Mechanisms for (Porphinato)manganese(III)-Catalyzed Oxygenation and Reduction of Styrenes in Benzene–Ethanol Containing Sodium Borohydride

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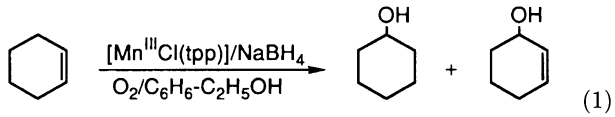
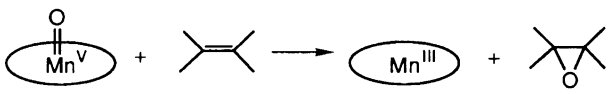
1-Phenylethanol, acetophenone, 2,3-diphenylbutane, and ethylbenzene are produced in the (porphinato)-manganese(III)-catalyzed reaction of styrene with $NaBH_4$ in aerobic benzene–ethanol. Chloro(5,10,15,20-tetraphenylporphinato)manganese(III) ([Mn^{III}Cl(tpp)]) and chloro[5,10,15,20-tetrakis(2,4,6-trimethylphenyl)porphinato]manganese(III) ([Mn^{III}Cl(tmp)]) have been used as the catalysts. It is suggested that the [Mn^{III}(tpp)]-mediated reaction of styrene with $NaBH_4$ yields 1-phenylethyl radical and [Mn^{II}(tpp)]. The 1-phenylethyl radical reacts with dioxygen to generate a peroxyl radical, $(C_6H_5)(CH_3)CHOO\cdot$, which is stabilized by coordinating to [Mn^{II}(tpp)]. [Mn^{III}[$OOCH(CH_3)(C_6H_5)$](tpp)] thus formed may yield [Mn^{III}OH(tpp)] and acetophenone which is readily reduced to 1-phenylethanol with $NaBH_4$. The coupling and disproportionation reactions of the 1-phenylethyl radicals afford 2,3-diphenylbutane and ethylbenzene, respectively. Slower reaction of styrene observed in the catalysis by $[Mn^{III}(tmp)]^+$ can be interpreted in terms of a steric hindrace in the formation of the radical and [Mn^{II}(tmp)]. Similarly, all results obtained for α-methylstyrene can be explained by the formation of the 1-methyl-1-phenylethyl radical which is less reactive than the 1-phenylethyl radical and is free from the interaction with the manganese complex. The reaction mechanism involving the free radicals has been supported by the results on the effects of TEMPO.

(Porphinato)manganese complexes have widely been used as catalysts in model reactions of cytochrome P-450. Tabushi and Koga[1] studied the cytochrome P-450 model oxygenation of alkenes using [Mn^{III}Cl(tpp)] (tpp: 5,10,15,20-tetraphenylporphine dianion) as a catalyst and $NaBH_4$ as a reductant. The oxygenation products of cyclohexene are cyclohexanol and cyclohexen-2-ol:



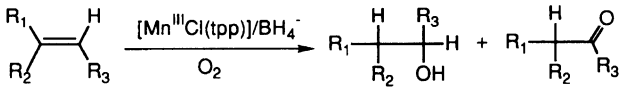
(1)

They assumed cyclohexene oxide as an initial oxygenation product, though its formation could not be detected.[1] Although the similar reaction system has been applied for biomimic oxidation of alkenes with dioxygen,[2] no detailed study on the reaction mechanism has been carried out. Besides dioxygen,[3] several oxidants such as iodosylbenzene and pentafluoroiodosylbenzene,[4] alkyl hydroperoxides,[5] *m*-chloroperbenzoic acid,[6] $KHSO_5$,[7] H_2O_2,[8] $NaClO_x$,[9] and *p*-cyano-*N*,*N*-dimethylaniline *N*-oxide[10] have been utilized in the (porphinato)manganese-catalyzed oxidation of alkanes and alkenes. A high-valent oxomanganese(V) complex has been believed as an active species in the oxidation of alkenes to give corresponding epoxides:[3c,4d,5,6,8b]



(2)

After the study by Tabushi and Koga,[1] the (porphinato)manganese-catalyzed oxygenation of various alkenes in the presence of BH_4^- has been examined.[2] These studies reveal that the corresponding ketones are also formed together with the hydroxylated compounds and that the epoxides are not formed in this reaction system:[2]



