The Effect of Axial Ligand on the Reactivity of Oxomanganese(V) Corrole

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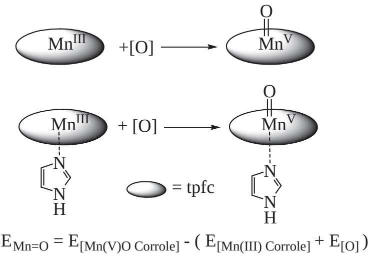
The effect of axial ligand on the reactivity of oxomanganese(V) 5,10,15-tris(pentafluorophenyl)corrole (tpfc)$Mn^{V}O$ had been investigated by kinetic method. It was found the reactivity of (tpfc)$Mn^{V}O$ towards styrene could be greatly enhanced by axial coordination interaction. Catalytic experiments indicated that the turnover frequency (TOF) of (tpfc)Mn^{III}-catalyzed epoxidation of styrene with PhIO was increased about 7 times in the presence of imidazole (catalyst/ligand, 1:10). Theoretical calculations showed that axial coordination will lower the binding energy of Mn=O bond in (tpfc)$Mn^{V}O$.



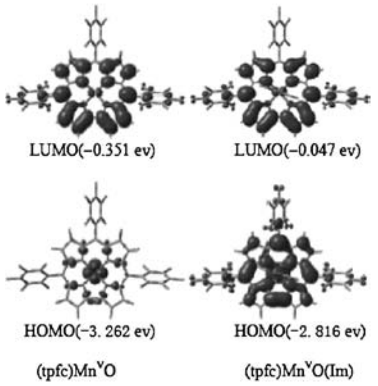
Scheme 1.

In recent years, study on corrole chemistry has received extensive interests.[1] Although it has been demonstrated that manganese corroles can catalyze the oxidation of alkene[2] and sulfide,[3] the mechansim of manganese corrole-catalyzed oxidation reaction is not fully understood so far. In the first investigation of manganese corrole-catalyzed oxidation of alkenes with PhIO, Gross et al.[2] had succesfully isolated oxomanganese(V) 5,10,15-tris(pentafluorophenyl)corrole (tpfc)$Mn^{V}O$. The lack of reactivity of (tpfc)$Mn^{V}O$ towards alkenes led to the proposal that the active oxidant in the catalytic reactions was possibly a higher valent $Mn^{VI}O$ species generated by disproportion of $Mn^{V}O$ complex. β-Octakis(4-*tert*-butylphenyl)corrolazine manganese(III) complex (TBP_8CZ)Mn^{III} is an active catalyst for the oxidation of PhSMe or epoxidation of stilbene with PhIO, but oxomanganese(V) corrolazine (TBP_8CZ)$Mn^{V}O$ was also found not reactive to alkenes.[4] ^{18}O-Labeling experiments indicated that a new "third oxidant" (TBP_8CZ)$Mn^{V}O$(PhIO) was involved in the catalytic oxidation process. Thus, Goldberg and Kerber[5] had proposed the possibility that (tpfc)$Mn^{V}O$(PhIO) might be the true oxidant in the (tpfc)Mn^{III}-catalysed oxidation of alkenes with PhIO. To examine the role of (tpfc)Mn^{III} as catalyst in the epoxidation of alkenes, Collman et al.[6] had performed a competitive epoxidation of styrene/cyclooctene with different ArIO terminal oxidants (Ar = C_6H_5, C_6F_5, mesityl), and found the ratio of epoxides varied with the property of ArIO. It is suggested that both $Mn^{V}O$ and Mn^{III}—OIAr intermediates were the active oxidants in the catalytic processes. Chang et al.[7] had prepared a perfluorinated manganese corrole (F_8tpfc)Mn^{III}, and found the isolated (F_8tpfc)$Mn^{V}O$ is much more reactive than (tpfc)$Mn^{V}O$ in the direct reaction with cyclooctene. Recently, Newcomb et al.[8] had checked the reactivity of several $Mn^{V}O$ corroles bearing different substituents, (BPFMC)$Mn^{V}O$, (TPC)$Mn^{V}O$, and (tpfc)$Mn^{V}O$ (BPFMC = 5,15-bis(pentafluorophenyl)-10-(*p*-methoxyphenyl)corrole; TPC = 5,10,15-triphenylcorrole). The order of reactivity of these $Mn^{V}O$ corroles was found to be TPC > BPFMC > TPFC in self-decay reactions or in the reactions with substrates. This is inverted from the expected $Mn^{V}O$ reactivity based on the electron-demand of the ligands. Fryxelius et al.[9] reported manganese 5,10,15-tri(4-nitrophenyl)corrole [*t*(4-NO_2P)C]Mn^{III}(Py) could not catalyze the oxidation of stilbene with PhIO as terminal oxidant.

