Manganese(v)-oxo corroles in hydride-transfer reactions[†]

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Hydride transfer from dihydronicotinamide adenine dinucleotide (NADH) analogues to manganese(v)-oxo corroles proceeds *via* proton-coupled electron transfer, followed by rapid electron transfer. The redox potentials (E_{red}) of manganese(v)-oxo corroles exhibit a good correlation with their reactivity in hydride-transfer reactions.

High-valent metal–oxo species have been implicated as the key intermediates in the catalytic oxidation of organic substrates by metalloenzymes.¹ By synthesizing biomimetic metal–oxo complexes and investigating their structural, spectroscopic, and chemical properties, our understanding of the nature of the metal–oxo intermediates and the mechanistic details of oxygen atom transfer in oxidation reactions has been advanced greatly.² Especially, reactivities of heme and nonheme iron–oxo complexes are well investigated in biomimetic oxidation reactions.²

High-valent manganese(v)–oxo porphyrins have also been proposed as reactive intermediates in the oxidation of organic substrates by manganese(III) porphyrin catalysts.³ Very recently, manganese(v)–oxo porphyrins were characterized by various spectroscopic methods,^{4–6} and the ¹H NMR and resonance Raman data revealed that the manganese(v)–oxo porphyrins are *trans*-dioxomanganese(v) species.^{4e} Reactivities of the manganese(v)–oxo porphyrins have also been reported recently in hydride-transfer reactions using dihydronicotinamide adenine dinucleotide (NADH) analogues and in the oxidation of organic substrates.^{5,6a}

Manganese(v)–oxo corroles with triply bonded $Mn^{V} \equiv O$ moiety were successfully characterized with various spectroscopic techniques, especially resonance Raman spectroscopy.⁷ However, the reactivities of the manganese(v)–oxo corroles have been poorly investigated in oxidation reactions due to the low oxidizing power. In addition, fundamental redox potentials and hydride-transfer properties of manganese(v)–oxo corroles, which would provide valuable mechanistic insight into the chemical properties, have yet to be reported. In this communication, we report the first example of hydride transfer from NADH analogues to manganese(v)–oxo corroles together with the determination of redox potentials of the manganese(v)–oxo corroles. An acid effect on the reactivity

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and redox potential of the Mn(v)-oxo species has been discussed as well.

Manganese(v)-oxo corroles, Mn(v)(O)(TNPC) (1) (TNPC = 5,10,15-tris(4-nitrophenyl)corrolato trianion), Mn(v)(O)(TFMPC) (2) (TFMPC = 5,10,15-tris(3,5-trifluoromethylphenyl)corrolato trianion), and Mn(v)(O)(TPFC) (3) (TPFC = 5,10,15-tris-(pentafluorophenyl)corrolato trianion) (see structures in Chart 1, Mn(v)(O)(Cor) Complexes), were prepared by the published procedures;⁷ manganese(III) corroles were reacted with 2.0 equiv. iodosylbenzene (PhIO) in CH₃CN at 10 °C. The UV-vis spectrum of 1 exhibits a strong band at 405 nm, characteristic of Mn(v)-oxo corroles (Fig. 1a for 1; ESI¹, Fig. S1 for 2 and 3). 1 was stable enough to be used in reactivity studies at 10 °C ($t_{1/2} = \sim 2$ h). First, the reaction of 1 with NADH analogues, 10-methyl-9,10-dihydroacridine (AcrH₂) and its derivatives, was investigated (see Chart 1, Hydride Donors). Upon addition of substrates to a solution of 1, the intermediate reverted back to the starting manganese(III) corrole, showing UV-vis spectral changes with a clear isosbestic point at 438 nm (Fig. 1a). First-order rate constants, determined by the pseudo-first-order fitting of the kinetic data for the decay of 1, increased linearly with increasing the substrate concentration, leading us to determine the second-order rate constant of 8.2(3) \times 10 M⁻¹ s⁻¹ for AcrH₂ (Fig. 1b). By using the dideuterated compound, AcrD₂ (see Chart 1, Hydride Donors), a large kinetic isotope effect (KIE) value of 10(2) was obtained (Fig. 1b and c; ESI⁺, Table S1). Such a large KIE value indicates that the C-H bond activation of AcrH₂ by 1 is the rate-determining step in the hydride-transfer reaction.^{5c,8}