(3)

The absence of the epoxides in the oxygenation products suggests a mechanism which does not involve a oxomanganese(V) complex. Since the epoxides are hardly reduced by BH_4^-, these monooxygenated products should be detected if the oxomanganese(V) complex is an active species. Shimizu et al.[2c] proposed a reaction mechanism for the (porphinato)manganese-catalyzed oxygenation of alkenes involving a coordination of the alkene to (porphinato)manganese(II). We also studied the oxygenation of styrene catalyzed by a water-soluble (porphinato)iron in water containing $NaBH_4$ and assumed that an insertion of dioxygen to an alkyl(porphinato)iron complex formed via a hydride transfer from BH_4^- to styrene yields acetophenone which is reduced with $NaBH_4$ to 1-phenylethanol.[11] It is likely to occur that the alkyl(porphinato)manganese complex is also formed as a key intermediate in the (porphinato)-manganese-catalyzed oxygenation. The aim of the present study is clarification of the reaction mechanism for the (porphinato)manganese-catalyzed oxygenation of alkenes in benzene–ethanol in the presence of $NaBH_4$. Styrene and α-methylstyrene were used as the mechanistic probes.

Results and Discussion

Reaction Products. The reactions were followed by means of GLC when styrene in benzene–

ethanol (1:1) was stirred at ambient temperature in the presence of [$Mn^{III}Cl$(tpp)] and $NaBH_4$ [mol ratio: styrene/$NaBH_4$/[$Mn^{III}Cl$(tpp)]=10/20/1]. The reactions were carried out in air- and O_2-saturated and strictly degassed benzene-ethanol. The products and their yields are summarized in Table 1.

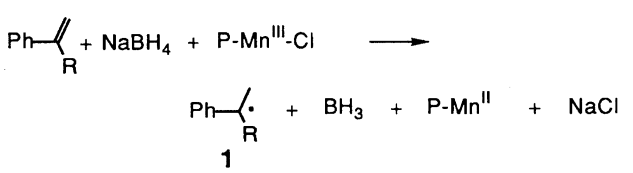
In the absence of O_2 (Entry 1), styrene is converted to ethylbenzene and 2,3-diphenylbutane in <1 and 4% yields, respectively. The reaction of styrene was saturated within 3 min and about 70% of styrene was changed to unknown product(s). Although polystyrene seems to be the main product in the reaction under anaerobic conditions, we failed the isolation of polystyrene. In this case, the formation of [Mn^{II}(tpp)] was observed by means of absorption spectroscopy (λ_{max}=607, 569, 434, and 415 nm (sh) for [Mn^{II}(tpp)]).[1] These results indicate that [Mn^{II}(tpp)] does not act as the catalyst for the reduction of styrene to ethylbenzene and 2,3-diphenylbutane. This is a contrast to the results for the [Fe(tpp)]-catalyzed reaction of styrene where ethylbenzene and 2,3-diphenylbutane are produced in 65 and 10% yields, respectively, in strictly degassed benzene–ethanol.[12]

Under the air-saturated conditions (Entry 2), the yields of ethylbenzene and 2,3-diphenylbutane increase to 8 and 39%, respectively, and an oxygenated product, 1-phenylethanol (12%), is also formed together with these reduction products. The formation of a trace amount of acetophenone was observed by means of GLC. In O_2-saturated benzene–ethanol (Entry 3), the main product is changed to 1-phenylethanol (74%) but the reduction products are still produced (2% for ethylbenzene and 10% for 2,3-diphenylbutane). When the air was bubbled into the reaction mixture during reaction (Entry 4), the results became almost the same as those for the O_2-saturated conditions. These findings clearly reveal that the oxygenation reaction to 1-phenylethanol occurs more rapidly than the reduction to ethylbenzene and 2,3-diphenylbutane when adequate amounts of dioxygen always exist in the solvent. Interestingly, the relative yield of ethylbenzene to 2,3-diphenylbutane is about 0.2 which is completely different from that for the [Fe(tpp)]-catalyzed reduction (ethylbenzene/2,3-diphenylbutane=6.5).[12] In the previous study,[12] we found that 2,3-diphenylbutane and ethylbenzene are formed via the alkyl(porphinato)iron(III) and alkyl(porphinato)iron(II) complexes [alkyl: $CH(CH_3)(C_6H_5)$], respectively. The organometallic iron(III) complex has a radical character to yield the coupling product while the alkyl(porphinato)iron(II) complex shows a carbanionic nature to give ethylbenzene through a proton transfer from ethanol. Judging from the product distribution, ethylbenzene in the [Mn(tpp)]-mediated reaction seems to be produced via a different pathway from that for the [Fe(tpp)]-mediated one. Ethylbenzene may be formed from the disproportionation of the 1-phenylethyl radicals (vide infra).

