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Multi-electron oxidation

Multi-Electron Oxidation of Anthracene Derivatives by Nonheme Manganese(IV)-Oxo Complexes

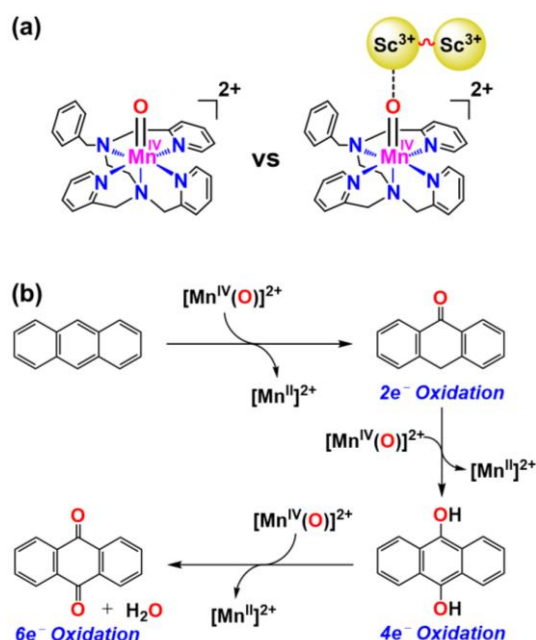
Namita Sharma,^[a] Jieun Jung,^[a] Yong-Min Lee,^[a] Mi Sook Seo,^[a] Wonwoo Nam,^{*,[a]} and Shunichi Fukuzumi^{*,[a,b]}

Abstract: Six-electron oxidation of anthracene to anthraquinone by a nonheme Mn(IV)-oxo complex, [(Bn-TPEN)Mn^{IV}(O)]²⁺, proceeds via the rate-determining electron transfer from anthracene to [(Bn-TPEN)Mn^{IV}(O)]²⁺, followed by subsequent fast oxidation reactions to give anthraquinone. The reduced Mn(II) complex [(Bn-TPEN)Mn^{II}] is oxidized by [(Bn-TPEN)Mn^{IV}(O)]²⁺ rapidly to produce the μ -oxo dimer [(Bn-TPEN)Mn^{III}-O-Mn^{III}(Bn-TPEN)]⁴⁺. The oxygen atoms of the anthraquinone product were found to derive from the manganese-oxo species by the ¹⁸O labelling experiments. In the presence of Sc³⁺ ion, formation of anthracene radical cation was directly detected in electron

transfer from anthracene to a Sc³⁺ ion-bound Mn^{IV}(O) complex, [(Bn-TPEN)Mn^{IV}(O)-(Sc(OTf)₃)₂]²⁺, followed by subsequent further oxidation to yield anthraquinone. When anthracene was replaced by 9,10-dimethylantracene, electron transfer from 9,10-dimethylantracene to [(Bn-TPEN)Mn^{IV}(O)-(Sc(OTf)₃)₂]²⁺ occurred rapidly to produce stable 9,10-dimethylantracene radical cation. The driving force dependence of the rate constants of electron transfer from anthracene derivatives to [(Bn-TPEN)Mn^{IV}(O)]²⁺ and [(Bn-TPEN)Mn^{IV}(O)-(Sc(OTf)₃)₂]²⁺ was well evaluated in light of the Marcus theory of electron transfer.

Introduction

Multi-electron transfer is of major importance in a wide range of fields including renewable energy and bioinspired catalysis. For example, natural photosynthesis proceeds via multi-electron transfer processes such as four-electron oxidation of water and multi-electron reduction of CO₂.^[1-9] Unlike single electron transfer, mechanisms of multi-electron transfer reactions have yet to be elucidated clearly.^[11-10] Among multi-electron oxidations of various substrates, the oxidation of anthracene and its derivatives merits special attention, because the number of electrons to be transferred is different depending on the substituents of anthracene derivatives.^[11-13] For example, six-electron oxidation of anthracene affords anthraquinone, whereas one-electron oxidation of 9,10-disubstituted anthracene results in formation of its stable radical cation.^[12] Although there are a few reports on the oxidation of anthracene and its derivatives by high-valent metal-oxo complexes,^[14,15] mechanism(s) of the multi-electron oxidation reactions has yet to be clarified.



Scheme 1. a) Molecular structure of [(Bn-TPEN)Mn^{IV}(O)]²⁺ (1) and [(Bn-TPEN)Mn^{IV}(O)-(Sc(OTf)₃)₂]²⁺ (2). b) Multi-electron oxidation of anthracene by 1 and 2.

