Mn^{II}-THIOPHENOLATE AND -SELENOPHENOLATE COMPLEXES AS CATALYST IN AIR OXIDATION OF BENZOIN, BENZALDEHYDE AND HYDRAZOBENZENE

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Catalytic air oxidation of benzoin to benzil in N,N-dimethylformamide (DMF) occurred in the presence of $[Mn(SePh)_4]^{2-}$ or $[Mn(SPh)_4]^{2-}$ (with conversion of 70% and 45%, respectively ([complex]/[benzoin] = 1/20, 50 h, 20 °C)). Similar oxidation of other substrates, e.g. hydrazobenzene, benzaldehyde, and benzhydrol, was also found.

The well known importance of Mn in biological transformation implies Mn-thiolate and Mn-selenolate species to be active in biological redox reactions. There is not much evidence for manganese binding to sulfur donor groups in metalloproteins, but the chemistry of this class of complexes is interesting in its own right. The chemical similarity of Fe^{III} and Mn^{III} and the biological importance of iron-sulfur systems also prompts further investigation of manganese complexes with sulfur ligands. Selenolate ligands also play important roles in some biological systems involving selenocysteine ligation e.g. formate dehydrogenase [1], and glutathione peroxidase [2].

Mn^{II}-thiolate complexes are readily oxidized in solution by dioxygen under neutral conditions at ambient temperature. Except for a report by Kaneko et al. [3], little is known about the catalytic activity of Mn^{II}-thiolate and -selenolate complexes for air oxidations of these organic compounds. They have investigated the catalytic activity of a polynuclear toluenedithiolato-Mn complex on oxidative polymerization of 2,6-dimethylphenol under basic conditions in a heterogeneous system. We have examined oxygenation of other substrates under neutral conditions in a homogeneous system. The reaction of Mn^{II}-thiolate complexes with dioxygen is the first step of the catalysis and therefore investigated separately. In particular, catalytic air oxidation of benzoin, benzaldehyde, benzhydrol and hydrazobenzene in the presence of $[Me_4N]_2[Mn(SePh)_4]$ (**1**) and $[Me_4N]_2[Mn(SPh)_4]$ (**2**) was examined in DMF and methanol.

All of preparation of complexes were carried out under argon atmosphere: $[Me_4N]_2[Mn(SePh)_4]$ was prepared by the reaction reported in the previous paper

Table 1
Air oxidation of substrates in the presence of $[Mn(XPh)_4]^{2-}$

Substrates *	Products	Time, h	Solvent	Conv., % X: Se	S
Benzoin	Benzil	50	DMF	70	45
		50	MeOH	30	25
Hydrazobenzene	Azobenzene	2	DMF	20	15
		2	MeOH	80	60
Benzaldehyde	Benzoic acid	1	DMF	50	52
4-Chlorobenzaldehyde	4-Chlorobenzoic acid	1	DMF	40	53
2,4-Dimethoxybenzaldehyde	2,4-Dimethoxybenzoic acid	20	DMF	≃ 0	≃ 0
Benzhydrol	Benzophenone	10	DMF	1	4
4,4′-Dichlorobenzhydrol	4,4′-Dichlorobenzophenone	10	DMF	12	10
4,4′-Dimethoxybenzhydrol	4,4′-Dimethoxybenzophenone	10	DMF	3	6

Reaction conditions: [Substrate] = 20 mM, [Complex] = 1 mM; 20 °C.

* Benzaldehyde and p-Cl-benzaldehyde converted to respective benzoic acid in air in DMF about 10% in 10 hours. 2,4-Dimethoxybenzaldehyde is stable over 20 hours in air in DMF solution. Other substrates are stable in air in this time scale.

[4]; and $[Me_4N]_2[Mn(SPh)_4]$ by the modification of the procedure reported by Holah et al. [5] and Costa et al. [6]. Catalytic air oxidation in the presence of Mn^{II}-thiophenolate and -selenophenolate complexes was carried out in DMF and methanol in air with stirring at 20 °C. The molar ratio [complex]/[substrate] was 1/20. The yield of product were determined by using HPLC.

As seen in table 1, **1** and **2** showed catalytic activity in the oxidations of benzoin, benzaldehyde, benzhydrol and hydrazobenzene. Time conversion curves showed similar feature for all substrates. Initially, the observed oxidation rates with both catalysts were high, and gradually decreased. The catalytic activity corresponds to the oxidation potential of the complexes as indicated by electrochemical measurement. The cyclic voltamograms of **1** and **2** showed an irreversible oxidation peak at +0.01 V (vs. SCE) and at +0.24 V (vs. SCE), respectively in DMF under argon. The difference (230 mV) between **1** and **2** indicates higher reactivity of **1** to dioxygen. This difference is thought to cause the observed higher efficiency of **1**. Solvent effects were also observed as shown in table 1. Benzoin was converted to benzil faster in DMF than in methanol. Contrary to the case of benzoin, hydrazobenzene was converted to azobenzene faster in methanol. These differences are probably caused by the difference of coordination mode of the substrates with manganese species. The catalytic activity of **1** and **2** for the air oxidation of other organic substrates is also tabulated in table 1. Benzaldehyde was oxidized to benzoic acid catalytically. Substituent effects were similar to the

