Mechanisms for (porphyrinato)iron(III)-catalyzed oxygenation of styrenes by O_2 in presence of BH_4^-

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Abstract

Mechanisms have been proposed for the (porphyrinato)iron(III)-catalyzed oxidation of styrene and α-methylstyrene by O_2 in benzene–ethanol containing $NaBH_4$. The product analysis and the deuterium incorporation using $NaBD_4$ suggest that the (σ-alkyl)Fe^{III}–Por complex, $[C_6H_5CH(CH_3)]Fe^{III}$–Por, is formed as an intermediate in the reaction of styrene. Insertion of O_2 to the (σ-alkyl)Fe^{III}–Por complex having a radical character yields a (peroxy)iron(III) complex, $[C_6H_5CH(CH_3)OO]Fe^{III}$–Por. The homolytic fission of the O–O bond followed by the hydrogen abstraction within the radical pair affords acetophenone and (HO)Fe^{III}–Por. Acetophenone is readily reduced with $NaBH_4$ to give 1-phenylethanol. Meanwhile, the reaction of α-methylstyrene with BH_4^- in the presence of Por–Fe^{III}Cl may also yield the (σ-alkyl)Fe^{III}–Por complex, which takes up O_2 to form a (peroxy)iron(III) complex, $(C_6H_5C(CH_3)_2OO)Fe^{III}$–Por. The (peroxy)iron(III) complex is directly reduced by BH_4^- to give 2-phenyl-2-propanol and (HO)Fe^{III}–Por. In the reaction of styrene, such direct reduction of the (peroxy)iron(III) complex as a minor pathway competes with the homolytic fission of its O–O bond.

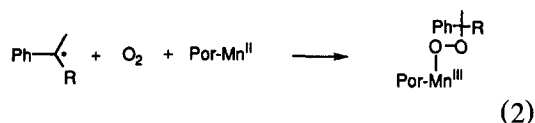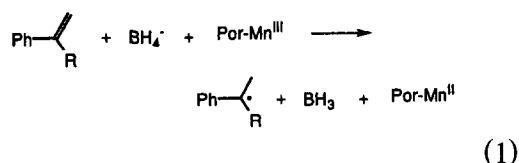Keywords: Porphyrin complexes; Oxygenation; Styrenes; Borohydride ion

1. Introduction

Cytochrome P-450 is a monooxygenase which activates dioxygen to oxidize a wide variety of hydrocarbons [1]. It has been elucidated that Por–Fe^{III} (Por: porphyrin dianion) is reduced to Por–Fe^{II} via an electron transfer from NADPH. The iron(II) complex reacts with O_2 to afford an oxygen adduct which further accepts an electron and two protons to form a high-valent (oxo)iron porphyrin species such as $O=Fe^V$–Por or $[O=Fe^{IV}$–Por$]^{+\cdot}$ [2,3]. Since such an oxygen activation in biological system is very interesting to chemists, much effort has been made to mimic the P-450-catalyzed oxygenation in artificial systems [4]. In most model systems, the studies have been focused on the preparation of high-valent (oxo)iron porphyrins using various oxygen transfer agents such as iodosobenzenes [5], hypochlorites [6], N,N-dimethylaniline N-oxides [7], percarboxylic acids [8], $KHSO_5$ [9], alkyl hydroperoxide [10], H_2O_2 [11], and O_2 in the presence of reducing agents [12–15].

As one of the P-450-model systems, Tabushi and Koga [16] developed a system composed of

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$Mn^{III}(TPP)$, BH_4^-, and O_2 (TPP: 5,10,15,20-tetraphenylporphyrin dianion). In this model system, cyclohexene in benzene–ethanol reacts with O_2 to afford cyclohexanol and cyclohexen-2-ol. They briefly mentioned that cyclohexene oxide is the primary product which is reduced by $NaBH_4$ to yield cyclohexanol. The model system proposed by Tabushi and Koga has further been studied by several groups [17]. On the basis of the product analysis, Shimizu et al. [17] concluded that a high-valent (oxo)manganese porphyrin is not the active species of this reaction. Recently, we traced this model system and demonstrated that the oxygenation of styrene and α-methylstyrene by O_2 in benzene–ethanol containing $Por–Mn^{III}$ and $NaBH_4$ occurs via the 1-phenylethyl and 2-phenyl-2-propyl radicals, respectively [18]:

