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Oxidation of Benzoin to Benzil and of *p*-Substituted Benzyl Alcohol to the Corresponding Benzaldehyde Catalyzed by Iron(II) Thiolate Complexes. A Proposed Reaction Mechanism

Wei-Yin Sun, Norikazu Ueyama, and Akira Nakamura*

Department of Macromolecular Science, Faculty of Science, Osaka University,
Toyonaka, Osaka 560, Japan

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Abstract: The catalytic *p*-benzoquinone or air oxidation of benzoin to benzil was carried out in the presence of $[Fe^{II}(S_2\text{-}o\text{-xyl})_2]^{2-}$ (*o*-xyl = *o*-xylene-α, α'-dithiolate) or $[Fe^{II}(S\text{-}t\text{-Bu})_4]^{2-}$ in a ratio [benzoin]/[catalyst] = 20/1 in DMF at 25 °C Under such mild reaction conditions, the Fe(II) thiolate complex exhibited high catalytic activity In the reaction catalyzed by $[Fe^{II}(S_2\text{-}o\text{-xyl})_2]^{2-}$, 64% and 93% of benzoin was oxidized to benzil in 25 h by air and *p*-benzoquinone, respectively In the air oxidation of benzyl alcohol catalyzed by $[Fe^{II}(S_2\text{-}o\text{-xyl})_2]^{2-}$, benzaldehyde was formed specifically without formation of benzoic acid Furthermore, *p*-substituent effect (Cl > H > OMe) was found in the catalytic air oxidation of *p*-substituted benzyl alcohol The catalytic oxidation is first order with respect to each of substrate and the catalyst at initial stage A reaction mechanism was proposed and the rate-determining step is at the release of the methine hydrogen as a proton which is based on the kinetic isotope effect (k_H/k_D was 4 3 by *p*-benzoquinone oxidation and 5 0 by air oxidation, respectively) and *p*-substituent effect of substrate in the presence of $[Fe^{II}(S_2\text{-}o\text{-xyl})_2]^{2-}$

INTRODUCTION

Many transition metal thiolate complexes such as $[MoO^{V}(SR)_4]^-$, $[Mn^{II}(SR)_4]^{2-}$ and $[Fe_4S_4(SR)_4]^{2-}$,[1-3] and metal acetate complex such as $[Ni^{II}(OCOCH_3)_2]$ [4] have been reported to exhibit catalytic activity in the oxidation of alcohol to ketone or aldehyde Most of these metal thiolate complexes were synthesized as model of native metalloproteins in structural and/or reactivity aspect.[5] The studies of reaction catalyzed by metal thiolate complexes provide information for the mechanisms of catalytic oxidation and would be useful in understanding the oxidation process of native proteins. Recently, the simple Fe(II) thiolate, e.g. $[Fe(SPh)_4]^{2-}$, and cysteine-containing oligopeptide-Fe(II) complexes as, $[Fe(Z\text{-cys-Gly-Val-OMe})_4]^{2-}$ and $[Fe(Z\text{-cys-Pro-Leu-cys-Gly-Val-OMe})_2]^{2-}$, which were model of rubredoxin, were found to be catalytically active in the air oxidation of methyl *DL*-mandelate to methyl benzoylformate, *p*-substituted benzhydrol to the corresponding benzophenone and benzoin to benzil.[6,7] The reaction mechanisms catalyzed by Fe(II) thiolate complex are considered to be very important since the native rubredoxin functions as electron-transfer mediators using a Fe(II)/Fe(III) redox couple in biological systems.[8]

As reported previously, the Fe(II) thiolate complexes showed higher catalytic activity than that of Mn(II) analogue and the reaction rate is very fast at the initial stage.[6,7,9] The Fe(III) species was proposed to be involved in the catalytic reaction since the reaction of Fe(II) thiolate complexes with air or *p*-benzoquinone gives the corresponding Fe(III) complexes.[7] However, most of Fe(III) thiolate complexes are thermally unstable due to the oxidation of thiol ligands to give disulfide and Fe(II) complex[10] except for a few reported examples with chelate ligands as, $[Fe^{III}(S_2\text{-}o\text{-xyl})_2]^-$ or with bulky ligands as, $[Fe^{III}(S\text{-}2,3,5,6\text{-}Me_4C_6H)_4]^-$ [11,12] In this paper, we report the results of the stoichiometric reaction of $[Fe^{III}(S_2\text{-}o\text{-xyl})_2]^-$ with benzoin together with the catalytic *p*-benzoquinone or air oxidation of benzoin to benzil and also *p*-substituted benzyl alcohol to the corresponding benzaldehyde in the presence of $[Fe^{II}(S_2\text{-}o\text{-xyl})_2]^{2-}$ An oxidation mechanism was proposed based on the kinetic isotope effect in the oxidation of benzoin, α-C-deuterated benzoin and on the *p*-substituent effect in the oxidation of *p*-substituted benzyl alcohol.