We herein report the mechanisms of six-electron oxidation of anthracene as well as four-electron oxidation of 9-methylantracene and one- or two-electron oxidation of 9,10-dimethylantracene by mononuclear nonheme manganese(IV)-oxo complexes, [(Bn-TPEN)Mn^{IV}(O)]²⁺ (1, Bn-TPEN = *N*-benzyl-*N,N',N'*-tris(2-pyridylmethyl)-1,2-diaminoethane)^[16] and Sc³⁺ ion-

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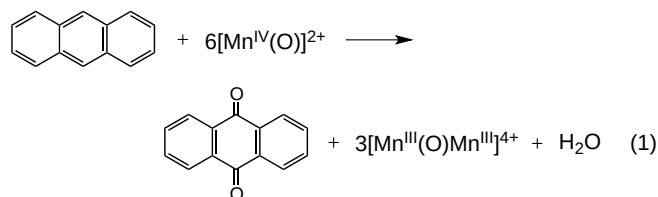
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bound Mn(IV)-oxo complex, $[(\text{Bn-TPEN})\text{Mn}^{\text{IV}}(\text{O})-(\text{Sc}(\text{OTf})_3)_2]^{2+}$ (**2**),^[17,18] (Scheme 1a for the molecular structure of **1** and **2** and Scheme 1b for the reactions of anthracene by **1** and **2**); the mechanisms were proposed based on the kinetics study and the detection of anthracene radical cation intermediate. This is the first example to clarify the mechanism of the multi-electron oxidation of substrates by high-valent metal-oxo complexes, although the mechanisms of two-electron oxidation of substrates by high valent metal-oxo complexes have been extensively studied.^[17-21] The driving force dependence of logarithm of rate constants of electron transfer ($\log k_{\text{et}}$) from anthracene derivatives to $[(\text{Bn-TPEN})\text{Mn}^{\text{IV}}(\text{O})]^{2+}$ (**1**) and $[(\text{Bn-TPEN})\text{Mn}^{\text{IV}}(\text{O})-(\text{Sc}(\text{OTf})_3)_2]^{2+}$ (**2**), is compared with that of electron-transfer reactions of **1** and **2** with one-electron reductants, such as ferrocene derivatives, in light of the Marcus theory of electron transfer.^[21]

Results and Discussion

Oxidation of anthracene by $[(\text{Bn-TPEN})\text{Mn}^{\text{IV}}(\text{O})]^{2+}$

Anthracene was fully oxidized upon addition of six equivalents of **1** in a solvent mixture of trifluoroethanol (TFE) and acetonitrile (MeCN) ($v/v = 1:1$) at 273 K, in which the absorption band at 1020 nm due to **1** disappeared completely (Figure 1). The stoichiometry of the reaction is given by Eq. (1), where anthracene is oxi-



dized to anthraquinone (six-electron oxidized product) and **1** was reduced by one electron to produce Mn^{III} species. The Mn^{III} product was confirmed by cold spray ionization (CSI) mass spectrometry as shown in Figure 2 together with EPR silence (Table 1; Supporting Information (SI), Figure S1). The Mn^{III} species was probably produced via a μ -oxo dimer, $[(\text{Bn-TPEN})\text{Mn}^{\text{III}}-\text{O}-\text{Mn}^{\text{III}}(\text{Bn-TPEN})]^{4+}$, because CSI mass spectrum as shown in Figure 2 was virtually identical to that of the product obtained in the reaction of $[(\text{Bn-TPEN})\text{Mn}^{\text{IV}}(\text{O})]^{2+}$ with $[(\text{Bn-TPEN})\text{Mn}^{\text{II}}]^{2+}$ (SI, Figure S2).

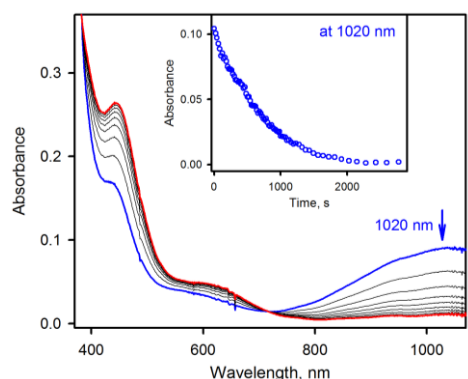


Figure 1. UV-visible absorption changes in the six-electron oxidation of anthracene (0.10 mM) by six equivalents of **1** (0.60 mM) in TFE/MeCN ($v/v = 1:1$) at 273 K.

Table 1. Doubly integrated values of EPR signals of the reduced species of $[(\text{Bn-TPEN})\text{Mn}^{\text{IV}}(\text{O})]^{2+}$ (**1**) by the reduction with anthracene derivatives in comparison with those of manganese(II) acetate at 77 K.

Mn complex	substrate	doubly integrated value	yield, ^a %
1 (0.6 mM)	anthracene (0.1 mM)	7.4×10^5	0.2
1 (0.8 mM)	9-methylanthracene (0.2 mM)	1.5×10^6	0.3
1 (0.5 mM)	9,10-dimethylanthracene (0.5 mM)	9.9×10^5	0.3
$\text{Mn}^{\text{II}}(\text{CH}_3\text{CO}_2)_2$ (0.5 mM)	—	3.6×10^8	—

^a Spin amount of Mn^{II} complex ($S = 1/2$ state) formed in the reactions was compared with that of $\text{Mn}^{\text{II}}(\text{CH}_3\text{CO}_2)_2$.