$$Ph\!-\!\!\!<_R + BH_4^{\cdot} + Por\text{-}Mn^{III} \longrightarrow$$
$$Ph\!-\!\!\!<_R^{\cdot} + BH_3 + Por\text{-}Mn^{II}$$

$$(1)$$

$$Ph\!-\!\!\!<_R^{\cdot} + O_2 + Por\text{-}Mn^{II} \longrightarrow \begin{array}{c} Ph\!\!\mid\!\!R \\ O\text{-}O \\ | \\ Por\text{-}Mn^{III} \end{array}$$

$$(2)$$

Homolytic fission of an O–O bond of the (alkylperoxo)manganese(III) complex formed from styrene gives $(HO)Mn^{III}$–Por and acetophenone which is readily reduced to 1-phenylethanol by BH_4^-. In the case of α-methylstyrene, the (alkylperoxo)manganese(III) complex is directly reduced by BH_4^- to afford 2-phenyl-2-propanol and $(HO)Mn^{III}$–Por. Such a radical mechanism is very similar to that for the (porphyrinato)-cobalt(II)-catalyzed oxygenation of styrenes [19].

Although it has been known that similar oxygenation occurs when $Fe^{III}(TPP)Cl$ is used in place of $Por–Mn^{III}Cl$ [17,20], no detailed mechanism has been studied for the $Por–Fe^{III}$-catalyzed oxidation of alkenes. The oxygenation

product of the $Fe^{III}(TPP)$-catalyzed oxidation of styrene is 1-phenylethanol, not styrene oxide. Since styrene oxide is hardly reduced to 1-phenylethanol by $NaBH_4$, the mechanism involving a high valent (oxo)iron porphyrin complex [20] is very doubtful. In the present study, we have tried to clarify the mechanism for the (porphyrinato)iron-catalyzed oxidation of alkenes by O_2 in benzene–ethanol containing $NaBH_4$. In a previous paper [21], we reported the reduction of alkenes by $NaBH_4$ in anaerobic benzene–ethanol containing $Por–Fe^{III}$ complexes. In the case of styrene, ethylbenzene and 2,3-diphenylbutane are the reduction products which are assumed to be produced via the $[C_6H_5CH(CH_3)]Fe^{II}$–Por and $[C_6H_5CH(CH_3)]Fe^{III}$–Por complexes (1), respectively. We demonstrated that $(\sigma\text{-alkyl})Fe^{II}$–Por and $(\sigma\text{-alkyl})Fe^{III}$–Por have alkyl anion and alkyl radical characters, respectively. Since the reaction conditions of the present oxygenation of alkenes are quite the same as those of the previous reduction except for the existence of O_2, it is reasonable to consider that the $(\sigma\text{-alkyl})Fe^{III}$–Por complex is formed as an intermediate in the (porphyrinato)iron-catalyzed oxygenation. Our previous communication briefly mentioned the reaction mechanism [22].

2. Experimental

2.1. Materials

5,10,15,20-Tetraphenylporphyrin $(TPPH_2)$ [23], 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin $(TPFPPH_2)$ [24], 5,10,15,20-tetrakis(2,4,6-trimethylphenyl)porphyrin $(TMPH_2)$ [25], and 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin $(TDCPPH_2)$ [26] were prepared by the procedures described in the literature. $Fe^{III}(TPP)Cl$, $Fe^{III}(TPFPP)Cl$, $Fe^{III}(TMP)Cl$, and $Fe^{III}(TDCPP)Cl$ were synthesized using a standard procedure [27]. Styrene and α-methyl-

styrene (Nacalai) were purified by passing through alumina columns to remove oxidized products. $NaBH_4$ (Nacalai), $NaBD_4$ (CEA), diphenyl disulfide (Nacalai), 4,4'-dichlorodiphenyl disulfide (Tokyo Kasei), imidazole, 1-methylimidazole, and 2-methylimidazole (Nacalai) were purchased and used without further purification. 4,4'-Dimethyldiphenyl disulfide (Tokyo Kasei) was recrystallized from benzene–methanol. All solvents were used after drying by the appropriate methods and distilled before use.

2.2. Instrumentation

The 400 MHz ^1H NMR spectra were measured on a JEOL JNM-GX400 spectrometer at 23°C. TMS was used as an internal standard. The GC–MS spectra were taken on a Shimadzu QP2000 spectrometer with the use of electron-impact ionization at an energy of 70 eV. For GLC analysis, a Shimadzu GC-8A gas chromatograph having a Thermon 1000 glass column (1 m) was used.