RESULTS

Catalytic Oxidation of Benzoin to Benzil by Air or p-Benzoquinone in the Presence of Fe(II) Thiolate Complexes

The aerial oxidation of benzoin catalyzed by $[Fe(S_2\text{-}o\text{-xyl})_2]^{2-}$ (**1**), $[Fe(SPh)_4]^{2-}$ (**2**) and $[Fe(S\text{-}t\text{-Bu})_4]^{2-}$ (**3**) was carried out in mild conditions (in DMF at 25 °C and ambient pressure) with a ratio: [substrate] [catalyst] = 20 : 1, (see experimental section) The representative runs of these reactions are shown in Figure 1. All of these Fe(II) complexes exhibit high catalytic activity with very fast initial oxidation rate 64% (catalytic yield, 1280%), 66% (catalytic yield, 1320%) and 73% (catalytic yield, 1460%) of benzoin was oxidized to benzil in 25 h in the presence of catalyst of **1**, **2** and **3**, respectively, which were similar to those catalyzed by cysteine peptide thiolate Fe(II) complexes [7]

In contrast to the air oxidation reaction, the initial reaction rate became somewhat slow when *p*-benzoquinone was used as an oxidant As shown in the Figure 1, the time course of the $[Fe(S_2\text{-}o\text{-xyl})_2]^{2-}$, benzoin and *p*-benzoquinone system

(1 : 20 : 40) indicates a smooth oxidation process without obvious deactivation of the catalyst. The yield of benzil was 93% (catalytic yield, 1860%) in the *p*-benzoquinone oxidation catalyzed by complex **1** in 25 h which was higher than that of air oxidation after the same period as mentioned above. The rapid deactivation of catalyst in the air oxidation is caused by the formation of water during the reaction[7] since the iron-thiolato complex is unstable in water.[20]

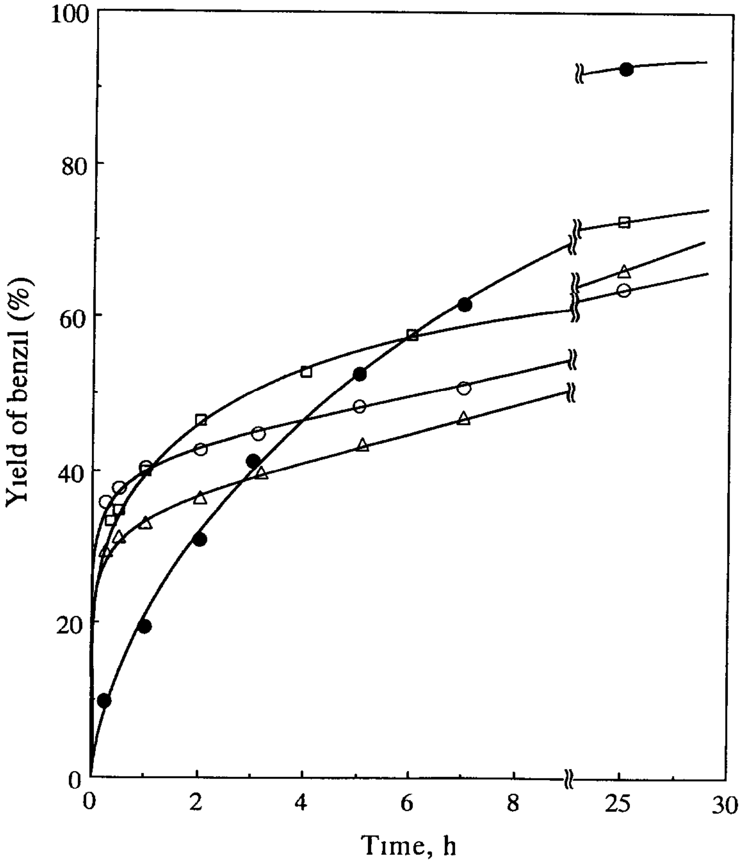

Figure 1. Time course for the catalytic oxidation of benzoin to benzil. (●) *p*-benzoquinone (40 mM) oxidation catalyzed by $[Fe(S_2\text{-}o\text{-}xyl)_2]^{2-}$ (**1**), (○) air oxidation catalyzed by $[Fe(S_2\text{-}o\text{-}xyl)_2]^{2-}$ (**1**), (Δ) air oxidation catalyzed by $[Fe(SPh)_4]^{2-}$ (**2**) and (❑) air oxidation catalyzed by $[Fe(S\text{-}t\text{-}Bu)_4]^{2-}$ (**3**). [Benzoin] = 20 mM, [Catalyst] = 1 mM, in DMF at 25 °C.

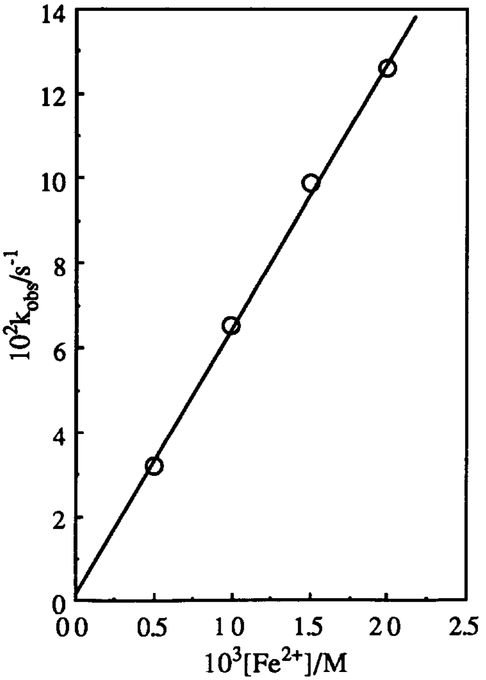

Figure 2. Dependence on the concentration of $[Fe(S_2\text{-}o\text{-}xyl)_2]^{2-}$ for the observed rate constants at initial stage for the *p*-benzoquinone oxidation of benzoin (20 mM) in DMF at 25 °C.