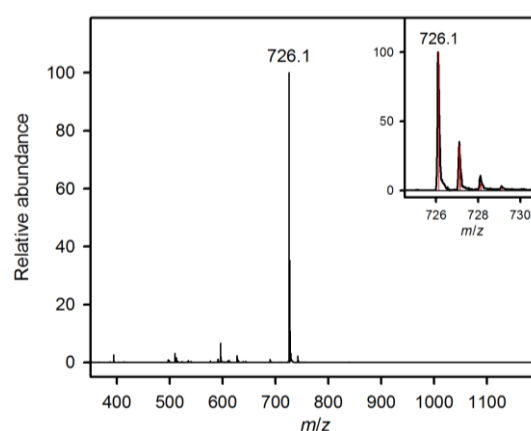


Figure 2. CSI mass spectrum of the reaction product obtained in the oxidation of anthracene (0.10 mM) by $[(\text{Bn-TPEN})\text{Mn}^{\text{IV}}(\text{O})]^{2+}$ (0.60 mM) in TFE/MeCN ($v/v = 1:1$) at 273 K. The ion peak at $m/z = 726.1$ corresponds to $[\text{Mn}^{\text{III}}(\text{BrTPEN})(\text{CF}_3\text{CH}_2\text{O})(\text{CF}_3\text{SO}_3)]^+$ (calculated $m/z = 726.1$). Inset shows the experimental (black line) and calculated (red bars) isotope distribution patterns of the peak at $m/z = 726.1$.

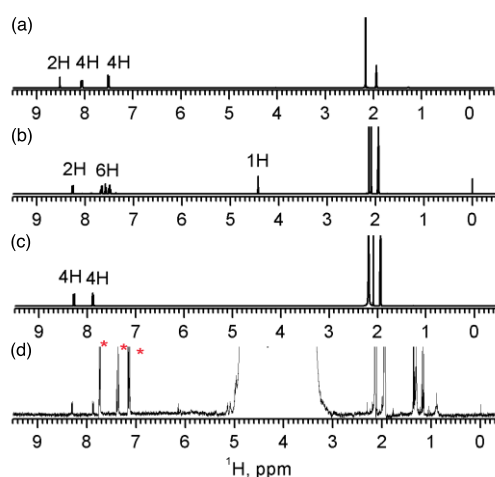


Figure 3. ^1H NMR spectra of the authentic references [a] anthracene (10 mM), [b] anthrone (10 mM), [c] anthraquinone (10 mM)], and [d] the reaction products obtained in the oxidation of anthracene (0.20 mM) by **1** (1.2 mM) in TFE/MeCN- d_3 ($v/v = 1:1$) at 273 K. The peaks marked with asterisks (*) in (d) are from PhIO, which was formed in the generation of **1** by PhIO.

Further, the formation of anthraquinone (100% yield based on anthracene) as an oxidized product of anthracene was confirmed by taking ^1H NMR spectra of the reaction solution (Figure 3). It was confirmed that no oxidation of anthracene was observed when **1** was replaced by $\text{Mn}^{\text{II}}(\text{OTf})_2$ under otherwise the same conditions. The direct oxidation of anthracene by a hypervalent iodine oxidant required high temperature such as 373 K.^[22]

When the anthracene oxidation was performed with ^{18}O -labeled **1** ($1\text{-}^{18}\text{O}$), which was prepared by exchanging the oxygen atom of $1\text{-}^{16}\text{O}$ with H_2^{18}O ,^[18] the oxygen atoms of the anthraquinone product were found to derive from the Mn^{IV} -oxo species; the ratio of two ^{18}O to one ^{16}O in anthraquinone was virtually the same as the ratio derived from $1\text{-}^{18}\text{O}$: $1\text{-}^{16}\text{O}$ (SI, Figure S3) as shown by the CSI mass spectra of anthraquinone in Figure 4.

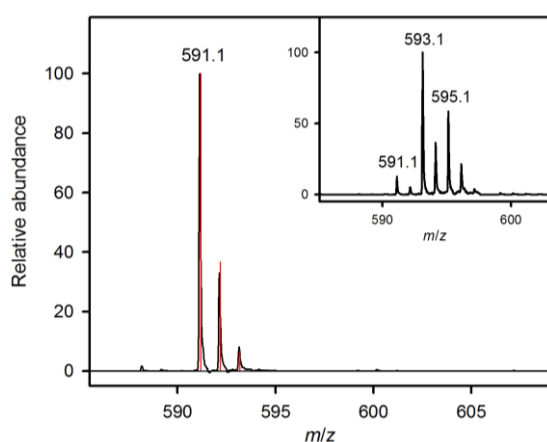


Figure 4. CSI mass spectrum of the reaction product (black line) obtained in the oxidation of anthracene (0.50 mM) with $[(\text{Bn-TPEN})\text{Mn}^{\text{IV}}(\text{O})]^{2+}$ (**1**; 0.50 mM) in TFE/MeCN ($v/v = 1:1$) at 273 K. The peak at $m/z = 591.1$ corresponds to $[(\text{anthraquinone})(\text{anthracene})(\text{CF}_3\text{CH}_2\text{OH})(\text{CH}_3\text{CN})_2(\text{Na})]^+$ ($= [^{16}\text{O}, ^{16}\text{O}\text{-labeled anthraquinone}]^+$; calculated $m/z = 591.2$). The red bars show the calculated isotope distribution patterns of the peak at $m/z = 591.1$. Inset shows CSI mass spectrum of the complete reaction solution obtained in the oxidation of anthracene (0.50 mM) with $[(\text{Bn-TPEN})\text{Mn}^{\text{IV}}(^{18}\text{O})]^{2+}$ ($1\text{-}^{18}\text{O}$; 0.50 mM) in TFE/MeCN ($v/v = 1:1$) at 273 K. The peaks at $m/z = 591.1$, 593.1 and 595.1 correspond to $[^{16}\text{O}, ^{16}\text{O}\text{-labeled anthraquinone}]^+$ (calculated $m/z = 591.2$), $[^{16}\text{O}, ^{18}\text{O}\text{-labeled anthraquinone}]^+$ (calculated $m/z = 593.2$) and $[^{18}\text{O}, ^{18}\text{O}\text{-labeled anthraquinone}]^+$ (calculated $m/z = 595.2$), respectively. The mass intensity ratio of $m/z = 591.1$, 593.1 and 595.1 was 8.0 : 58 : 34. The formation of significant amount of ^{18}O , ^{18}O -labeled anthraquinone indicates that oxygen in anthraquinone derived from $[(\text{Bn-TPEN})\text{Mn}^{\text{IV}}(^{18}\text{O})]^{2+}$.