2.3. General procedure of reaction

A typical example of the oxygenation of alkene is shown below. A mixture of $Fe^{III}(TPP)Cl$ (10 mg, 0.014 mmol), $NaBH_4$ (54 mg, 1.4 mmol), and n-eicosane (25 mg, an internal standard for GLC) was placed in a 30-ml two-necked flask with a balloon filled with O_2. The reaction system was evacuated by a water pump and filled with O_2 in the balloon. After four cycles of evacuation–charging with O_2, styrene (146 mg, 1.4 mmol) in 8 ml of aerobic benzene–ethanol (1:1) was injected into the reaction vessel using a syringe to start the oxygenation reaction. The reaction mixture was stirred under the O_2 atmosphere at room temperature. The reaction was followed by means of GLC. After the reaction was completed, the products were isolated by silica gel column chromatography with benzene and analyzed by means of ^1H NMR and GC–MS spectroscopies.

3. Results and discussion

3.1. Oxygenation of styrene

(Porphyrinato)iron-catalyzed oxygenation of styrene was carried out in a benzene–ethanol (1:1) mixed solvent containing $NaBH_4$ (mol ratio: styrene/$NaBH_4$/catalyst = 100/100/1). Table 1 shows the results. No oxygenation takes place if one of the components of this system (O_2, $NaBH_4$, or Por–$Fe^{III}Cl$) is eliminated.

The relatively slow oxidation of styrene occurs to yield 1-phenylethanol and acetophenone when $Fe^{III}(TPP)Cl$ is used as a catalyst (entry 1). In the $Fe^{III}(TPFPP)$-catalyzed oxidation, styrene was consumed completely within 30 min and ethylbenzene and 2,3-diphenylbutane were formed as the reduction products together with the oxidation product, 1-phenylethanol (entry 2). The time course of the reaction is shown in Fig. 1, which demonstrates that acetophenone is produced at an initial stage of the reaction and an induction period is observed for the formation of 1-phenylethanol. These findings indicate that acetophenone is the primary product of the oxygenation of styrene. The similar pathway has been assumed for the (porphyrinato)-manganese-catalyzed oxidation of styrene [17,18]. In the previous paper, we

Table 1
(Porphyrinato)iron(III)-catalyzed reactions of styrene in O_2-saturated benzene–ethanol (1:1) containing $NaBH_4$ [a]

Entry	Catalyst	Reaction time / hr	Conversion / %	Yield[b] / %			
-------	----------	--------------------	----------------	Ph—⟨OH	Ph⟩⟨Ph	Ph—/	Ph—⟨O
1	Fe^{III}(TPP)Cl	3	45	33	0	0	<1
2	Fe^{III}(TPFPP)Cl	0.5	100	54	17	4	0
3	Fe^{III}(TMP)Cl	3	14	5	0	0	0
4	Fe^{III}(TDCPP)Cl	3	33	9	2	0	0

[a] The reaction conditions are shown in Experimental section in text.
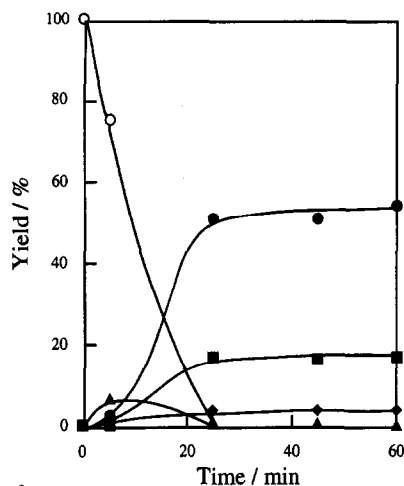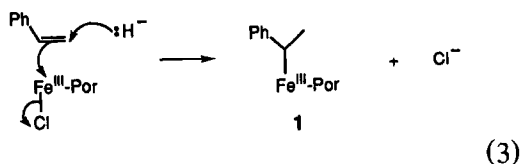[b] Yields based on an initial concentration of styrene.