The oxidation rate constant (k_{obs}) was obtained at initial stage of the reaction for both of air and *p*-benzoquinone oxidation of benzoin. The k_{obs} of the air oxidation was found to be about 15-folds larger than that of *p*-benzoquinone oxidation catalyzed by complex **1** (Figure 1). The correlation between the k_{obs} and concentration of catalyst was examined. For example, as shown in the Figure 2, a linear relation was found in the case of *p*-benzoquinone oxidation. This indicates that the oxidation reaction rate is proportional to the concentration of the catalyst. Furthermore, the order with respect to the benzoin was investigated and the logarithmic plot of benzoin concentration against time is also linear (Figure 3). Therefore, the reaction is first order with respect to each concentration of benzoin and the catalyst, that which is the same as in cases of oxidation of benzoin catalyzed by 4Fe4S cluster and $[Ni(OCOCH_3)_2]$ [3,4]

The deuterium kinetic isotope effect is important for investigation of the oxidation mechanism. Oxidation of α-deuterobenzoin by *p*-benzoquinone or air in the presence of complex **1** was carried out under the same conditions as the reaction of benzoin. The observed k_H/k_D was 4.3 (oxidized by *p*-benzoquinone) and 5.0 (oxidized by air), respectively. This indicates that cleavage of the α-C-H bond of benzoin is involved in the rate-determining step [7]

Catalytic Air Oxidation of p-Substituted Benzyl Alcohol to the Corresponding Benzaldehyde in the Presence of $[Fe(S_2\text{-}o\text{-}xyl)_2]^{2-}$

The *p*-substituted benzoin or benzhydrol have been used to examine the electronic influence on the oxidation reaction catalyzed by metal thiolate complexes as $[Fe(SPh)_4]^{2-}$, $[Fe(Z\text{-}cys\text{-}Gly\text{-}Val\text{-}OMe)_4]^{2-}$, $[Fe_4S_4(tipbt)_4]^{2-}$ (tipbt = 2,4,6-triisopropylbenzenethiolate) and $[Mn(SPh)_4]^{2-}$ *etc* [2,6,7,9] In these cases, the electron-

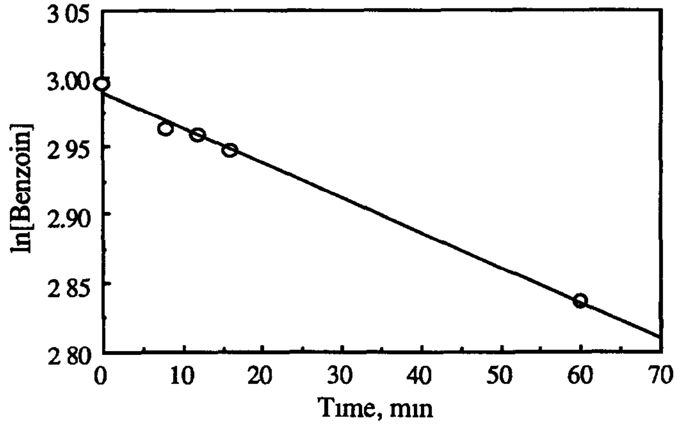

Figure 3. Relation of ln[Benzoin] *vs* time in the *p*-benzoquinone oxidation of benzoin in the presence of $[Fe(S_2\text{-}o\text{-}xyl)_2]^{2-}$ (0.5 mM) in DMF at 25 °C.

Table I. Catalytic air oxidation of *p*-substituted benzyl alcohol in the presence of $[Fe(S_2\text{-}o\text{-}xyl)_2]^{2-}$ in DMF at 25 °C.

substrate	product	yield (%)
4,4'-dichlorobenzyl alcohol	4,4'-dichlorobenzaldehyde	10
benzyl alcohol	benzaldehyde	7
4,4'-dimethoxybenzyl alcohol	4,4'-dimethoxybenzaldehyde	6

Reaction conditions: [substrates] = 20 mM, [catalyst] = 1 mM, reaction time, 2 h.

withdrawing group as Cl or Br accelerates the oxidation while the electron-donating one as CH_3 or OCH_3 works opposite. In this study, we investigated the air oxidation of *p*-substituted benzyl alcohol in the presence of complex **1** and the results are listed in Table I. Similar *p*-substituent effect was observed in these air oxidation reactions. The *p*-chloro-substituted substrate is oxidized more easily than the *p*-methoxy one. The observed *p*-substituent effect indicates that the α-hydrogen of benzyl alcohol was released as a proton in the rate-determining step

The oxidation product was investigated by ^{13}C-NMR spectroscopy. In our reaction conditions, the oxidation was found to stop at aldehyde specifically, since only a carbonyl carbon signal of benzaldehyde (Ph*C(H)=O) at 192 ppm (in $Me_2SO\text{-}d_6$ at 30 °C) was detected, no signal due to the carbonyl carbon of benzoic acid was observed which should appear at 173 ppm Absence of benzoic acid was also confirmed by HPLC analysis In the absence of catalyst, no detectable *p*-substituted benzaldehyde was formed in 2 h. The combined results of the kinetic isotope effect and the *p*-substituent effect indicate that the oxidation reaction involves transport of both protons and electrons during the catalytic oxidation cycles.

The air oxidation of benzaldehyde catalyzed by Fe(II) thiolate complex was also carried out in the same conditions as the catalytic air oxidation of benzyl alcohol. However, no benzoic acid was produced in 20 h Thus the Fe(II) thiolate complex was found to be catalytically inactive in the air oxidation of aldehyde to carboxylic acid.