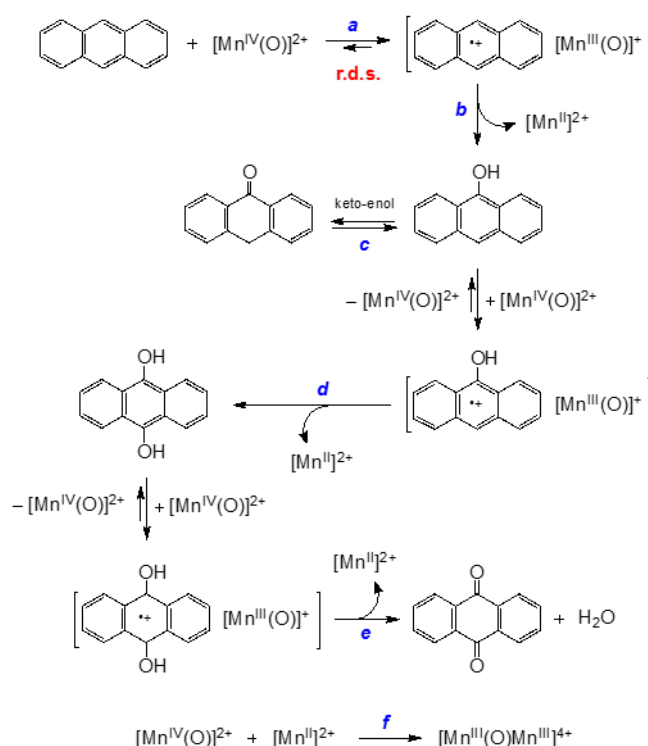
The decay rate of **1** in the presence of excess anthracene obeyed first-order kinetics (SI, Figure S4a) and the first-order rate constants were proportional to the concentration of anthracene (SI, Figure S5a). If one assumes that the first electron transfer from anthracene to **1** is the rate-determining step in the six-electron oxidation of anthracene by **1**, the decay rate of **1** is given by Eq. (2),

$$-d[\text{Mn}^{\text{IV}}(\text{O})]/dt = 6k_{\text{et}}[\text{Mn}^{\text{IV}}(\text{O})][\text{An}] \quad (2)$$

where k_{et} is the rate constant of the first electron transfer and "An" denotes anthracene. Once the first electron transfer from anthracene to **1** occurs, six equivalents of **1** disappears due to the stoichiometry in Eq. (1). The k_{et} value of electron transfer from anthracene to **1** was determined from the slope (k_2) of the pseudo-

first-order rate constant (k_1) vs. concentration of large excess anthracene ($k_2 = 6k_{\text{et}}$) to be $0.20 \text{ M}^{-1} \text{ s}^{-1}$ in TFE/MeCN ($v/v = 1:1$) at 273 K.

The mechanism of the oxidation of anthracene by **1** is proposed as follows: First, six-electron oxidation of anthracene by **1** proceeds via the rate-determining initial electron transfer from anthracene to **1**, affording anthracene radical cation and $[(\text{Bn-TPEN})\text{Mn}^{\text{III}}(\text{O})]^+$, as shown in Scheme 2 (reaction pathway a), followed by the further oxidation (pathways b – e). The Gibbs energy change of electron transfer (ΔG_{et}) is positive (0.41 eV judging from the one-electron oxidation potential of anthracene (1.19 V vs. SCE; SI, Figure S6) and the one-electron reduction potential of **1** (0.78 V vs. SCE).^[16] In such a case, no anthracene radical cation was observed during the reaction. In competition with the back electron transfer from $[(\text{Bn-TPEN})\text{Mn}^{\text{III}}(\text{O})]^+$ to anthracene radical cation, fast O^- transfer from $[\text{Mn}^{\text{III}}(\text{O})]^+$ to anthracene radical cation may occur to produce 9-hydroxyanthracene (the enol form; Scheme 2, reaction pathway b),^[23] which is known to be tautomerized to anthrone (the keto form; Scheme 2, reaction pathway c),^[24] and $[\text{Mn}^{\text{II}}]^{2+}$. Anthrone in equilibrium with 9-hydroxyanthracene is further oxidized via electron transfer from 9-hydroxyanthracene to $[\text{Mn}^{\text{IV}}(\text{O})]^{2+}$, followed by fast O^- transfer and intramolecular hydrogen atom transfer to produce anthrahydroquinone and $[\text{Mn}^{\text{II}}]^{2+}$ (Scheme 2, reaction pathway d). Anthrahydroquinone is further oxidized via electron transfer from anthrahydroquinone to $[\text{Mn}^{\text{IV}}(\text{O})]^{2+}$, followed by proton transfer and hydrogen atom transfer to produce anthraquinone, $[\text{Mn}^{\text{II}}]^{2+}$ and H_2O (Scheme 2, reaction pathway e). Anthrone (the initial two-electron oxidized product of anthracene) was also oxidized by four equivalents of **1** to produce anthraquinone. The rate constant of oxidation of anthrone by **1** in TFE/MeCN ($v/v = 1:1$) at 273 K was determined to be $6.0 \text{ M}^{-1} \text{ s}^{-1}$ (SI, Figure S5b). The k value of oxidation of anthrone by **1** is much larger than the k_2