Fig. 1. Progress in the disappearance of styrene (O) and in the formation of 1-phenylethanol (●), acetophenone (▲), 2,3-diphenylbutane (■), and ethylbenzene (♦) in the reaction of styrene (1.4 mmol) in O_2-saturated benzene–ethanol (1:1, 8 ml) containing (TPFPP)Fe^{III}Cl (0.014 mmol) and $NaBH_4$ (1.4 mmol) at room temperature.

proposed that the (σ-alkyl)Fe^{III}–Por complex **1** is formed in the reduction of styrene with $NaBH_4$ in the presence of Fe^{III}(TPP)Cl under anaerobic conditions [21]. The only difference in the experimental conditions between the present oxidation and the previous reduction is whether O_2 exists or not. Therefore, it is quite reasonable to consider that **1** is also formed in the present oxidation reaction as an intermediate. The fact that the rate of the Fe(TPFPP)-catalyzed reaction is much faster than that of the Fe(TPP)-catalyzed one suggests a transition state stabilized by the electron-withdrawing groups attached to the benzene rings at the periphery of the porphyrin. The following transition state to **1** seems to be stabilized by the electron-deficient (porphyrinato)iron(III):

$$\text{Ph}\diagdown\diagup\diagdown\!\!H^- \longrightarrow \text{Ph}\diagdown\!\!\diagup \quad + \quad Cl^-$$
$$\underset{\displaystyle Cl}{Fe^{III}\text{-Por}} \qquad\qquad \underset{\displaystyle \mathbf{1}}{Fe^{III}\text{-Por}}$$

(3)

Therefore, it is reasonable to assume the complex **1** as an intermediate of the reaction. The intermediate **1** is known to have a radical char-

acter and to be the precursor of 2,3-diphenylbutane [21]. Although we could not obtain any direct evidence for forming the (σ-alkyl)Fe^{III}–Por complex, this complex could be regarded as a hypothetical intermediate. The validity of this hypothesis will be examined in this study.

The reaction was retarded when Fe^{III}(TMP)Cl was used as the catalyst (entry 3). Two reasons can be considered for this retardation. One of them is destabilization of the transition state to **1** by the electron-donating groups attached to the porphyrin periphery. Another reason is the steric hindrance due to the methyl groups attached to the ortho positions of the benzene rings of the porphyrin. Although Fe^{III}(TDCPP)Cl is an electron-deficient ironporphyrin, the Fe^{III}(TDCPP)Cl-catalyzed reaction proceeds more slowly than the Fe(TPP)-catalyzed one (entry 4). The yield of 1-phenylethanol is very low compared with those in the reactions catalyzed by Fe^{III}(TPP)Cl and Fe^{III}(TPFPP)Cl. Slow consumption of styrene seems to be ascribed to the steric hindrance due to the Cl groups of this porphyrin. Since the formation of **1** is expected to be affected by steric hindrance, the results obtained support our assumption that the (σ-alkyl)Fe^{III} porphyrin complex **1** is the reaction intermediate.

The deuterium incorporation using $NaBD_4$ was examined. The reaction conditions were the same as those described in the Experimental section, except for the use of $NaBD_4$ in place of $NaBH_4$. The reaction mixture was withdrawn at appropriate times and diluted with acetone. The samples thus obtained were analyzed by means of GC–MS spectroscopy. After 6 h, two molecular-ion peaks were observed at $m/e = 123$ and 124 (relative intensity: 1:1.2), which correspond to $C_6H_5CH(OH)(CH_2D)$ and $C_6H_5CD(OH)(CH_2D)$, respectively. The fragment peaks due to the $C_6H_5CH(OH)$ and $C_6H_5CD(OH)$ radical ions were also observed at $m/e = 107$ and 108 (relative intensity: 1:2), respectively. If 1-phenylethanol is necessarily formed via acetophenone, the molecular-ion peak should be observed only at $m/e = 124$.

The result of deuterium incorporation indicates that there are, at least, two pathways for formation of 1-phenylethanol. Since the mass spectroscopy applied in this study (EI, 70 eV) cannot provide the correct ratio of $C_6H_5CH(OH)(CH_2D)$ to $C_6H_5CD(OH)(CH_2D)$ [28], the reaction products were analyzed by means of ^1H NMR spectroscopy. After the reaction, the solvent was removed in vacuo and the residue was distilled using a glass-tube oven under a reduced pressure. The distillate in $CDCl_3$ was analyzed by means of ^1H NMR spectroscopy. The NMR signals were assigned to $C_6H_5CD(OH)(CH_2D)$ and $C_6H_5CH(OH)(CH_2D)$ and no signals due to other products were observed. The signal due to $-CH(OH)-$ appeared at 4.97 ppm. The comparison of the signal intensity at 4.97 ppm due to $-CH(OH)-$ with that at 1.80 ppm due to $-OH$ suggests that the ratio of the formation of $C_6H_5CD(OH)(CH_2D)$ to $C_6H_5CH(OH)(CH_2D)$ is 3:1. The experiment using C_2H_5OD indicates that no proton transfer from the protic solvent occurs in the formation of 1-phenylethanol.