Oxidation of Fe(II) Thiolate Complexes by Air or p-Benzoquinone

Stoichiometric reaction of $[Fe^{II}(S_2\text{-}o\text{-xyl})_2]^{2-}$ with dioxygen or *p*-benzoquinone was studied by measurements of absorption spectra. For example, a new absorption maximum was observed immediately at 478 nm when the dioxygen (about 2 equivalents) was injected into a DMF solution of complex **1** The result indicates that the Fe(III) complex of *o*-xylene-α, α'-dithiolate was formed in solution since $[Fe^{III}(S_2\text{-}o\text{-xyl})_2]^-$ has been reported to exhibit an absorption band at 486 nm.[11] The formation of Fe(III) thiolate complex by air oxidation of the corresponding Fe(II) analogue has been reported[7,21] and in a few cases, air oxidation of Fe(II) complex has been used to synthesize the corresponding Fe(III) complex [11,12]

Spectral change also occurred in a reaction between complex **1** and *p*-benzoquinone (1 · 1) in DMF solution which is similar with that of air oxidation as described above. Observation of two absorption maxima at 480 and 690 nm confirms the formation of Fe(III) species [11] In addition, maxima at 426 and 455 nm were also detected in this reaction at first and the intensity was decreased gradually and disappeared finally (in about 5 h), while the absorption maxima at 480 and 690 nm were stable and showed a little change after one day The absorption maxima at 426 and 455 nm were supposed to be due to the one-electron reduced product of *p*-benzoquinone About 90% Fe(III) complex was formed in situ as estimated from the absorption coefficient in both cases of dioxygen and *p*-benzoquinone oxidation reactions

Stoichiometric Reaction of $[Fe^{III}(S_2\text{-}o\text{-}xyl)_2]^-$ with Benzoin

This reaction was investigated by ^{1}H-NMR spectroscopy in an acetonitrile-d_3 solution at 30 °C and the results are presented in Figure 4 No isotropically shifted signals were observed in the ^{1}H-NMR spectrum of $[Fe^{III}(S_2\text{-}o\text{-xyl})_2]^-$ due to the high paramagnetism of high-spin Fe(III) as discussed for the oxidized rubredoxin [22] However, when one equivalent of benzoin was added to the solution, signals at 108.8 and 91.7 ppm were observed in about 20 min (Figure 4a) and the increase of intensity of these two signals indicates progress of the reaction Almost the same signals were found in the ^{1}H-NMR spectrum of complex $[Fe_2(S_2\text{-}o\text{-xyl})_3]^{2-}$ (see experimental section) The result implicates that a binuclear Fe(II) thiolate complex was formed by this reaction No signal was found at about 264 ppm (Figure 4) which was due to the CH_2 protons of a mononuclear complex, $[Fe^{II}(S_2\text{-}o\text{-xyl})_2]^{2-}$. The result indicates no formation of $[Fe^{II}(S_2\text{-}o\text{-xyl})_2]^{2-}$ during the reaction of $[Fe^{III}(S_2\text{-}o\text{-xyl})_2]^{-}$ with benzoin.

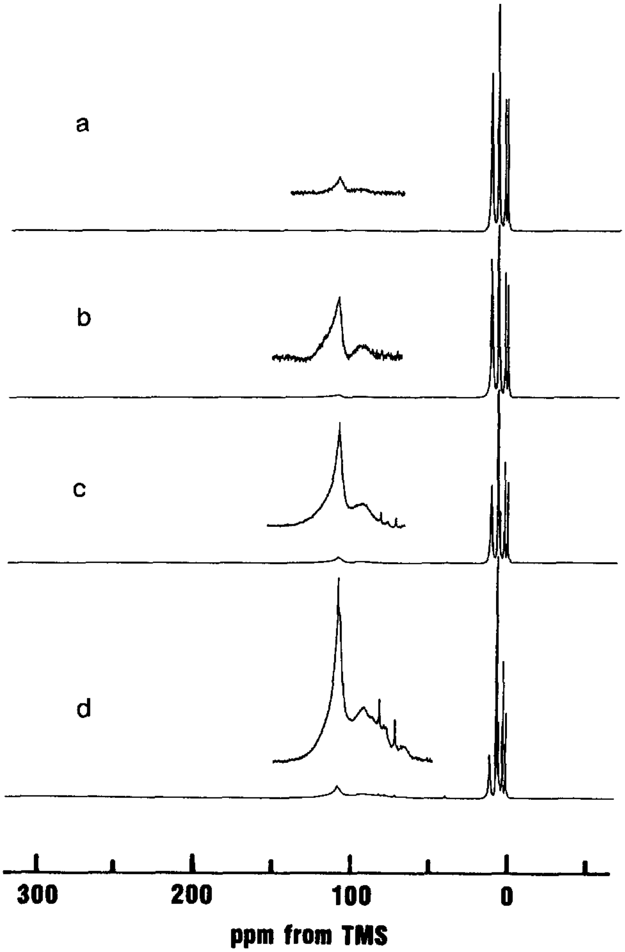

Figure 4. ^{1}H-NMR spectra of reaction of $[Fe^{III}(S_2\text{-}o\text{-xyl})_2]^{-}$ with benzoin (1 . 1) in acetonitrile-d_3 at 30 °C. a) Reaction time, 20 min, b) 50 min, c) 150 min and d) 40 h

