, competitive oxygenation of norbornylene and α-methylstyrene by **2b** and **3b** showed preferable oxidation of less hindered norbornylene with almost identical selectivity (100 : 30—35), suggesting very similar oxygenation mechanisms by **2** and **3**.[34]

Implication of Biological Use of Porphyrin π-Cation Radicals. Heme enzymes such as peroxidases and catalase are known to use two-electron oxidized intermediates, called compound **I**. Many spectroscopic studies support the formulation of compound **I** as an oxoiron(IV) porphyrin π-cation radical.[6—10] In the case of P-450, the active species responsible for the monooxygenations are still obscure and the subject of intensive investigations.[11] While Champion pointed out a possible description of ·O–Fe(IV) (one extreme structure of O=Fe(V)) as the active species of P-450,[14] Egawa et al. suggested formation of a compound **I** type intermediate on the basis of their rapid scan measurements.[13] There are two important conclusions from our studies; i) UV-vis spectra of the O=Fe^{V} complexes are almost identical to those of O=Fe(IV) species, compound **II**. Therefore, one must be very careful to assign compound **II** on the basis of UV-vis spectroscopy. ii) O=Fe(V) porphyrins are less reactive than the corresponding O=Fe(IV) porphyrin π-cation radicals. The results are suggestive of the biological role of porphyrin π-cation radicals in compound **I** of peroxidases, catalase, and possibly in the active species of P-450.

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