3.2. Oxygenation of α-methylstyrene

In the reaction of styrene, there are two pathways for forming 1-phenylethanol. The oxygenation of α-methylstyrene under the same conditions is expected to proceed without formation of ketone. The results of the oxygenation of α-methylstyrene are summarized in Table 2. In the Fe(TPP)-catalyzed reaction, the rate of oxidation of α-methylstyrene to 2-phenyl-2-propanol is faster than that of styrene to 1-phenylethanol. If demethylation occurs to yield acetophenone, 1-phenylethanol should be formed. However, 2-phenyl-2-propanol is the sole oxidation product[1].

We have to consider whether the (σ-alkyl)Fe^{III}–Por complex, $[C_6H_5C(CH_3)_2]Fe^{III}$–TPP **2**, is also formed in the reaction of α-methylstyrene through a reaction similar to Eq. 3. The carbanion formed from α-methylstyrene, 2-phenyl-2-propanide, should be more unstable than that from styrene. In addition, the center of the complex **2** is more crowded than that of complex **1** because of two bulky methyl groups of 2-phenyl-2-propanide. It is predicted, therefore, that the complex **2** is more unstable than the complex **1**. However, the Fe^{III}(TPP)-catalyzed oxidation of α-methylstyrene occurs more rapidly than that of styrene.

Does such inconsistency indicate that **2** is not the intermediate in the reaction of α-methylstyrene? In the previous study, we demonstrated that the (σ-alkyl)Fe^{III}–Por complex has a radical character [21]:

$$\tag{4}$$
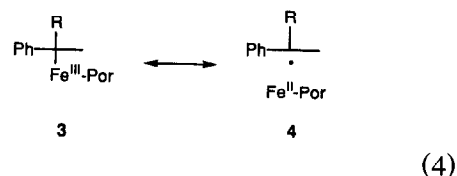
The experimental results obtained in this study can be explained reasonably by assuming the

Table 2
(Porphyrinato)iron(III)-catalyzed reactions of α-methylstyrene in O_2-saturated benzene–ethanol (1:1) containing $NaBH_4$ [a]

Entry	Catalyst	Reation time / hr	Conversion / %	Product (yield[a] / %)		
				Ph—OH	Ph——Ph	Ph—<
5	Fe^{III}(TPP)Cl	3	78	55	0	0
6	Fe^{III}(TPFPP)Cl	0.5	100	45	26	4
7	Fe^{III}(TMP)Cl	3	35	7	0	0
8	Fe^{III}(TDCPP)Cl	3	65	27	10	0

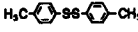[a] The reaction conditions are shown in Experimental section in the text.
[b] Yields based on an initial concentration of α-methylstyrene.
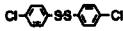
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[1] The demethylation was observed in the reaction of α-methylstyrene in dichloromethane. Details of this reaction have not yet been elucidated.

structure **4** as the (σ-alkyl)Fe^{III}–Por complex. Namely, the 2-phenyl-2-propyl radical formed from α-methylstyrene is more stable than the 1-phenylethyl radical from styrene. We are thinking that **2** is the complex whose character is represented by the structure **4**.

The reduction products, cumene and 2,3-dimethyl-2,3-diphenylbutane, are formed in the Fe^{III}(TPFPP)-catalyzed reaction (entry 6). The total yield of the reduction products in the reaction of α-methylstyrene is higher than that of styrene. This can be interpreted in terms of the difference in the radical stability. The 2-phenyl-2-propyl radical is more stable than the 1-phenylethyl radical. It is reasonable to assume, therefore, that the 2-phenyl-2-propyl radical which loosely coordinates to Por–Fe^{II} is the intermediate of both the oxidation and reduction reactions of α-methylstyrene. As the case of styrene, the bulky groups attached to the ortho positions of the benzene rings of porphyrin retard the reaction (entries 7 and 8).

In the oxygenation of α-methylstyrene in the presence of NaBD$_4$, C$_6$H$_5$C(CH$_3$)(CH$_2$D)(OH) is the sole oxygenation product.