The hydride-transfer reaction was also investigated with other AcrH₂ derivatives bearing a substituent R at the C-9 position, such as AcrHMe and AcrHEt (see the structure of AcrHR in Chart 1, *Hydride Donors*), and the reaction rates were found to vary depending on the substituent R of AcrHR (Fig. 1b). This result is similar to those observed in the hydride-transfer reactions by heme and non-heme Fe(Iv)-oxo

Mn(V)(O)(Cor) Complexes



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Fig. 1 (a) UV-vis spectral changes of $1 (3 \times 10^{-5} \text{ M})$, blue line) upon addition of AcrH₂ (6 × 10⁻⁴ M). Inset shows time course of the decay of 1 monitored at 405 nm (blue) and the formation of [Mn^{III}(TNPC)] monitored at 659 nm (red). (b) Plots of k_{obs} versus concentrations of AcrH₂ (black circles), AcrD₂ (red circles), AcrHMe (blue circles), and AcrHEt (green circles) to determine the second-order rate constants. (c) Plots of log k_2 of 1 (black circles), 2 (red circles), and 3 (blue circles) in the reactions of NADH analogues at 10 °C versus log k_2 of [Mn^V(O)₂(TPFPP)]⁻ in the reactions of NADH analogues at 25 °C.^{5c}

and Mn(v)-oxo porphyrins;^{5c,8b,c} the reactivity of AcrHR bearing an electron-donating R group is lower than that of AcrH₂, suggesting that the hydride-transfer reaction does not occur *via* a one-step hydride-transfer mechanism.⁹

The effect of corrole ligands on the reactivity of Mn(v)–oxo corroles was investigated in hydride-transfer reactions, and the second-order rate constants of 82(3), 49(3), and 8.8(3) × $10^2 \text{ M}^{-1} \text{ s}^{-1}$ were obtained in the reactions of AcrH₂ with **1**, **2**, and **3**, respectively (Fig. 1c; ESI[†], Table S1). The reactivity order of **3** > **1** > **2** suggests that a Mn(v)–oxo complex bearing an electron-deficient corrole ligand is more reactive in hydride-transfer reactions. The reactivity order of **3** > **1** > **2** was observed in the oxidation of AcrH₂ derivatives as well (Fig. 1c). In addition, large KIE values of 11(2) and 7.5(4) were obtained in the reactions of **2** and **3**, respectively,

with $AcrH_2$ and its dideuterated compound, $AcrD_2$ (Fig. 1c; ESI⁺, Table S1).

It has been proposed previously that hydride transfer from NADH analogues to Mn(v)-oxo porphyrins occurs via proton-coupled electron transfer (PCET), followed by rapid electron transfer.^{5c} We therefore compared k_2 values obtained in the hydride-transfer reactions by Mn(v)-oxo corrole and Mn(v)-oxo porphyrin complexes (see Fig. 1c). The observation of a linear correlation in the reactivity comparisons implies that hydride transfer from AcrH₂ and its derivatives to $Mn^{V}(O)(Cor)$ follows the mechanism proposed in the hydridetransfer reactions by [Mn^V(O)₂(Porp)]⁻ (see Scheme 1).^{5c,8-10} Further, the reactivity of Mn^V(O)(Cor) turned out to be greater than that of [Mn^V(O)₂(Porp)]⁻. For example, the reactivity of 3 determined at 10 °C is ~ 60 times greater than that of $[Mn(v)(O)_2(TPFPP)]^-$ (TPFPP=meso-tetrakis-(pentafluorophenyl)porphinato dianion) determined at 25 °C (compare k_2 values of Mn^V(O)(Cor) and [Mn^V(O)₂(TPFPP)]⁻ in ESI[†], Table S1).