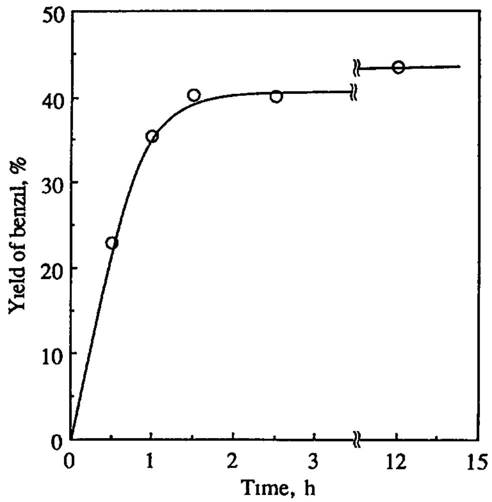

Figure 5. Time course for the stoichiometric reaction between $[Fe^{III}(S_2\text{-}o\text{-}xyl)_2]^-$ and benzoin (1 : 1) in DMF at 25 °C.

The CH_2 protons of $[Fe_2(SCH_2CH_3)_6]^{2-}$ have been reported to be observed at 69 ppm at 24 °C and at 59.9 and 57.6 ppm at -30 °C in acetonitrile-d_3.[18] The CH_2 signals (108.8 and 91.7 ppm at 30 °C) of $[Fe_2(S_2\text{-}o\text{-}xyl)_3]^{2-}$ were observed at lower field than those (69 ppm at 24 °C) of $[Fe_2(SCH_2CH_3)_6]^{2-}$ This trend was similar to the CH_2 signals observed in mononuclear complexes of $[Fe(S_2\text{-}o\text{-}xyl)_2]^{2-}$ (264 ppm in acetonitrile-d_3 at 30 °C, down field shifted) and $[Fe(SCH_2CH_3)_4]^{2-}$ (196 ppm in acetonitrile-d_3 at 27 °C)[20]

The formation of a binuclear complex from reaction of the *o*-xyl Fe(III) complex with benzoin was considered to be caused by the presence of protons (H^+) of benzoin. The stoichiometry of the reaction is given in equation (**1**)

$$PhCH(OH)COPh + 2(Et_4N)[Fe^{III}(S_2\text{-}o\text{-}xyl)_2] \longrightarrow PhCOCOPh + (Et_4N)_2[Fe_2^{II}(S_2\text{-}o\text{-}xyl)_3] + 1,2\text{-}C_6H_4(CH_2SH)_2 \quad (\mathbf{1})$$

One equivalent of *o*-xylene-α, α'-dithiol formed by this reaction was confirmed by ^1H-NMR spectroscopy. The formation of benzil was detected by HPLC. The results indicate that the Fe(III) complex can oxidize benzoin to give benzil with concomitant formation of a binuclear Fe(II) species

The same reaction was also carried out in DMF at 25 °C The time course of conversion of benzoin to benzil which was analyzed by HPLC is shown in Figure 5. In a stoichiometric reaction of $[Fe^{III}(S_2\text{-}o\text{-xyl})_2]^-$ with benzoin (1 : 1), just about half amounts of benzoin (50%) was oxidized to benzil. The result indicates that two moles of Fe(III) thiolate complexes oxidizes one mole of benzoin as shown in the equation (1). This reaction was also monitored by ^{1}H-NMR in DMF-d_7, two isotropically shifted signals at 113.8 and 94.6 ppm were observed which were very similar to those observed in acetonitrile-d_3 as shown in Figure 4.

The stoichiometric reaction between $[Fe^{III}(S_2\text{-}o\text{-xyl})_2]^-$ and o-xylene-α, α'-dithiol has been reported to produce the reduced state (Fe^{2+}) as evidenced by electronic spectral results.[23]

DISCUSSION

Both air and p-benzoquinone can oxidize some Fe(II) thiolate complexes to Fe(III) state as confirmed by absorption spectroscopy, and the Fe(III) complex reacts with a suitable substrate such as benzoin to give benzil as shown by the stoichiometric reaction of $[Fe^{III}(S_2\text{-}o\text{-xyl})_2]^-$ with benzoin. Thus, the catalytic oxidation of benzoin in the presence of Fe(II) thiolate complexes was considered to proceed through the same reaction mechanism in both cases of air and p-benzoquinone oxidation and the Fe(III) complex formed in situ is the active species, although the initial reaction rate was quite different between air and p-benzoquinone oxidation. A probable oxidation mechanism is illustrated in Figure 6.

In the present catalytic oxidation of benzoin, the Fe(II) thiolate complex was firstly oxidized to Fe(III) state by air or p-benzoquinone since the Fe(II) complex does not react with benzoin as proven by electronic spectroscopy which was the same as in the case of oxidation of benzoin catalyzed by some of the 4Fe4S clusters.[3] In the second step, the substrate coordinates to metal ion through alcoholic and ketyl oxygen atoms to form a six coordinated Fe(III) complex as proposed previously.[7] In the cases of catalytic air oxidation of benzyl alcohol and benzhydrol which was reported previously, a solvent molecule may coordinate to Fe(III) instead of the ketonic oxygen atom in this step. A similar coordination of substrate to metal ion has been reported in the cases of 4Fe4S cluster,[3] $[Ni(OCOCH_3)_2]$,[4] *etc* as catalyst The anionic alcoholic oxygen atom (CH-O$^-$) coordinates to metal ion since the catalytic oxidation of benzoin ethyl ether does not occur as reported in the case of $[Mo^{VI}O_2(cysS\text{-}OMe)_2]$ as a catalyst.[24] Then, one-electron oxidation of benzoin occurred to form an intermediate as shown in Figure 6a and the methine hydrogen of benzoin was released as a proton The rate of this step probably controls the rate of whole oxidation, because this is the rate determining step based on the kinetic isotope effect and p-substituent effect of substrate. The hydrogens from alcoholic OH group and methine hydrogen of benzoin are oxidized by dioxygen and p-benzoquinone to give water and hydroquinone, respectively