The reactivity of $Mn^{V}O$ corroles observed by different research groups is somewhat puzzling. As $Mn^{V}O$ corrole may play a key role in the catalytic oxidation process, to explore the reactivity of $Mn^{V}O$ corroles at different conditions is certainly helpful in understanding the mechanism of manganese corrole-catalyzed oxidation reactions. We herein wish to report the effect of axial ligand on the reactivity of $Mn^{V}O$ corrole.

5,10,15-Tris(pentafluorophenyl)corrole (tpfc) can be easily prepared by Gross's solvent-free method,[10] and its oxomanganese(V) complex (tpfc)$Mn^{V}O$ is even stable enough to run a flash chromatography for purification.[7] For convenience, we choose (tpfc)$Mn^{V}O$ (see Scheme 1) as model $Mn^{V}O$ corrole and imidazole as axial ligand. (tpfc)Mn^{III} can form 1:1 complex with imidazole, the binding constant turned out to be 2.05×10^{5} M^{-1} (25 ± 0.1 °C) in CH_2Cl_2. In UV–vis spectra of (tpfc)Mn^{III}, a strong absorption appeared at 484 nm with the addition of imidazole (Figure S1).[14] When PhIO was added to (tpfc)Mn^{III}(Im) in CH_2Cl_2, the colour of solution would gradually turns from green to red, which is similar to (tpfc)Mn^{III} case,[2] indicating the formation of (tpfc)$Mn^{V}O$(Im). The UV–vis spectra of (tpfc)$Mn^{V}O$(Im) is nearly the same to that of (tpfc)$Mn^{V}O$. However, the self decay rate of (tpfc)$Mn^{V}O$(Im) is much faster than (tpfc)$Mn^{V}O$, and it will finally return to (tpfc)Mn^{III}(Im) in itself decay reaction as indicated by UV–vis spectra (Figure S2).[14] In the presence of styrene, the decay of (tpfc)$Mn^{V}O$(Im) can be remarkably accelerated further (Figure S3).[14]

To make a quantitative comparison, a (tpfc)$Mn^{V}O$ solution of ca. 5.0×10^{-3} M was prepared for kinetic study.[15] At 25($\pm$0.1) °C, the self decay reaction constant of (tpfc)$Mn^{V}O$ in CH_2Cl_2 is $2.07 \times 10^{-4}\,s^{-1}$, and (tpfc)$Mn^{V}O$ returned to (tpfc)Mn^{III} completely after 300 min. The self decay reaction constant of (tpfc)$Mn^{V}O$ will increase to $9.30 \times 10^{-4}\,s^{-1}$ in the presence of imidazole (0.3 M), and (tpfc)$Mn^{V}O$ became (tpfc)Mn^{III}(Im) atfer 70 min. This suggests axial binding of imidazole can significantly affects the stability of (tpfc)$Mn^{V}O$. Pseudo-first-order reaction rate constant between (tpfc)$Mn^{V}O$



Scheme 2.

and styrene (0.3 M) in CH_2Cl_2 is $3.24 \times 10^{-4}\,s^{-1}$ ($25 \pm 0.1\,°C$). It will increase up to $31.3 \times 10^{-4}\,s^{-1}$ in the presence of imidazole (0.3 M). Such a remarkable increase of the pseudo-first-order reaction rate constant between (tpfc)Mn^VO and styrene in the presence of imidazole indicates the reactivity of (tpfc)Mn^VO could be greatly enhanced by coordination of an axial ligand.