Scheme 2. Proposed reaction mechanisms.

value of oxidation of anthracene by **1** ($0.20 \text{ M}^{-1} \text{ s}^{-1}$, vide supra). Thus, it was confirmed that the initial oxidation of anthracene to anthrone was the rate-determining step for the six-electron oxidation of anthracene by **1**.

It was confirmed that $[(\text{Bn-TPEN})\text{Mn}^{\text{II}}]^{2+}$ was rapidly oxidized by **1** to produce the Mn^{III} species (SI, Figure S2) via the μ -oxo dimer $[(\text{Mn}^{\text{III}}(\text{O})\text{Mn}^{\text{III}})]^{4+}$ complex (Scheme 2, reaction pathway f) as shown in Figure 5a. The rate of the bimolecular reaction of $[(\text{Bn-TPEN})\text{Mn}^{\text{II}}]^{2+}$ with equimolar **1** obeyed the second-order kinetics and the second-order plot (Figure 5b) afforded the second-order rate constant k_2 of $6.8 \text{ M}^{-1} \text{ s}^{-1}$ at 273 K. This value is larger than the k_2 value of electron transfer from anthracene to **1** (vide supra). In such a case, the overall stoichiometry is given by Eq. (1) although the initial product is $[(\text{Bn-TPEN})\text{Mn}^{\text{II}}]^{2+}$ (Scheme 2).

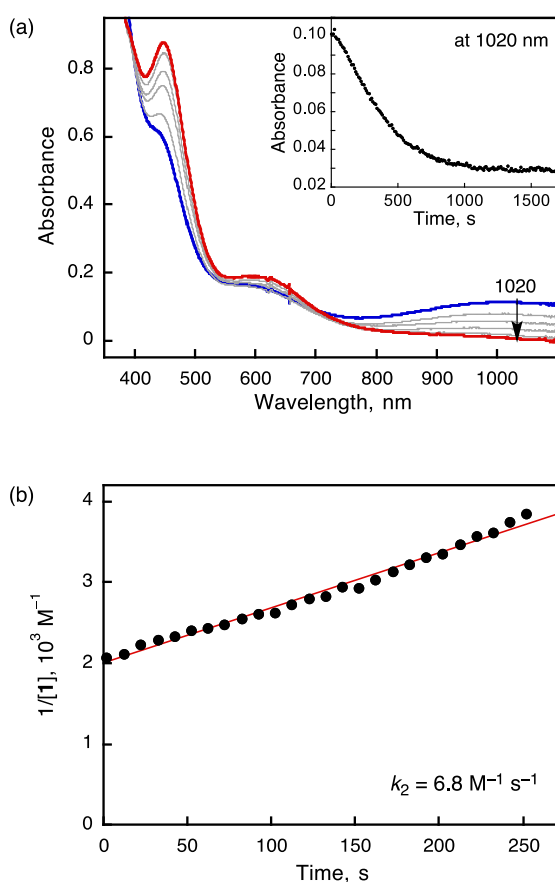


Figure 5. a) Visible spectral change observed in the reaction of $[(\text{Bn-TPEN})\text{Mn}^{\text{IV}}(\text{O})]^{2+}$ (**1**: blue line, 0.50 mM) with $[(\text{Bn-TPEN})\text{Mn}^{\text{II}}]^{2+}$ (0.50 mM) in TFE/MeCN ($v/v = 1:1$) at 273 K. Inset shows the time course of absorbance change monitored at 1020 nm due to the decay of **1**. b) Second-order plot of $1/[\text{1}]$ vs. time for the reaction of **1** (0.50 mM) with $[(\text{Bn-TPEN})\text{Mn}^{\text{II}}]^{2+}$ (0.50 mM) in TFE/MeCN ($v/v = 1:1$) at 273 K.

When anthracene was replaced by 9-methylanthracene ($E_{\text{ox}} = 1.10 \text{ V}$ vs. SCE; SI, Figure S7), four-electron oxidation of 9-methylanthracene occurred by four equivalents of **1** (SI, Figure S8), whereas in the case of 9,10-dimethylanthracene ($E_{\text{ox}} = 1.04 \text{ V}$ vs. SCE; SI, Figure S9), two-electron oxidation occurred by two equivalents of **1** (SI, Figure S10). The rate constants of electron transfer (k_{et}) from 9-methylanthracene and 9,10-dimethylanthracene were determined from slopes (k_2) of plots of k_1 vs. concentrations of 9-methylanthracene and 9,10-