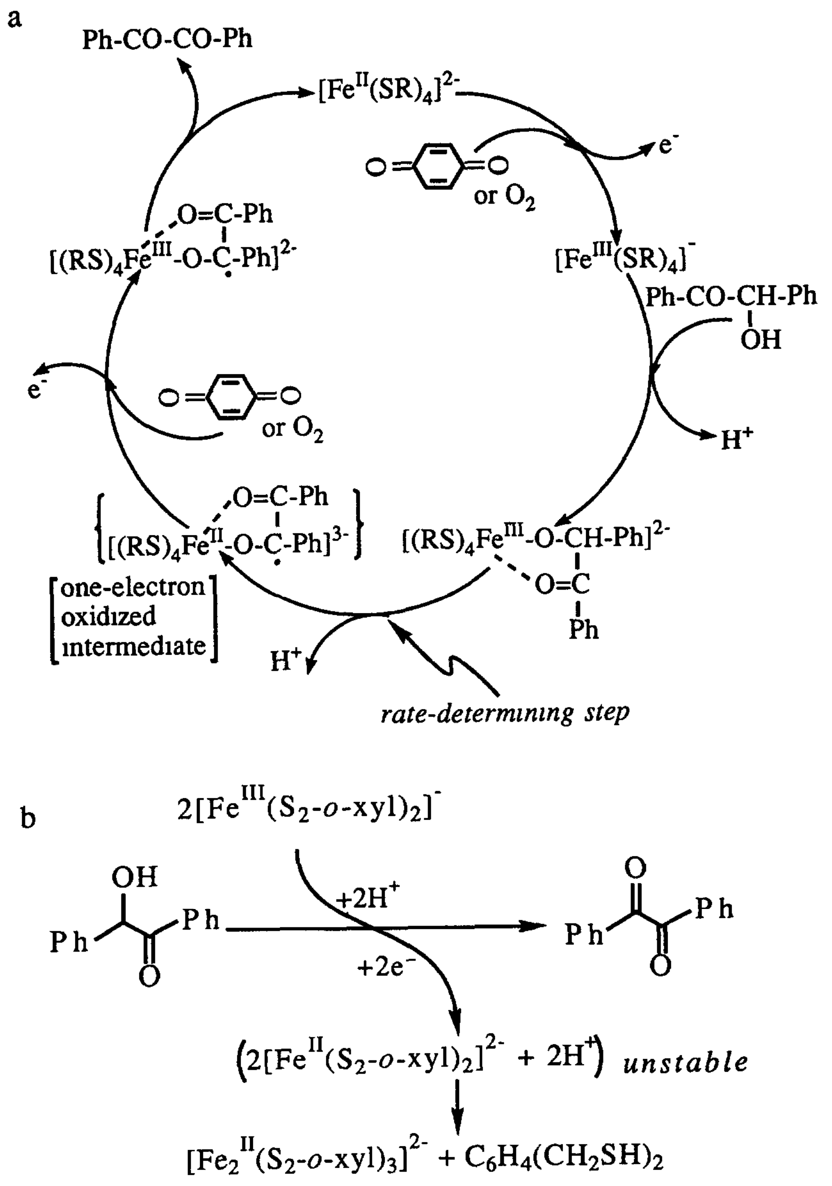

Figure 6. a) Proposed catalytic cycle for the oxidation of benzoin by air or *p*-benzoquinone in the presence of $[Fe^{II}(SR)_4]^{2-}$; b) Scheme for the stoichiometric reaction between $[Fe^{III}(S_2\text{-}o\text{-xyl})_2]^-$ and benzoin

As shown in Figure 2, the oxidation is first order to the concentration of catalyst, thus the two-electron oxidation of benzoin is considered to occur in two steps, not two moles of the catalyst oxidize one mole of benzoin simultaneously. In the latter case, the observed rate constant should be proportional to square of the concentration of the catalyst (i.e second order dependence)

In the stoichiometric reaction of the Fe(III) complex with benzoin, two protons from substrate exist in the system since there is no suitable proton-acceptor. These protons cause the conversion of mononuclear Fe(II) thiolate complex to binuclear analogue (Figure 6b). The formation of $(Et_4N)_2[Fe_2^{II}(S_2\text{-}o\text{-}xyl)_3]$ from $(Et_4N)_2[Fe^{II}(S_2\text{-}o\text{-}xyl)_2]$ has been reported to occur in a protic solvent such as ethanol[11]

The oxidation benzyl alcohol has been reported to be catalyzed by bis(pyridine)cobalt(II) complex, $[Co^{II}(bpy)_2](ClO_4)_2$[25] This Co(II) complex also exhibits catalytic activity in the oxidation of benzaldehyde to benzoic acid.[25] A Mn(II) thiolate complex, $[Mn(SPh)_4]^{2-}$, has also been reported to be catalytically active in the oxidation of benzaldehyde to benzoic acid[9] However, the Fe(II) thiolate complex catalyzed the oxidation of alcohol to aldehyde selectively This specificity is considered to be an important feature of Fe(II) thiolate complex as a model of rubredoxin.