Table 3
Effects of axial ligands on (TPP)Fe^{III}-catalyzed oxygenation of styrene [a]

Entry	Ligand	Yield[b]/%		
		Ph—⟨OH	Ph—⟨OH	Ph—⟨Ph
9	none	64 (80)	0	0
10	⟨⟩-SS-⟨⟩	62 (62)	19 (19)	0
11	Cl-⟨⟩-SS-⟨⟩-Cl	50 (50)	20 (20)	6 (6)
12	H₃C-⟨⟩-SS-⟨⟩-CH₃	59 (59)	20 (20)	0
13	N⌒NH	80 (80)	0	0
14	N⌒NCH₃	52 (89)	0	0
15	N⌒NH CH₃	49 (83)	0	0

[a] The reactions were carried out for 24 hr at room temperature in O$_2$-saturated benzene–ethanol (1:1) under the following conditions: styrene: 1.4 mmol, (TPP)Fe^{III}Cl: 0.014 mmol, NaBH$_4$: 1.4 mmol, axial ligand: 0.14 mmol.

[b] Yields based on an initial concentration of α-methylstyrene. The values in parentheses are the yields based on the consumed styrene.
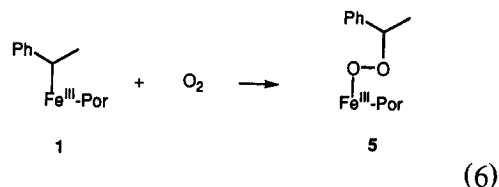
3.3. Effects of axial ligands

Table 3 shows the effects of the axial ligands in the Fe^{III}(TPP)-catalyzed reactions of styrene. We found that diphenyl disulfide is reduced by NaBH$_4$ [29]:

$$\langle\rangle\text{-S-S-}\langle\rangle + \text{BH}_4^- \longrightarrow \langle\rangle\text{S}^- + \langle\rangle\text{SH} + \text{BH}_3$$

(5)
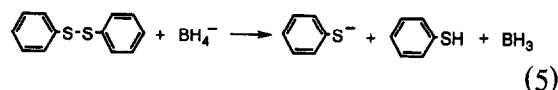
Therefore, the thiophenolate ion can act as an axial ligand. In the presence of diphenyl disulfide and its derivatives (entries 10, 11, and 12), benzyl alcohol is produced in ca. 20% yield together with 1-phenylethanol (50–60% yields). Meanwhile, the yield of 1-phenylethanol increases when imidazole is added as a ligand. Both 1- and 2-methylimidazoles retard the oxygenation reaction.
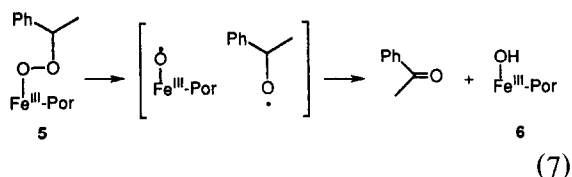
3.4. Reaction mechanisms

In general, styrene is not reduced by NaBH$_4$ in solutions. In the presence of Por–Fe^{III}Cl, however, styrene is readily reduced in benzene–ethanol to give ethylbenzene and 2,3-diphenylbutane [21]. We have demonstrated that the reduction to 2,3-diphenylbutane occurs through the formation of the (σ-alkyl)Fe^{III}–Por complex **1** having a radical character. It is quite reasonable to assume, therefore, that the complex **1** is also the intermediate of the oxygenation reaction of styrene. It has been known that dioxygen inserts into the iron(III)–carbon bond of (σ-alkyl)Fe^{III}–Por complex [30]:

$$\text{Ph}\diagup\text{Fe}^{III}\text{-Por} + O_2 \longrightarrow \text{Ph}\diagup\text{O-O}\diagup\text{Fe}^{III}\text{-Por}$$

1   **5**

(6)

The radical character of **1** seems to be adequate to the formation of **5** [31]. The O–O bond of the (alkylperoxo)iron(III) complex **5** derived from styrene may homolytically dissociate to form a

radical pair, followed by the hydrogen abstraction within a cage to afford acetophenone and a (hydroxo)iron(III) porphyrin complex **6**:


$$(7)$$

The formation of acetophenone is understood by this mechanism, which is just the same as the hypothetical one proposed in our previous communication [22].