We then investigated electron-transfer (ET) reactions with $Mn^{V}(O)(Cor)$ and ferrocene derivatives to determine the redox potentials of Mn(v)–oxo corroles. Upon addition of 1,1'-dimethylferrocene (DiMeFc) to the solution of 1 at 10 °C, the absorption band at 405 nm due to 1 decreased, accompanied by an increase in the absorption bands at 481 and 659 nm due to $Mn^{III}(TNPC)$ (ESI†, Fig. S2). This result indicates that two-electron reduction of 1 by DiMeFc took place. Interestingly, the ET between 1 and the reductant was in equilibrium [eqn (1)],¹¹ where the final concentration of $Mn^{III}(TNPC)$ produced in the ET reduction of 1 increased with an increase in the initial concentration of DiMeFc, [DiMeFc]₀.

$$2\text{DiMeFc} + \text{Mn}^{V}(\text{O})(\text{Cor}) \stackrel{K_{\text{et}}}{=} 2\text{DiMeFc}^{+} + \text{Mn}^{\text{III}}(\text{Cor})$$
(1)

The equilibrium constant (K_{et}) in eqn (1) was determined to be 5.0×10^{-2} at 10 °C by fitting the plot (ESI†, Fig. S3a). The apparent reduction potential, E_{red} , of **1** was then determined with K_{et} value and the E_{ox} value of DiMeFc (0.26 V versus SCE)¹² using eqn (2), where *n* is the number of electrons transferred. The E_{red}

$$E_{\rm red} = E_{\rm ox} + (RT/nF) \ln K_{\rm et}$$
(2)

of 1 was calculated to be 0.22 V versus SCE. The ET reactions from DiMeFc to other $Mn^{V}(O)Cor$ species were also in



Scheme 1 Proposed mechanism of the hydride transfer from $AcrH_2$ to a manganese(v)-oxo corrole complex.

equilibrium (ESI[†], Fig. S4), and the equilibrium constants (K_{et}) for **2** and **3** were 5.0 × 10⁻³ and 1.5 at 10 °C, respectively. Consequently, the E_{red} values of **2** and **3** were determined to be 0.19 and 0.27 V versus SCE, respectively. The E_{red} values are in a good correlation with their reactivities, suggesting that Mn(v)–oxo corroles with a high E_{red} is a more powerful oxidant.

Interestingly, in the presence of an acid (*i.e.*, HClO₄; 10 equiv., 3.0×10^{-4} M), **1** showed a reactivity with bromoferrocene (BrFc; $E_{ox} = 0.54$ V versus SCE); **1** did not react with BrFc in the absence of the acid. In addition, we found that there was an equilibrium between **1** and BrFc, where the final concentration of Mn^{III}(TNPC) produced in the ET reduction of **1** increased with an increase in the initial concentration of BrFc, [BrFc]₀. The equilibrium constant (K_{et}) of 3.0×10^{-1} was determined at 10 °C by fitting the plot (ESI[†], Fig. S3b). The apparent reduction potential, E_{red} , of **1** in the presence of acid is then calculated with K_{et} value and the E_{ox} value of BrFc by eqn (2). The E_{red} of **1** in the presence of HClO₄ is 0.52 V versus SCE, which is 0.30 V higher than that of **1** in the absence of HClO₄. Similar trends were actually reported in the non-heme Fe^{IV}(O) system.¹³

The hydride transfer from NADH analogues to Mn(v)-oxo corroles was also dependent significantly on the presence of HClO₄. Upon addition of 20 equiv. AcrHEt (6.0 \times 10⁻⁴ M) to a solution of 1 (3.0 \times 10⁻⁵ M) containing 10 equiv. HClO₄ $(3.0 \times 10^{-4} \text{ M})$, 1 reverted back to the starting Mn^{III}(TNPC) with the concomitant formation of AcrEt⁺ ion from AcrHEt (ESI[†], Fig. S5a). In the absence of HClO₄, AcrEt(OH) was the final product (see ESI[†], Experimental section). First-order rate constant (k_{obs}), determined by the pseudo-first-order fitting of the kinetic data for the decay of **1** or the formation of AcrEt⁺, was $5.8 \times 10^{-2} \text{ s}^{-1}$; the rate constant is 100 times greater than that determined in the absence of HClO₄ ($k_{obs} = 5.6 \times 10^{-4} \text{ s}^{-1}$, Fig. 1b and ESI[†], Fig. S5b). This result is in line with the observation that the presence of an acid increased the redox potential of 1 (vide supra). We also found that the first-order rate constant increased proportionally with increasing the acid concentration (ESI[†], S5b). Such acceleration of the rate results from the enhancement of the ET process in Scheme 1 due to the protonation of [Mn^{IV}(O)(Cor)]⁻ (PCET).