EXPERIMENTAL

Materials — Substrates, benzoin was from Wako Pure Chemical Industries and purified by recrystallization, 4,4'-dichlorobenzyl alcohol, benzyl alcohol and 4,4'-dimethoxybenzyl alcohol were purchased from Tokyo Kasei Co. Ltd and purified by recrystallization or by distillation before use *p*-Benzoquinone was also recrystallized and stored in the dark. α-C-deuterated benzoin was prepared by a reported method[13] All spectral measurements and operations except for air oxidation reactions were carried out under inert gas atmosphere All solvents, e g DMF (*N*, *N'*-dimethylformamide), acetonitrile-d_3, were purified by distillation

Synthesis of Fe(II) and Fe(III) Thiolate Compounds — The complexes employed in this study, $(Et_4N)_2[Fe^{II}(S_2\text{-}o\text{-}xyl)_2]$ (**1**),[11] $(Et_4N)_2[Fe(SPh)_4]$ (**2**),[14,15] $(Et_4N)_2[Fe(S\text{-}t\text{-}Bu)_4]$ (**3**),[16] $(Et_4N)[Fe^{III}(S_2\text{-}o\text{-}xyl)_2]$[17] and $(Et_4N)_2[Fe_2^{II}(S_2\text{-}o\text{-}xyl)_3]$,[11,17] were prepared by methods reported in the literatures. The ^{1}H-NMR spectral measurements were carried out for the mono- and bi-nuclear Fe(II) *o*-xylene-α, α'-dithiolate complexes in acetonitrile-d_3 solution at 30 °C and the results are given below $[Fe^{II}(S_2\text{-}o\text{-}xyl)_2]^{2-}$ 264 ppm (α-CH_2 protons), 9 42 and 8.77 ppm (benzene ring protons). The peaks at 108 7 and 92 4 ppm (ca 1 · 2) of $[Fe_2^{II}(S_2\text{-}o\text{-}xyl)_3]^{2-}$ are due to the bridging and terminal CH_2 protons, respectively, as in the case of $[Fe_2(SEt)_6]^{2-}$.[18] No isotropically shifted signals downfield from 20 ppm were observed for $[Fe^{III}(S_2\text{-}o\text{-}xyl)_2]^-$ at the same conditions.

Typical Procedure for Catalytic Air Oxidation of Benzoin in the Presence of Fe(II) Thiolate Complexes — A solution of $[Fe^{II}(S_2\text{-}o\text{-}xyl)_2]^{2-}$ (1.30 mg, 2 X 10^{-6} mol) in DMF (1 ml) was added to a DMF (1 ml) solution of benzoin (8.49 mg, 4 X 10^{-5} mol) and the mixture was stirred vigorously at 25 °C under an argon atmosphere. The reaction was started by exposing the reaction mixture to air. After a given period, about 0.1 ml of the reaction solution was taken out and added to a mixture of diethyl ether and water (2 : 1) to extract benzil and unreacted benzoin to the diethyl ether layer. The yield of benzil was determined by HPLC using a COSMOSIL 5C18-AR column (150 mm X 4.6 mm inside diameter)

The air oxidation of benzoin to benzil catalyzed by $(Et_4N)_2[Fe(S\text{-}t\text{-}Bu)_4]$ or $(Et_4N)_2[Fe(SPh)_4]$ was also carried out in the same way

The catalytic air oxidation of α-C-deuterated benzoin in the presence of $[Fe^{II}(S_2\text{-}o\text{-}xyl)_2]^{2-}$ was carried out under the same conditions as the reaction of benzoin.

Catalytic Oxidation of Benzoin by *p*-Benzoquinone in the Presence of $[Fe^{II}(S_2\text{-}o\text{-}xyl)_2]^{2-}$ — A DMF (1 ml) solution of Fe(II) complex, $[Fe^{II}(S_2\text{-}o\text{-}xyl)_2]^{2-}$, (2.61 mg, 4 X 10^{-6} mol) was added to a DMF (1 ml) solution of benzoin (17.0 mg, 8 X 10^{-5} mol) at 25 °C The mixture was stirred vigorously and the reaction was started by addition of a DMF (2 ml) solution of *p*-benzoquinone (17.3 mg, 1.6 X 10^{-4} mol). After a prescribed reaction time, the product was extracted with diethyl ether and analyzed by HPLC.

The *p*-benzoquinone oxidation of α-C-deuterated benzoin catalyzed by $[Fe^{II}(S_2\text{-}o\text{-}xyl)_2]^{2-}$ was also carried out under the same conditions as mentioned above.

Catalytic Air Oxidation of *p*-Substituted Benzyl Alcohol to the Corresponding Benzaldehyde in the Presence of $[Fe(S_2\text{-}o\text{-}xyl)_2]^{2-}$ — To a DMF solution (1 ml) of $[Fe(S_2\text{-}o\text{-}xyl)_2]^{2-}$ (2 X 10^{-6} mol) was added 1 ml of *p*-substituted benzyl alcohol (4 X 10^{-5} mol) in DMF with stirring and then air was bubbled into the mixture and stirred at 25 °C. The other procedure was same as the case of air oxidation of benzoin as described above. The reaction mixture were extracted with diethyl ether and analyzed by HPLC immediately or cooled to a lower temperature (-20 °C) before HPLC analysis to avoid the autoxidation of benzyl alcohol by air.