Table 2. One-electron oxidation potentials (E_{ox}) of anthracene, 9-methylanthracene and 9,10-dimethylanthracene and second-order rate constants of electron transfer from anthracene derivatives to **1** and **2** in TFE/MeCN ($v/v = 1:1$) at 273 K.

substrate	E_{ox} , V vs. SCE	1 k_{et} , $\text{M}^{-1} \text{ s}^{-1}$	2 k_{et} , $\text{M}^{-1} \text{ s}^{-1}$
anthracene	1.19	0.20	5.2×10^4
9-methylanthracene	1.10	0.28	4.8×10^5
9,10-dimethylanthracene	1.04	6.1	8.3×10^5

^a The k_{et} values for the electron transfer from anthracene, 9-methylanthracene and 9,10-dimethylanthracene to **1** were obtained by dividing the second-order rate constants (k_2) by the numbers of electron for the multi-electron oxidation ($k_2 = 6k_{\text{et}}$ for anthracene, $k_2 = 4k_{\text{et}}$ for 9-methylanthracene and $k_2 = 2k_{\text{et}}$ for 9,10-dimethylanthracene, respectively).

dimethylanthracene as shown in SI, Figures S4b and S4c, respectively. It should be noted that $k_2 = 4k_{\text{et}}$ for 9-methylanthracene and $k_2 = 2k_{\text{et}}$ for 9,10-dimethylanthracene based on the stoichiometry mentioned above. The k_{et} values are listed in Table 2.

We have also investigated the reactions of **2**, $[(\text{Br-TPEN})\text{Mn}^{\text{IV}}(\text{O})-(\text{Sc}(\text{OTf})_3)_2]^{2+}$; $E_{\text{red}} = 1.36 \text{ V}$ vs. SCE,^[17] with anthracene and its derivatives. Since electron transfer from anthracene to **2** becomes exergonic ($\Delta G_{\text{et}} = -0.17 \text{ eV}$), electron transfer from anthracene to **2** occurred to produce anthracene radical cation, where the absorption band at 710 nm due to anthracene radical cation was clearly observed upon mixing anthracene and **2**, and then the anthracene radical cation decayed at fast rate (Figure 6).^[12,25,26] Since the decay rate constants in these cases increased with an increase in the anthracene concentration (SI, Figure S11), the rate constant of electron transfer (k_{et}) from anthracene to **2** was determined from the slope of the decay rate constants vs. concentration of anthracene.^[27] In contrast, electron transfer from 9,10-dimethylanthracene to **2** occurred to produce the corresponding radical cation, which is stable (Figure 7). In the case of 9,10-dimethylanthracene, the rate of formation of 9,10-dimethylanthracene radical cation was determined directly from the increase in absorbance at 660 nm due to the radical cation (Figure 7; SI, Figure S12). The rate of formation of 9-methyl-

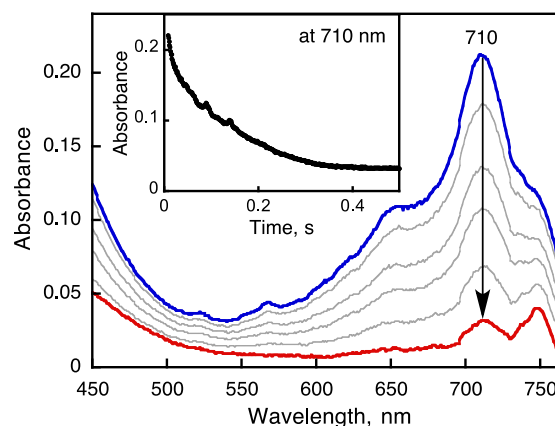


Figure 6. UV-visible absorption change in the six-electron oxidation of anthracene (0.10 mM) by six equivalents of **2** (0.60 mM) in TFE/MeCN ($v/v = 1:1$) at 273 K.

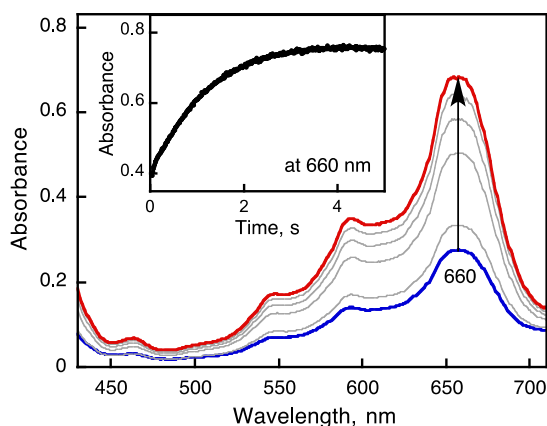


Figure 7. UV-visible absorption change in the two-electron oxidation of 9,10-dimethylantracene (0.10 mM) by **2** (0.10 mM) in TFE/MeCN ($v/v = 1:1$) at 273 K.

anthracene radical cation was also determined directly from the increase in absorbance at 685 nm due to the radical cation (SI, Figure S13). The rate constants of electron transfer (k_{et}) of **2** together with those of **1** are listed in Table 2. It was also confirmed that $[(\text{Bn-TPEN})\text{Mn}^{\text{II}}]^{2+}$ was rapidly oxidized by **2** to produce the μ -oxo dimer $[(\text{Mn}^{\text{III}}(\text{O})\text{Mn}^{\text{III}})]^{4+}$ complex (Scheme 2, reaction pathway *f*) with the second-order rate constant k_2 of $68 \text{ M}^{-1} \text{ s}^{-1}$ at 273 K as shown in SI, Figure S14.