In conclusion, we have reported the first example of the oxidation of NADH analogues by manganese(v)–oxo corroles. We have also demonstrated that hydride transfer from AcrH₂ and its derivatives to Mn^V(O)(Cor) occurs *via* PCET, followed by rapid electron transfer, as reported previously in the reaction of [Mn^V(O)₂(Prop)]^{-,5c} The redox potentials of manganese(v)–oxo corroles were determined for the first time using 1,1'-dimethyl-ferrocene as a one-electron reductant in the redox titration experiments, and the $E_{\rm red}$ values were in a good correlation with their reactivities in hydride-transfer reactions; the manganese-(v)–oxo corroles with a high $E_{\rm red}$ showed a greater reactivity. Finally, we have demonstrated that the presence of acid in reaction solutions increases the redox potential of manganese-(v)–oxo corroles and the rate of the hydride transfer from hydride donors to manganese(v)–oxo corroles.

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Notes and references

- (a) P. C. A. Bruijnincx, G. van Koten and R. J. M. Klein Gebbink, Chem. Soc. Rev., 2008, 37, 2716; (b) W. Nam, Acc. Chem. Res., 2007, 40, 465, and review articles in the special issue; (c) P. R. Ortiz de Montellano, Cytochrome P450: Structure, Mechanism, and Biochemistry, Kluwer Academic/Plenum Publishers, New York, 3rd edn, 2005; (d) M. M. Abu-Omar, A. Loaiza and N. Hontzeas, Chem. Rev., 2005, 105, 2227; (e) I. G. Denisov, T. M. Makris, S. G. Sligar and I. Schlichting, Chem. Rev., 2005, 105, 2253; (f) B. Meunier, S. P. de Visser and S. Shaik, Chem. Rev., 2004, 104, 3947.
- 2 (a) A. Gunay and K. H. Theopold, Chem. Rev., 2010, 110, 1060;
 (b) R. van Eldik, Coord. Chem. Rev., 2007, 251, 1649; (c) W. Nam, Acc. Chem. Res., 2007, 40, 522; (d) Y. Watanabe, H. Nakajima and T. Ueno, Acc. Chem. Res., 2007, 40, 554; (e) J. T. Groves, Proc. Natl. Acad. Sci. U. S. A., 2003, 100, 3569; (f) S. Fukuzumi, Y. Morimoto, H. Kotani, P. Naumov, Y.-M. Lee and W. Nam, Nat. Chem, 2010, 2, 756.
- 3 B. Meunier, A. Robert, G. Pratviel and J. Bernadou, *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, San Diego, 2000, vol. 4, ch. 31, pp. 119–187.
- 4 (a) J. T. Groves, J. Lee and S. S. Marla, J. Am. Chem. Soc., 1997, 119, 6269; (b) N. Jin and J. T. Groves, J. Am. Chem. Soc., 1999, 121, 2923; (c) N. Jin, J. L. Bourassa, S. C. Tizio and J. T. Groves, Angew. Chem., Int. Ed., 2000, 39, 3849; (d) D. Lahaye and J. T. Groves, J. Inorg. Biochem., 2007, 101, 1786; (e) N. Jin, M. Ibrahim, T. G. Spiro and J. T. Groves, J. Am. Chem. Soc., 2007, 129, 12416.