Stoichiometric reaction of $(Et_4N)[Fe^{III}(S_2\text{-}o\text{-}xyl)_2]$ with Benzoin in DMF or Acetonitrile Solution — A solution of Fe(III) complex (5 X 10^{-6} mol) in DMF (1 ml) and a solution of benzoin (5 X 10^{-6} mol) in DMF (1 ml) were mixed and stirred at 25 °C. The formation of benzil was determined by HPLC and the result was presented in Figure 5.

In order to examine the product from reaction of $[Fe^{III}(S_2\text{-}o\text{-xyl})_2]^-$ with benzoin, the ^{1}H-NMR spectral measurements were carried out using 15 mmol of $(Et_4N)[Fe^{III}(S_2\text{-}o\text{-xyl})_2]$ and 15 mmol of benzoin in DMF-d_7 (0.6 ml) or in acetonitrile-d_3 (0.6 ml) at 30 °C.

Physical Measurements — Absorption spectra were measured on a JASCO Ubest-30 spectrophotometer in visible region, using a 1 mm cell. The sample concentrations were 1.0 mM. 400 MHz ^{1}H-NMR and 100 MHz ^{13}C-NMR spectral measurements were carried out on a JEOL GSX-400 FT NMR spectrometer. Chemical shifts downfield of TMS (tetramethylsilane) standard are defined as positive. The details of experimental conditions for ^{1}H-NMR spectral measurements of Fe(II) thiolate complexes have been given in the previous papers [16,19]

REFERENCES

1. Nakamura, A.; Ueyama, N.; Okamura, T., Zaima, H and Yoshinaga, N. *J Mol. Catal* **1989,** *55,* 276
2. Kaneko, M. and Yamada, A. *Makromol Chem* **1981,** *182,* 101.
3 (a) Ueyama, N.; Sugawara, T ; Kajiwara, A. and Nakamura, A *J Chem Soc , Chem. Commun* **1986**, 434 (b) Sugawara, T., Ueyama, N. and Nakamura, A. *J. Chem Soc., Dalton Trans* **1991**, 249
4 Hammond, G. S and Wu, C -H S *J Am Chem. Soc* **1973,** *95,* 8215.
5 Ueyama, N. and Nakamura, A *Macromolecular Complexes, Dynamic Interactions and Electronic Processes,* Tsuchida, E., Ed.; VCH Publishers, Inc.: New York, 1991, pp 315-328
6 Sun, W Y.; Ueyama, N. and Nakamura, A. *J Mol Catal* **1992,** *71,* 391
7. Sun, W. Y.; Ueyama, N and Nakamura, A. *Tetrahedron* **1992,** *48,* 1557.
8 (a) Eaton, W A and Lovenberg, W *Iron-Sulfur-Proteins,* Lovenberg, W., Ed., Academic, New York, **1973**; Vol II, pp131-162 (b) Jensen, L. H *Iron-Sulfur Proteins,* Lovenberg, W , Ed , Academic Press New York, 1973; Vol II, pp 163-194.
9 Kajiwara, A., Ueyama, N and Nakamura, A *Catal Lett* **1989,** *3,* 25.
10 (a) Ueyama, N., Nakata, M and Nakamura, A *Bull, Chem Soc Jpn* **1981,** *54,* 1727. (b) Nakata, M , Ueyama, N , Terakawa, T. and Nakamura, A. *Bull, Chem Soc Jpn* **1983,** *56,* 3647
11. Lane, R W ; Ibers, J. A., Frankel, R B , Papaefthymiou, G C and Holm, R H. *J Am Chem Soc* **1977,** *99,* 84
12 Millar, M ; Lee, J F , Koch, S A and Fikar, R *Inorg Chem* **1982,** *21,* 4105

13. Harrison, A. G. and Kallury, R. K. M. R *Org Mass Spectrom.* **1980**, *15*, 249.
14. Holah, D. G and Coucouvanis, D. *J Am Chem Soc* **1975**, *97*, 6917.
15 Hagen, K. S ; Reynolds, J. G. and Holm, R. H. *J Am Chem Soc.* **1981**, *103*, 4054.
16. Ueyama, N.; Sun, W. Y and Nakamura, A. *Inorg Chem.* **1992**, *31*, 4053.
17. Lane, R. W , Ibers, J. A ; Frankel, R. B and Holm, R H. *Proc Natl Acad. Sci U S A* **1975**, *72*, 2868.
18. Hagen, K. S. and Holm, R. H. *Inorg Chem.* **1984**, *23*, 418.
19. Sun, W. Y ; Ueyama, N. and Nakamura, A. *Inorg Chem* **1991**, *30*, 4026
20. Hagen, K S ; Watson, A. D. and Holm, R. H. *J Am Chem. Soc* **1983**, *105*, 3905
21. Yanada, K.; Nagano, T. and Hirobe, M. *Chem. Pharm Bull* **1988**, *36*, 535.
22. Werth, M T ; Kurtz, Jr , D M ; Moura, I and LeGall, J. *J Am Chem. Soc* **1987**, *109*, 273
23 Yanada, K ; Nagano, T and Hirobe, M *Tetrahedron Lett* **1986**, *27*, 5113.
24 Ueyama, N , Kamabuchi, K and Nakamura, A *J Chem Soc , Dalton Trans* **1985**, 635.
25. Sobkowiak, A and Sawyer, D T *J Am Chem Soc.* **1991**, *113*, 9520.