The rate constants of outer-sphere electron-transfer reactions are fitted by the Marcus theory of electron transfer [Eq. (3)],

$$k_{et} = Z \exp[-(\lambda/4)(1 + \Delta G_{et}/\lambda)^2/k_B T] \quad (3)$$

where Z is the collision frequency taken as $1.0 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$, λ is the reorganization energy of electron transfer, k_B is the Boltzmann constant, and T is the absolute temperature.^[16,28]

The driving force dependence of k_{et} of electron transfer from one-electron reductants to **1** and **2** is well fitted by the blue line in Figure 8 using Eq. (3) with the λ value of 2.18 eV.^[17,29] The rate constants of electron transfer from anthracene derivatives to **1** and **2** are also plotted against $-\Delta G_{et}$ values in Figure 8 (red circles and triangles), where the driving force dependence is similar to that of outer-sphere electron transfer, although the λ value is somewhat smaller (1.70 eV) probably due to the small bond reorganization energy of anthracene derivatives which are delocalized π -compounds. The agreement of the observed rate constants with the Marcus line in Figure 8 (red line) indicates that the multi-electron oxidation of anthracene derivatives by both **1** and **2** proceeds via the rate-determining initial electron transfer from anthracene derivatives to **1** and **2**, followed by rapid further oxidation.

Conclusion

Six-electron oxidation of anthracene to anthraquinone by **1** proceeds via the rate-determining electron transfer from anthracene to **1**, followed by the subsequent fast oxidation reactions all the way to anthraquinone through the formation of anthrone and anthrahydroquinone as transient products. In the presence of Sc^{3+} ion, electron transfer from anthracene and its derivatives to **2** becomes exergonic to produce anthracene radical cations, which

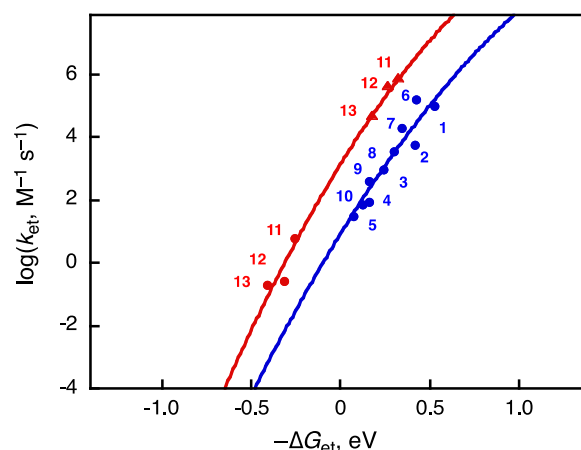


Figure 8. Driving force ($-\Delta G_{et}$) dependence of $\log k_{et}$ of electron transfer from ferrocene derivatives [(1) dimethylferrocene, (2) ferrocene, (3) bromoferrocene (4) acetylferrocene, (5) dibromoferrocene] to **1** and from coordinatively saturated metal complexes [(6) $[\text{Fe}^{\text{II}}(\text{Me}_2\text{phen})_3]^{2+}$, (7) $[\text{Fe}^{\text{II}}(\text{Ph}_2\text{phen})_3]^{2+}$, (8) $[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$, (9) $[\text{Fe}^{\text{II}}(5\text{-Clphen})_3]^{2+}$, and (10) $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$] to **2** (blue circles) and that of $\log k_{et}$ of electron transfer from anthracene derivatives [(11) 9,10-dimethylantracene, (12) 9-methylantracene, and (13) anthracene] to **1** (red circles) and **2** (red triangles) in TFE/MeCN ($v/v = 1:1$) at 273 K. The blue and red lines are drawn according to Eq. (3) with the λ values of 2.18 and 1.70 eV respectively.

were detected and decayed by a further oxidation by the Sc^{3+} ion-bound $\text{Mn}^{\text{IV}}(\text{O})$ complex. The rate constants of initial electron transfer from anthracene and its derivatives to both **1** and **2** fit well with those predicted by the Marcus theory of electron transfer. This study provides the first valuable mechanistic insight into multi-electron oxidation of substrates by high-valent metal-oxo complexes initiated by the rate-determining first electron transfer step.

Experimental Section

Materials

Commercially available chemicals were used without further purification unless otherwise indicated. Anthracene derivatives such as anthracene, anthrone, 9-methylantracene, 9,10-dimethylantracene, and scandium(III) triflate ($\text{Sc}(\text{CF}_3\text{SO}_3)_3$) were purchased from Aldrich Chemical Co. and used as received. Solvents were dried according to published procedures and distilled under Ar prior to use.^[31] Iodosylbenzene (PhIO) was prepared by literature method.^[32] Ligand (Bn-TPEN = *N*-benzyl-*N,N',N'*-tris(2-pyridylmethyl)-1,2-diaminoethane) and manganese(II) complex, $[\text{Mn}^{\text{II}}(\text{CF}_3\text{SO}_3)_2] \cdot 2\text{CH}_3\text{CN}$, were prepared by literature methods.^[33] The synthesis of $[(\text{Bn-TPEN})\text{Mn}^{\text{II}}]^{2+}$ was carried out in dry box. Bn-TPEN (0.47 mmol, 200 mg) and $[\text{Mn}^{\text{II}}(\text{CF}_3\text{SO}_3)_2] \cdot 2\text{CH}_3\text{CN}$ (0.57 mmol, 247 mg) were dissolved in CH_3CN and stirred at ambient temperature overnight. The resulting solution was filtered and added to a large volume of Et_2O . The product was obtained as a white solid in 85% yield (0.375 g). $[(\text{Bn-TPEN})\text{Mn}^{\text{IV}}(\text{O})]^{2+}$ was generated by the published method.^[34]