Free Radical Intermediates. Table 2 shows the results of the reactions of styrene and α-methylstyrene in O_2-saturated benzene–ethanol (1:1) containing [$Mn^{III}Cl$(tpp)] or [$Mn^{III}Cl$(tmp)] [tmp: 5,10,15,20-tetrakis(2,4,6-trimethylphenyl)porphine dianion] and $NaBH_4$ (mol ratio: substrate/$NaBH_4$/catalyst=100/200/1). The reaction conditions are identical to those described in Table 1 except for the amounts of the catalyst.

In the reactions of styrene, lowering the amounts of the catalyst causes the disappearance of the reduction products (compare the results shown in Entry 3 of Table 1 with those exhibited in Entries 1 and 3 of Table 2). Assuming the 1-phenylethyl radical as an intermediate, the results can be explained reasonably. The rate of formation of the 1-phenylethyl radical should be decelerated upon lowering the amounts of catalyst leading to lower probability of collision of the radicals. In the reaction of α-methylstyrene, however, a radical coupling product, 2,3-dimethyl-2,3-diphenylbutane, is formed besides an oxygenation product, 2-phenyl-2-propanol (Entries 2 and 4). In the case of the [Mn^{III}(tpp)]$^+$-catalyzed reaction (Entry 2), cumene and 1-phenylethanol were also obtained as the by-products. The formation of 2,3-dimethyl-2,3-diphenylbutane strongly suggests that the 1-methyl-1-phenylethyl radical is generated in this reaction. If the rate of formation of the 1-methyl-1-phenylethyl radical is fast, the coupling and disproportionation reactions of this radical which yield 2,3-dimethyl-2,3-diphenylbutane and cumene, respectively, can compete with the oxygenation reaction. The progressive changes of the reactions of α-methylstyrene catalyzed by [Mn^{III}(tpp)]$^+$ and [Mn^{III}(tmp)]$^+$ (Entries 2 and 4) are shown in Fig. 1. The [Mn^{III}(tpp)]$^+$-catalyzed reaction of α-methylstyrene (Entry 2) is much faster than the [Mn^{III}(tmp)]$^+$-catalyzed one. The faster reaction causes the higher yield of the radical coupling product, 2,3-dimethyl-2,3-diphenylbutane. The rapid generation of the 1-methyl-1-phenylethyl radical seems to be a reason for formation of 2,3-dimethyl-2,3-diphenylbutane as well as cumene in the [Mn^{III}(tpp)]$^+$-catalyzed reaction.

Let us consider whether the reactions exhibited in Table 2 can totally be explained by the formation of the alkyl radicals **1**:



1 (4)

Effects of TEMPO. In order to confirm the generation of the 1-phenylethyl and 1-methyl-1-phenylethyl radicals in the (porphinato)manganese(III)-catalyzed reactions of styrene and α-methylstyrene, respectively,

Table 1. $[Mn^{III}(tpp)]^+$-Catalyzed Reactions of Styrene in Benzene–Ethanol (1 : 1) under Various Conditions at Room Temperature[a)]

Entry	System[b)]	Reaction time[c)]/min	Yield[d)]/%		
			Ph—/	Ph, Ph	Ph—OH
1	A	3	<1	4(28)	0
2	B	90	8(8)	39(39)	12(12)
3	C	15	2(2)	10(10)	74(74)
4	D	15	<1	4(4)	80(80)

a) A mixture of styrene (1.5 mmol), $NaBH_4$ (3.0 mmol), and $[Mn^{III}Cl(tpp)]$ (0.15 mmol) in 8 mL of benzene–ethanol (1 : 1) was stirred at ambient temperature. b) Reactions were carried out in strictly degassed (system A), aerobic (system B), and O_2-saturated benzene–ethanol (system C). In system D, the reaction was done by bubbling the air into the solution. c) Times for finishing the reactions. d) Yields based on the initial concentration of styrene. The values in parentheses are the yields based on the consumed styrene.