In the case of α-methylstyrene, the reaction shown in Eq. 7 does not occur. Probably, the direct reduction of the (alkylperoxo)iron(III) porphyrin complex **7** with $NaBH_4$ takes place:


$$(8)$$

$$(9)$$
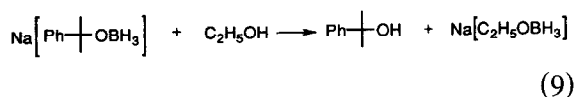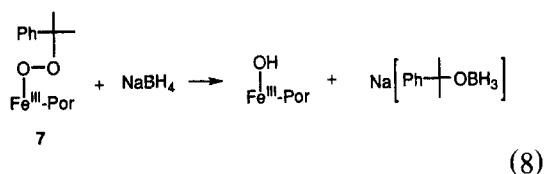
In the reaction of styrene, the direct reduction of the (peroxo)iron(III) complex **5** also proceeds to afford 1-phenylethanol as a minor pathway. The results of the deuterium incorporation for the reaction of styrene can be understood by these two mechanisms.

We have to consider the mechanisms for the effects of the axial ligands. In the presence of diphenyl disulfide and its derivatives, benzyl alcohol is formed in the oxygenation of styrene (entries 10, 11, and 12). It is known that the 1-phenylethoxyl radical dissociates into benzaldehyde and a methyl radical [32]:

$$(10)$$
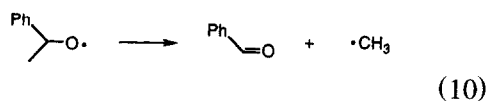
The porphyrin radical in the radical pair shown in Eq. 7 is equivalent to the (oxo)iron(IV) porphyrin complex **8**. Such a high valent (oxo)iron(IV) porphyrin complex should be stabilized by the axial ligand such as $C_6H_5S^-$:


$$(11)$$
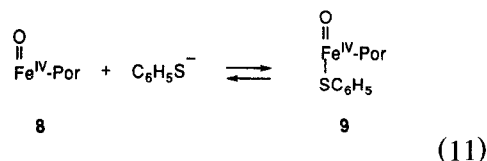
The ability of **8** to abstract a hydrogen from the 1-phenylethoxyl radical within the cage (Eq. 7) is weakened by coordination of the thiophenolate ion as an axial ligand. Therefore, the 1-phenylethoxyl radical moves out from the cage to dissociate spontaneously yielding benzaldehyde which is readily reduced to benzyl alcohol with $NaBH_4$.

The deceleration effect by 1- and 2-methylimidazoles may be interpreted in terms of the destabilization of the complex **1**. The electron-donating nature of these ligands should increase the activation energy for the reaction shown in Eq. 3.

The reduction products of styrene and α-methylstyrene are produced only when the electron-deficient porphyrin complexes are used as the catalysts (entries 2, 4, 6, and 8). The (σ-alkyl)Fe^{III}–Por complex is stabilized when the porphyrin ligand has the electron-withdrawing groups at its periphery. Therefore, the bimolecular reactions of such a (σ-alkyl)Fe^{III}–Por complex should occur to afford 2,3-diphenylbutane and ethylbenzene in the case of styrene and 2,3-dimethyl-2,3-diphenylbutane and cumene in the case of α-methylstyrene. We have demonstrated previously that ethylbenzene is formed through a proton transfer from ethanol to the (σ-alkyl)Fe^{II}–Por complex having a carbanion character under the anaerobic conditions [21]. Under the O_2-saturated conditions, however, the (σ-alkyl)Fe^{II}–Por complex is easily oxidized to the (σ-alkyl)Fe^{III}–Por complex [33]. Therefore,

it is reasonable to assume that ethylbenzene or cumene is formed via a disproportionation reaction of the corresponding (σ-alkyl)Fe^{III}–Por complex:

$$\text{(12)}$$
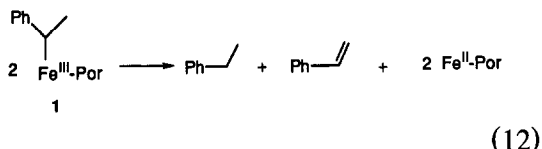
In this paper, we present the reliable mechanisms for the cytochrome P-450 model system where (porphyrinato)iron(III), O_2, and $NaBH_4$ are used as the catalyst, the oxidant, and the reductant, respectively. The remaining problem is the mechanism for formation of the (σ-alkyl)Fe^{III}–Por complex. A hydride iron complex, H–Fe^{III}–Por, may be a key species. Further investigation is needed to clarify this point.

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