Instrumentation

UV-vis spectra were recorded on Hewlett Packard 8453 diode array spectrophotometer equipped with a UNISOKU Scientific Instruments Cryostat USP-203A for the reactions of $[(\text{Bn-TPEN})\text{Mn}^{\text{IV}}(\text{O})]^{2+}$.

TPEN) $\text{Mn}^{\text{IV}}(\text{O})]^{2+}$ (**1**) with substrates or with a UNISOKU RSP-601 stopped-flow spectrometer equipped with a MOS-type highly sensitive photodiode-array for the reactions of $[(\text{Bn-TPEN})\text{Mn}^{\text{IV}}(\text{O})-(\text{Sc}(\text{OTf})_3)_2]^{2+}$ (**2**) with substrates. Cold spray ionization (CSI) mass spectra were collected on a JMS-T100CS (JEOL) mass spectrometer equipped with a CSI source. Typical measurement conditions are as follows: needle voltage, 2.2 kV; orifice 1 current, 50 – 500 nA; orifice 1 voltage, 0 to 20 V; ring lens voltage, 10 V; ion source temperature, 5 °C; spray temperature, – 40 °C. Electrospray ionization mass spectra (ESI-MS) were collected on a Thermo Finnigan (San Jose, CA, USA) LCQTM Advantage MAX quadrupole ion trap instrument, by infusing samples directly into the source at 20 $\mu\text{L}/\text{min}$ using a syringe pump. The spray voltage was set at 4.7 kV and the capillary temperature at 120 °C. X-band electron paramagnetic resonance (EPR) spectra were taken at 77 K using a JEOL X-band spectrometer (JES-FA100). The experimental parameters for EPR measurements with a JES-FA100 were as follows: microwave frequency = 9.028 GHz, microwave power = 1.0 mW, modulation amplitude = 1.0 mT, modulation frequency = 100 kHz and time constant = 0.03 s. ^1H nuclear magnetic resonance (NMR) spectra were measured with a Bruker model digital AVANCE III 400 FT-NMR spectrometer. Product analysis was performed with an Agilent Technologies 6890N gas chromatograph (GC). Electrochemical measurements were performed on a CHI630B electrochemical analyzer in a trifluoroethanol (TFE) and acetonitrile (MeCN) mixture solvent ($v/v = 1:1$) containing 0.1 M $n\text{-Bu}_4\text{NPF}_6$ (TBAPF₆) as a supporting electrolyte at 298 K. A conventional three-electrode cell was used with a platinum working electrode (surface area of 0.3 mm^2), a platinum wire as a counter electrode and an $\text{Ag}/\text{Ag}(\text{NO}_3)$ (0.01 M) electrode as a reference electrode. The platinum working electrode (BAS) was routinely polished with BAS polishing alumina suspension and rinsed with acetone and acetonitrile before use. The measured potentials were recorded with respect to an Ag/AgNO_3 (0.01 M) reference electrode. All potentials (vs. Ag/Ag^+) were converted to values vs. SCE by adding 0.29 V.^[35] All electrochemical measurements were carried out under Ar atmosphere.

¹⁸O-labeled Experiments

$[(\text{Bn-TPEN})\text{Mn}^{\text{IV}}(^{18}\text{O})]^{2+}$ (**1-¹⁸O**) was prepared by adding Ph^{18}O (4 equiv), which was prepared by adding H_2^{18}O (98%, 10 μL) to Ph^{16}O solution (80 μL), to a TFE/MeCN ($v/v = 1:1$) solution of $[(\text{Bn-TPEN})\text{Mn}^{\text{II}}]^{2+}$ (2.0 mL) at 298 K. Product analysis of the reaction solution obtained in the oxidation of anthracene (0.10 mM) by **1-¹⁸O** (0.60 mM) in a TFE/MeCN ($v/v = 1:1$) solution was performed by CSI mass. A sodium cation is a background ion to improve ESI responses.

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[30] Abbreviations: Me₂phen = 4,7-dimethyl-1,10-phenanthroline, Ph₂phen = 4,7-diphenyl-1,10-phenanthroline, bpy = 2,2'-bipyridyl, and 5-Clphen = 5-chloro-1,10-phenanthroline

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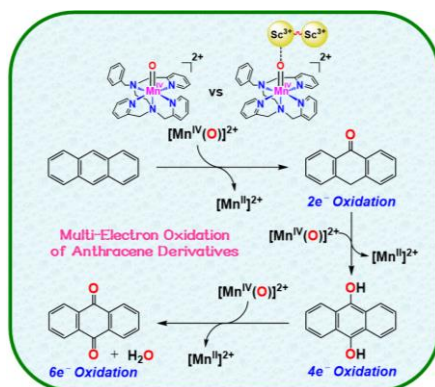
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