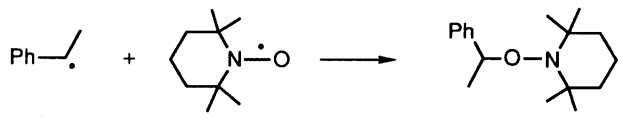
Table 2. (Porphinato)manganese(III)-Catalyzed Reactions of Styrene and α-Methylstyrene in O_2-Saturated Benzene–Ethanol (1 : 1) at Room Temperature[a)]

Entry	Catalyst	Substrate	Reaction time[b)]/min	Products (yields[c)]/%)
1	$[Mn^{III}Cl(tpp)]$	Ph—/	85	Ph—OH (86)
2	$[Mn^{III}Cl(tpp)]$	Ph—\	20	Ph—OH (69), Ph—Ph (26), Ph— (2), Ph—OH (<1)
3	$[Mn^{III}Cl(tmp)]$	Ph—/	180	Ph—OH (92)
4	$[Mn^{III}Cl(tmp)]$	Ph—\	35	Ph—OH (92), Ph—Ph (8)

a) The reaction conditions are shown in Experimental section in the text. b) Times for complete consumption of substrates. c) Yields based on the initial concentration of substrates.

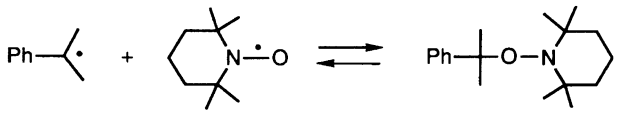
we studied the effects of a radical trap, TEMPO (2,2,6,6-tetramethylpiperidinyloxyl).[13)]

The results are summarized in Table 3. In the presence of TEMPO (100 mol% toward substrate), both oxygenation and reduction of styrene were completely inhibited and the coupling product of the 1-phenylethyl radical and TEMPO was obtained quantitatively (Entry 2):



(5)

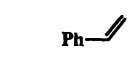
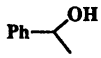
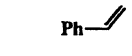
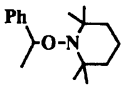
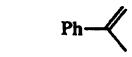
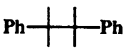
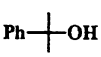
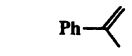
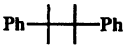
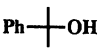
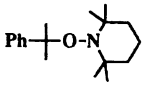
On the other hand, TEMPO does not inhibit the reactions of α-methylstyrene completely (Entry 4). In the presence of TEMPO, the reaction is decelerated and the yields of the products which are formed by the bimolecular reactions of the 1-methyl-1-phenylethyl radical (cumene and 2,3-dimethyl-2,3-diphenylbutane) become much lower than that of the oxygenation product (2-phenyl-2-propanol). Such insufficient inhibition by TEMPO can be understood by the following equilibrium:



(6)

The kinetics of the reversible reactions shown in Eq. 6 have been studied.[14)] The formation of the TEMPO adduct of the 1-methyl-1-phenylethyl radical competes with the oxygenation. The back reaction of the TEMPO adduct and the reaction of the 1-methyl-1-phenylethyl radical with dioxygen (oxygenation) seems to cause the consumption of the TEMPO adduct. Since the 1-phenylethyl radical is less stable than the 1-methyl-1-phenylethyl radical, the back reaction of the TEMPO adduct should be negligible. The results on

Table 3. Effects of TEMPO on $[Mn^{III}(tpp)]^+$-Catalyzed Reactions of Styrene and α-Methylstyrene in Aerobic Benzene–Ethanol (1 : 1) Containing $NaBH_4$ at Room Temperature[a)]