To further confirm the reactivity of (tpfc)Mn^VO could be enhanced by axial ligand, we have performed a theoretical calculations. The binding energy of $Mn^V{=}O$ bond in (tpfc)Mn^VO and (tpfc)Mn^VO(Im) is defined as shown in Scheme 1. Energies of all Mn^{III} ($S = 5$)[11] and Mn^VO ($S = 1$)[12] corrole species were calculated by B3PW91 method at STO-3G* level with Gaussian 03 program. The calculated binding energy of $Mn^V{=}O$ in (tpfc)Mn^VO and (tpfc)Mn^VO(Im) is −103.2 and −80.4 kcal/mol respectively. This indicates that (tpfc)Mn^VO is much more stable than (tpfc)Mn^VO(Im), that is (tpfc)Mn^VO(Im) is a more reactive oxidant than (tpfc)Mn^VO. The energies of HOMO and LUMO of (tpfc)Mn^VO(Im) are higher than that of (tpfc)Mn^VO. Calculated LUMOs of (tpfc)Mn^VO and (tpfc)Mn^VO(Im) are mainly localized on corrole nucleus and oxygen atom. Interestingly, the distribution of HOMO in (tpfc)Mn^VO(Im) is quite different from that in (tpfc)Mn^VO. HOMO of (tpfc)Mn^VO is localized on α carbons of corrole ring and manganese atom, while HOMO of (tpfc)Mn^VO(Im) is distributed extensively on manganese atom, axial ligand nitrogen atom, oxygen atom, and corrole nucleus (Scheme 2, Figure S4).[14] This indicates the axial coodination interaction could not only affect the energy level of Mn^VO corroles, but also the HOMO distributions.

The direct evidences that the reactivity of (tpfc)Mn^VO could be greatly increased by axial ligand also come from the catalytic oxidation of styrene by (tpfc)Mn^{III} with PhIO as terminal oxidant in the presence of imidazole. Catalytic experiments were carried out at following conditions: Styrene:PhIO:catalyst = 500:50:1 in 2-mL CH_2Cl_2 (catalyst, 2.4 μmol) under aerobic conditions at room temperature; Yield was determined by GC after 30 min based on the PhIO used; Axial ligand imidazole was added with a styrene/PhIO/catalyst/Im molar ratio of 500:50:1:10 in 2-mL CH_2Cl_2 (catalyst, 2.4 μmol); Turnover frequency (TOF) was calculated according to the reaction rate of the first 30 min.

The main product of catalytic oxidation reaction is styrene oxide (Figure S5).[14] TOF of (tpfc)Mn^{III}-catalyzed oxidation of styrene to styrene oxide is quite low ($4.8\,h^{-1}$), but it will increase to $34.5\,h^{-1}$ in the presence of imidazole. Such an increase in TOF basically matches the kinetic data mentioned above. When PhIO was added to the catalyst–substrate reaction mixtures, solutions would gradually turn from green to red colour. In the presence of imidazole, the solution would return green colour in 30 min, and the catalyst returned to (tpfc)Mn^{III}(Im) as detected by UV–vis spectra. But reaction mixture would keep red colour for more than 12 h without imidazole axial ligand. Catalytic experimental results indicate the oxygen atom transfer (OAT) rate between (tpfc)Mn^VO and styrene can be remarkably enhanced by axial ligand. The axial ligand induced rate acceleration of catalytic oxidation of substrates by metalloporphyrins is also well known.[13]

In summary, we have demonstrated that the reactivity of (tpfc)Mn^VO towards alkenes could be strongly enhanced by axial ligand. The axial coordination interaction would weaken Mn=O bond, raise the energy of HOMO and LUMO, as well as alter the HOMO distribution of (tpfc)Mn^VO significantly.

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14 Supporting Information is also available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

15 A (tpfc)Mn^{III} solution of 5.0×10^{-3} M in CH_2Cl_2 was used to prepare (tpfc)Mn^VO according to the method described in Ref. 7.

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