- 5 (a) W. Nam, I. Kim, M. H. Lim, H. J. Choi, J. S. Lee and H. G. Jang, *Chem.-Eur. J.*, 2002, **8**, 2067; (b) W. J. Song, M. S. Seo, S. D. George, T. Ohta, R. Song, M.-J. Kang, T. Tosha, T. Kitagawa, E. I. Solomon and W. Nam, *J. Am. Chem. Soc.*, 2007, **129**, 1268; (c) J. Y. Lee, Y.-M. Lee, H. Kotani, W. Nam and S. Fukuzumi, *Chem. Commun.*, 2009, 704; (d) C. Arunkumar, Y.-M. Lee, J. Y. Lee, S. Fukuzumi and W. Nam, *Chem.-Eur. J.*, 2009, **15**, 11482.
- 6 (a) R. Zhang, J. H. Horner and M. Newcomb, J. Am. Chem. Soc., 2005, **127**, 6573; (b) Y. Shimazaki, T. Nagano, H. Takesue, B.-H. Ye, F. Tani and Y. Naruta, Angew. Chem., Int. Ed., 2004, **43**, 98.
- 7 (a) Z. Gross, G. Golubkov and L. Simkhovich, Angew. Chem., Int. Ed., 2000, 39, 4045; (b) H.-Y. Liu, T.-S. Lai, L.-L. Yeung and C. K. Chang, Org. Lett., 2003, 5, 617; (c) H.-Y. Liu, F. Yam, Y.-T. Xie, X.-Y. Li and C. K. Chang, J. Am. Chem. Soc., 2009, 131, 12890; (d) Y. Gao, T. Akermark, J. Liu, L. Sun and B. Akermark, J. Am. Chem. Soc., 2009, 131, 8726; (e) S. H. Kim, H. Park, M. S. Seo, M. Kubo, T. Ogura, J. Klajn, D. T. Gryko, J. S. Valentine and W. Nam, J. Am. Chem. Soc., 2010, DOI: 10.1021/ja1066465, .
- 8 (a) X.-Q. Zhu, H.-R. Li, Q. Li, T. Ai, J.-Y. Lu, Y. Yang and J.-P. Cheng, *Chem.-Eur. J.*, 2003, **9**, 871; (b) S. Fukuzumi, H. Kotani, Y.-M. Lee and W. Nam, *J. Am. Chem. Soc.*, 2008, **130**, 15134; (c) Y. J. Jeong, Y. Kang, A.-R. Han, Y.-M. Lee, H. Kotani, S. Fukuzumi and W. Nam, *Angew. Chem., Int. Ed.*, 2008, **47**, 7321; (d) C. Fertinger, N. Hessenauer-Ilicheva, A. Franke and R. van Eldik, *Chem.-Eur. J.*, 2009, **15**, 13435; (e) L. Tahsini, M. Bagherzadeh, W. Nam and S. P. de Visser, *Inorg. Chem.*, 2009, **48**, 6661.
- 9 S. Fukuzumi, Y. Tokuda, T. Kitano, T. Okamoto and J. Otera, J. Am. Chem. Soc., 1993, 115, 8960.
- 10 (a) S. Fukuzumi, S. Koumitsu, K. Hironaka and T. Tanaka, J. Am. Chem. Soc., 1987, 109, 305; (b) S. Fukuzumi, K. Ohkubo, Y. Tokuda and T. Suenobu, J. Am. Chem. Soc., 2000, 122, 4286.
- 11 In the ET reaction, the oxo moeity is removed by the reaction with residual water. The K_{et} value in eqn (1) is defined including water.
- 12 (a) S. Fukuzumi, K. Okamoto, C. P. Gros and R. Guilard, J. Am. Chem. Soc., 2004, **126**, 10441; (b) Y.-M. Lee, H. Kotani, T. Suenobu, W. Nam and S. Fukuzumi, J. Am. Chem. Soc., 2008, **130**, 434.
- 13 S. Fukuzumi, H. Kotani, T. Suenobu, S. Hong, Y.-M. Lee and W. Nam, *Chem.-Eur. J.*, 2010, 16, 354.