Entry	Substrate	Reaction time/h	Product	Yield[b)]/%
1		2		12(12)
				8(8)
				39(39)
2		6		50(100)
3		1		4(4)
				34(34)
				53(53)
4		4		6(8)
				37(48)
				14(16)

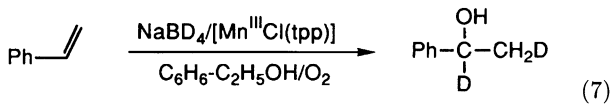
a) The reaction conditions are shown in Experimental Section in the text. In Entries 1 and 3, the reactions were carried out in the absence of TEMPO. In Entries 2 and 4, the reactions were carried out in the presence of TEMPO (100 mol% toward styrene). b) Yields based on an initial concentration of the substrates. The values in parentheses are the yields based on the consumed substrates.

the effects of TEMPO strongly support that the alkyl radicals **1** are common intermediates for oxygenation and reduction reactions of styrene or α-methylstyrene.

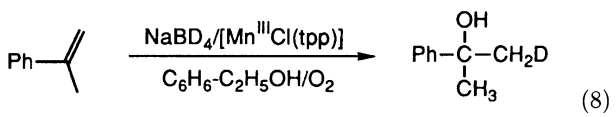
In the (porphinate)iron-mediated reduction of styrene in anaerobic benzene–ethanol, the formation of ethylbenzene through a proton transfer from ethanol to alkyl(porphinato)iron(II) having a carbanionic nature is scarcely affected by TEMPO while the formation of 2,3-diphenylbutane obtained from the coupling of alkyl(porphinato)iron(III) having a radical character is completely inhibited.[12)] The present result that TEMPO strongly inhibits even the formation of ethylbenzene suggest that ethylbenzene is formed by the disproportionation of the 1-phenylethyl radicals, not by the proton transfer from ethanol to the carbanion, 1-phenylethanide.

As Table 3 exhibits, the rates of the alkene disappearance are decelerated by TEMPO. This should be ascribed to the coordination of TEMPO to (porphinato)-manganese(III).[15)]

Deuterium Incorporation. As described above, the formation of a small amount of acetophenone was measured during the reaction of styrene. Therefore, it is quite reasonable to consider that acetophenone is the precursor of the final oxygenation product, 1-phenylethanol. In order to confirm this, the deuterium incorporation was studied using $NaBD_4$ (mol ratio: substrate/$NaBD_4$/$[Mn^{III}Cl(tpp)]$=100/200/1) under the O_2-saturated conditions. The structures of the oxygenation products of styrene and α-methylstyrene were determined by means of ^1H NMR and GC-MS. The results are revealed in Eqs. 7 and 8:



(7)



(8)

The formation of 1,2-dideuterio-1-phenylethanol from

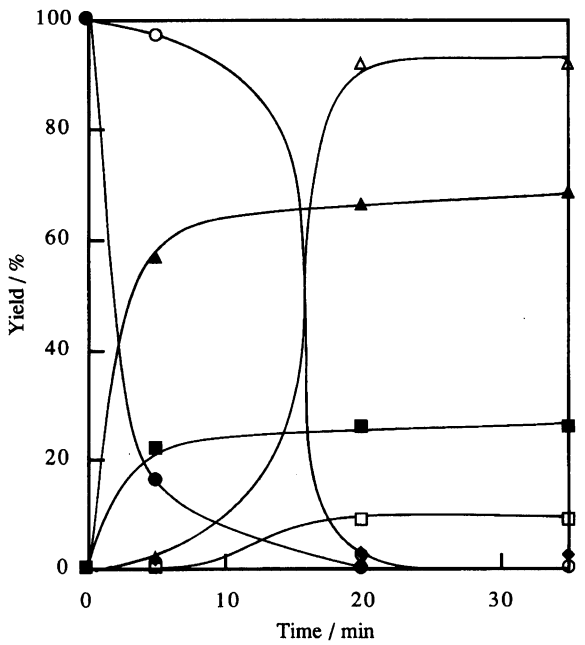
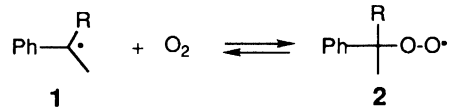