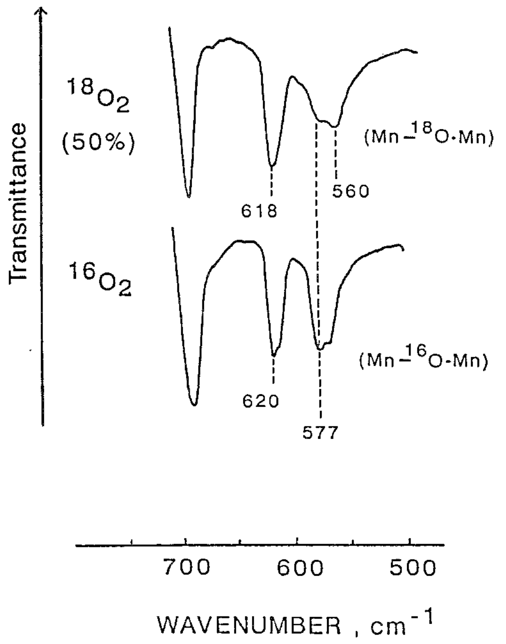

Fig. 1. IR spectra of $^{18}O_2$(50%) and $^{16}O_2$ oxidized species of $[Me_4N]_2[Mn(SPh)_4]$ **2** (KBr)

case of benzhydrol derivatives. Chloro-substituted derivatives are oxidized more easily than the methoxy derivatives.

Epoxidation of styrene did not occur in the presence of **1** and **2**. This result suggests a non-radical mechanism of the catalytic system containing **1** and **2** rather than the radical mechanism proposed on Mn-porphyrin-thiolate catalytic systems as cytochrome P-450 model [7]. It is possible that the thiolate and selenolate ligands activated the species containing Mn-O bonds which possibly formed by the reaction of **1** and **2** with dioxygen. The existence of Mn-O-Mn bonds was suggested by IR spectra of $^{18}O_2$ (50% content) oxidized species of **2** as shown in fig. 1. Isotopic absorptions ($^{16}O_2 \rightarrow {}^{18}O_2$) were observed at 1180, 618 and 560 cm^{-1}, while $^{16}O_2$ oxidized species had absorption at 1200, 620, and 577 cm^{-1}, respectively. The 560 cm^{-1}-absorption band could be assigned to Mn-^{18}O-Mn stretching mode as has been found for the Mn-O-Mn bond of a μ-oxo-di-μ-acetato bridged Mn dimer [8]. An absorption band assignable to terminal oxo (Mn = O) bond [9] was not observed.

These results of catalytic oxidation suggest that the active species are the air-oxidized species of the Mn^{II}-thiolate complexes. The absorption spectra of the oxidized species of **2** showed a weak shoulder ($\epsilon_M/Mn[M^{-1}cm^{-1}] \simeq 300$) near 420 nm in methanol just as that of oxo or hydroxo bridged dimanganese (III,III) complexes. It has been known that Mn^{III} μ-oxo-bridged dimers and tetramers show similar feature in 400–600 nm (d–d transition) region. Comparable absorption bands were observed in $[Mn^{III}_2O(O_2CCH_3)_2(HB(pz)_3)_2]$: [nm](ϵ_M/Mn^{III}

[$\mathrm{M^{-1}cm^{-1}}$]); in $\mathrm{CH_2Cl_2}$: 385sh(405), 458sh(165) [8], in $\mathrm{[Mn_2^{III}O(O_2CCH_3)_2(tacn)_2]^{2+}}$; in $\mathrm{CH_3CN}$: 486(337), 521(323) [10], and in $\mathrm{[Mn^{II}(EtOH)_4][Mn_2^{III}(sal)_4(pyr)_2]}$; in DMF: 460sh(274), 424(336) [11], and also in tetranuclear complexes, in $\mathrm{[Mn_4^{III}O_2(O_2CCH_3)_7(bipy)_2](ClO_4)3H_2O}$; in $\mathrm{CH_2Cl_2}$: 412(266), 447(268) [12]. These spectra differ from that of mononuclear $\mathrm{Mn^{III}}$ complex with sulfur ligands e.g. $\mathrm{[Mn^{III}(toluenditiolato)_2]^-}$; in DMF, 570sh(2200), 560(2300), 400sh(7400) [13] and $\mathrm{Mn^{III}}$(salps)MeOH; in $\mathrm{CH_2Cl_2}$, 370(24500), 418(17000) [14]. And also differ from that of μ-oxo bridged $\mathrm{Mn^{III}}$–$\mathrm{Mn^{IV}}$ [15,16] and $\mathrm{Mn^{II}}$-$\mathrm{Mn^{III}}$ [14,17] dimers and mononuclear $\mathrm{Mn^{IV}}$ complexes [18].

ESR spectra of the oxidized species of **2** in DMF or methanol at 77 K immediately after air oxidation at ambient temperature showed a broad and asymmetric signal with width of 3000 G. When the temperature was raised to 297 K for 10 min, air-oxidized species became ESR silent even at 77 K. These results indicated the existence of transient paramagnetic species and the transformation of these species to the air stable diamagnetic species. The air stable species would be the catalytically active species in consideration of the reaction time and temperature. It is well known that in the μ-oxo-bridged Mn-binuclear complexes, $\mathrm{Mn^{II}}$–$\mathrm{Mn^{III}}$ [14,19] and $\mathrm{Mn^{III}}$–$\mathrm{Mn^{IV}}$ [8,20] species show ESR signals but $\mathrm{Mn^{III}}$–$\mathrm{Mn^{III}}$ [8] species are inactive in ESR spectroscopy. The low temperature broad ESR signal and its conversion to a silent species suggest the formation of binuclear Mn species with considerable magnetic interaction between the Mn centers. And its conversion also suggests that the change of the formal oxidation states of Mn species during air oxidation of **2** probably are mononuclear $\mathrm{Mn^{II}}$ (under Ar) $\mathrm{Mn^{II}}$–$\mathrm{Mn^{III}}$ (broad signal) $\mathrm{Mn^{III}}$–$\mathrm{Mn^{III}}$ (absence of signal). Above suggestions are consistent with the results of IR and absorption spectra.

Further investigations of the catalytically active Mn-species are continuing.

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