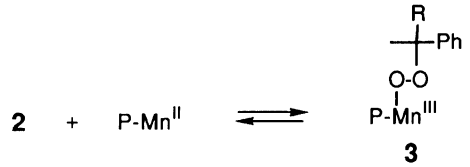
Fig. 1. Progress in the disappearance of α-methylstyrene (●,○) and in the formation of 2-phenyl-2-propanol (▲, △) and 2,3-dimethyl-2,3-diphenylbutane (■,□) in the [Mn^{III}(tpp)]- (●,▲,■) and [Mn^{III}(tmp)]-catalyzed reactions (○,△,□) of α-methylstyrene (1.5 mmol) in O_2-saturated benzene–ethanol (1:1, 8 ml) containing $NaBH_4$ (3.0 mmol) and the catalyst (0.015 mmol) at room temperature.

styrene can be understood by assuming acetophenone as a precursor. In the reaction of α-methylstyrene where carbonyl compound is hardly formed, 1-deuterio-2-phenyl-2-propanol was isolated. These results can be interpreted in terms of the radical mechanisms as described below.

Reaction Mechanisms. It seems that the 1-phenylethyl and 1-methyl-1-phenylethyl radicals are the common intermediates in the oxygenation and reduction of styrene and α-methylstyrene, respectively, which are catalyzed by (porphinato)manganese(III) complexes (Eq. 4). The radical **1** should easily react with dioxygen to yield alkylperoxyl radical **2**[16] which may be stabilized in a form of (alkylperoxo)-(porphinato) manganese(III) **3**:[17]

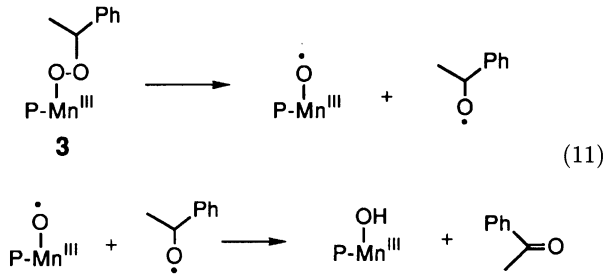


(9)



(10)

In the case of styrene, a homolitic O–O bond cleavage of the peroxomanganese(III) complex **3** may occur and is followed by the formation of acetophenone and hydroxo(porphinato)manganese(III) (P-Mn^{III}-OH):[18]

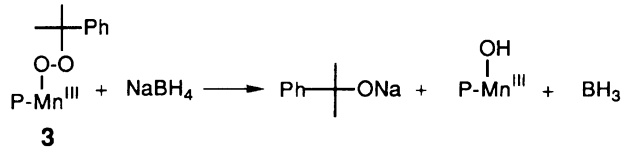


(11)

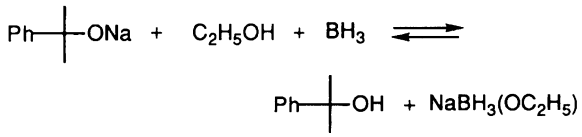
(12)

Acetophenone thus formed is readily reduced with $NaBH_4$ to afford 1-phenylethanol. When the enough amounts of the 1-phenylethyl radical are formed, the coupling and disproportionation reactions of the radicals occur to give 2,3-diphenylbutane and ethylbenzene, respectively.

Meanwhile, since the peroxo complex **3** generated from 1-methyl-1-phenylethyl radical cannot afford carbonyl compound, **3** may directly be reduced by $NaBH_4$ to yield 2-phenyl-2-propanol and P-Mn^{III}-OH:

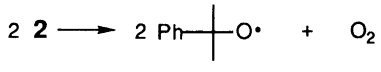


(13)

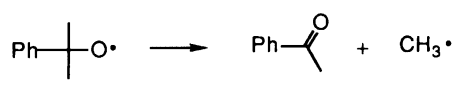


(14)

We confirmed that α-cumenyl hydroperoxide is readily reduced with $NaBH_4$ to 2-phenyl-2-propanol in a quantitative yield. We believe that the (alkylperoxo)-manganese(III) complex **3** shows the similar reactivity to α-cumenyl hydroperoxide (1-methyl-1-phenylethyl hydroperoxide) toward $NaBH_4$. The formation of a trace amount of 1-phenylethanol from α-methylstyrene (Entry 2 in Table 2) supports the generation of the 1-methyl-1-phenylethylperoxyl radical **2**. It has been known that the bimolecular reaction of **2** affords acetophenone[16] which is reduced with $NaBH_4$ to give 1-phenylethanol:



(15)



(16)

The recombination and disproportionation reactions of the 1-methyl-1-phenylethyl radical **1** give 2,3-dimethyl-

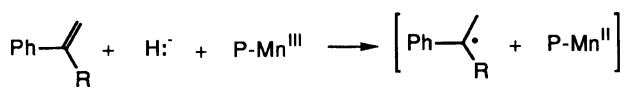
2,3-diphenylbutane and cumene, respectively. The relative rate of the recombination to the disproportionation of the radical **1** has been reported to be 19/1.[19] Therefore, the fact that the yield of 2,3-dimethyl-2,3-diphenylbutane is much higher than that of cumene (Entries 2 and 4 in Table 2) also supports the mechanism involving the radical **1**.

In the previous paper,[12] we reported the formation of the alkyl(porphinato)iron(III) and alkyl(porphinato)-iron(II) complexes, [Fe{$CH(CH_3)(C_6H_5)$}(tpp)], in the reduction of styrene with $NaBH_4$ to ethylbenzene and 2,3-diphenylbutane in anaerobic benzene–ethanol containing [Fe^{III}Cl(tpp)]. The alkyl(porphinato)iron-(III) complex has a radical character and yields 2, 3-diphenylbutane as a coupling product. The similar alkyl(porpninato)manganese(III) complex may be considered for the reaction of styrene catalyzed by $[Mn^{III}(tpp)]^+$ though no evidence for the formation of this organometallic compound has been obtained in this study. Judging from the Corey–Pauling–Koltum (CPK) molecular model, however, it seems that such alkyl(porpninato)manganese(III) complexes are hardly formed in the $[Mn^{III}(tmp)]^+$-catalyzed reactions because of the steric hindrance due to the methyl groups of the peripheral mesityl groups. We confirmed that the [Fe(tmp)]-mediated reduction of styrene with $NaBH_4$ proceeds very slowly compared with the [Fe(tpp)]-mediated one in anaerobic benzene–ethanol.[20] The slower rate in the [Fe(tmp)]-mediated reduction is ascribed to the higher activation energy for the formation of alkyl-(porphinato)iron(III) complex due to the larger steric hindrance compared with the case of the [Fe(tpp)]-mediated reduction. Especially, the steric hindrance in the formation of alkyl(porpninato)manganese(III) complex from α-methylstyrene is very serious. At least, therefore, the alkyl(porpninato)manganese(III) complex should not be an intermediate in the reaction of α-methylstyrene catalyzed by $[Mn^{III}(tmp)]$. The slower $[Mn^{III}(tmp)]$-catalyzed reactions observed in this study may be explained in terms of the steric hindrance in the reactions exhibited by Eq. 4. Although alkyl-(porphinato)iron complexes are widely known to be prepared using several methods,[21] little has been reported on the metal–carbon bonds of the (porphinato)-manganese complexes.[17,23]

Conclusion

In 1979, Tabushi and Koga[1] presented a cytochrome P-450 model composed of alkene, [Mn^{III}Cl(tpp)], $NaBH_4$, and O_2 in benzene–ethanol, though they did not carry out the detailed study on the reaction mechanism. The work done by Shimizu et al.[2c] is not also focused on the reaction mechanisms.

In this paper, we propose the mechanisms involving a pair of alkyl radical and (porphinato)manganese(II) which is formed by the reaction of alkene, a hydride, and (porphinato)manganese(III):



(17)

The radical reacts with dioxygen to form the (alkylperoxo)manganese(III) complex which is converted to acetophenone in the reaction of styrene and is directly reduced with $NaBH_4$ in the reaction of α-methylstyrene. The recombination and the disproportionation of the alkyl radicals yield $[(C_6H_5)(CH_3)(R)C\text{-}]_2$ and (C_6H_5)-$(CH_3)(R)CH$, respectively. No evidence for the formation of the alkyl(porpninato)manganese(III) complexes has been obtained in this study. Since no high-valent oxomanganese(V) complex is generated, the epoxidation does not proceed in this system.

Experimental

Chemicals. The 5,10,15,20-tetraphenylporphine[23] and 5,10,15,20-tetrakis(2,4,6-trimethylphenyl)porphine free bases[24] were prepared according to the procedures described in the literatures. [Mn^{III}Cl(tpp)] and [Mn^{III}Cl-(tmp)] were synthesized using an ordinary method.[25] Styrene and α-methylstyrene (Nacalai) were purified by passing through an alumina column to remove oxidized products. α-Cumenyl hydroperoxide (Nacalai, 70% purity), $NaBH_4$ (Nacalai), and TEMPO (Aldrich) were purchased and used without further purification. All solvents were used after drying by the appropriate methods and distilled prior to use.

Measurements. The electronic absorption spectra were measured by a Shimadzu UV200S spectrophotometer. The 400-MHz ^{1}H NMR and mass spectra of the reaction products were taken on a JEOL JNM-GX400 and a Hitachi M-80B or a Shimadzu QP2000 spectrometers, respectively. For GLC analysis, a Shimadzu GC-8A gas chromatograph having a Thermon 1000 glass column (1 m) was used.

General Procedures of Reaction. A typical example of the oxygenation and the reduction of alkene is shown below. A mixture of [Mn^{III}Cl(tpp)] (11 mg, 0.015 mmol), $NaBH_4$ (115 mg, 3.0 mmol), and biphenyl (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-time evacuation -charging with O_2 cycles, styrene (160 mg, 1.5 mmol) in 8 ml of aerobic benzene–ethanol (1 : 1) was injected into the vessel using a syringe to start the reaction. During reaction, the reaction mixture was stirred in O_2 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 IR, ^{1}H NMR, and GC-MS spectroscopies.

The reactions under the strictly degassed conditions were carried out using the same procedures described in the previous paper.[12]

Reactions of Styrene and α-Methylstyrene in Presence of TEMPO. A mixture of [Mn^{III}Cl(tpp)] (11 mg, 0.015 mmol), $NaBH_4$ (115 mg, 3.0 mmol), TEMPO (234 mg, 1.5 mmol), and biphenyl (25 mg, an internal standard for GLC) was placed in a 30-ml two-necked flask. Styrene

(160 mg, 1.5 mmol) in aerobic benzene–ethanol (1 : 1, 8 ml) was injected into the vessel using a syringe and the reaction mixture was stirred in air at ambient temperature. The progressive change of the reaction was followed by means of GLC. After the reaction, the TEMPO adduct [1-(1-phenylethoxy)-2,2,6,6-tetramethylpiperidine] was isolated using silica-gel column chromatography with chloroform. The structure of the adduct was determined by means of ^{1}H NMR and mass spectroscopies; mp 43—43.5 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = 1.02$ (s, 3H, TEMPO-CH_3), 1.16 (s, 3H, TEMPO-CH_3), 1.36 (s, 3H, TEMPO-CH_3), 1.46—1.56 (m, 6H, TEMPO-CH_2), 1.77 (d, 3H, CH_3), 4.77 (q, 1H, CH), 7.22—7.31 (m, 5H, C_6H_5). MS (EI, 70 eV) m/z (rel intensity) 262 (M^+, 0.3), 157 [$M^+ - C_6H_5CH(CH_3)$, 100], 105 (M^+ − TEMPO, 40).

The reaction of α-methylstyrene (180 mg, 1.5 mmol) in the presence of TEMPO was carried out by the same procedures as the case of styrene. After 4 h, the reaction mixture was passed through an alumina column to remove inorganic salts and the catalyst. The TEMPO adduct of the 1-methyl-1-phenylethyl radical was isolated by using GLC and analyzed by means of mass spectroscopy; MS (EI, 70 eV) m/z (rel intensity) 275 (M^+, 0.4), 260 ($M^+ - CH_3$, 1), 157 (TEMPO+1, 3), 119 (M^+ − TEMPO, 100). Since the TEMPO adduct of the 1-methyl-1-phenylethyl radical is unstable in solution, ^{1}H NMR of this compound could not be measured.

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