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Aromatic Hydroxylation of Anthracene Derivatives by a Chromium(III)-Superoxo Complex *via* Proton-Coupled Electron Transfer†

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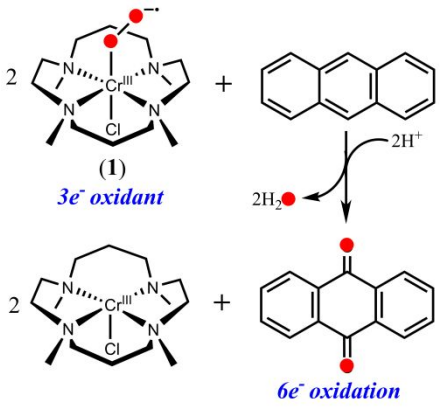
The chemistry of metal-superoxo intermediates started being unveiled in oxidation reactions by enzymes and their synthetic model compounds. However, aromatic hydroxylation reactions by the metal-superoxo species have yet to be demonstrated. In this study, we report for the first time that the hydroxylation of aromatic compounds such as anthracene and its derivatives by a mononuclear nonheme Cr(III)-superoxo complex, $[(Cl)(TMC)Cr^{III}(O_2)]^+$ (1), occurs in the presence of triflic acid (HOTf) *via* the rate-determining proton-coupled electron transfer (PCET) from anthracene to 1, followed by a fast further oxidation to give anthraquinone. The rate constants of electron transfer from anthracene derivatives to 1 in the presence of HOTf are well analyzed in light of the Marcus theory of electron transfer.

Metal-superoxo species have been proposed as the foremost intermediate generated during dioxygen activation process by the reduced metal centres in both heme and nonheme metalloenzymatic systems.[1-3] The intermediates have also been invoked as active oxidants in the C-H bond activation of organic substrates by nonheme enzymes containing iron (e.g., isopenicillin *N* synthase, *myo*-inositol oxygenase, 2-hydroxyethylphosphonate dioxygenase) and copper (e.g., dopamine β-monooxygenase, tyramine β-monooxygenase).[4] In succession to metal-superoxo species, metal-(hydro)peroxo and metal-oxo species are also proposed to be generated during substrate oxygenation *via* dioxygen activation in natural and model systems.[5-7] From the last few decades the high-valent metal-oxo species have been intensively investigated in a variety of oxidation reactions in heme and nonheme systems.[8] However, efforts have also been made by the bioinorganic and biomimetic communities recently to explore the chemistry of metal-superoxo intermediates. Thus, successful isolation and characterization of a number of metal-superoxo intermediates have been achieved in model systems[9] and their reactivity studies have been examined towards electrophilic hydrogen atom transfer (HAT), oxygen atom transfer (OAT), hydride transfer and nucleophilic aldehyde deformylation reactions.[10] It has also been reported very recently that chemical properties of the metal-superoxo species can be tuned by the presence of acid.[11] Although advances have been made in understanding reactivities of metal-superoxo species, their chemical properties still need to be fully explored and yet to be understood in broad aspects.



Scheme 1 Schematic representation of oxidation of anthracene by $[(Cl)(TMC)Cr^{III}(O_2)]^+$ (**1**) in the presence of triflic acid (HOTf).

Aromatic hydroxylation has been described as one of the most challenging chemical processes mediated by many metalloenzymes, including cytochromes P450 and nonheme iron mono- and dioxygenases for biotransformations of pharmaceuticals and other xenobiotics, and high-valent oxoiron(IV) species have been invoked as active oxidants in the aromatic hydroxylation reactions.[12] In biomimetic studies, high-valent metal-oxo species have shown reactivities in the aromatic hydroxylation reactions, and their mechanistic studies have also been investigated through a combined experimental and theoretical approach.[13] However, to the best of our knowledge, no report is available for a metal-superoxo species capable of hydroxylating aromatic compounds in both heme and nonheme systems.

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† Electronic Supplementary Information (ESI) available: Detailed experimental procedures, Tables S1 and S2, and Fig. S1-S10. See DOI: 10.1039/x0xx00000x

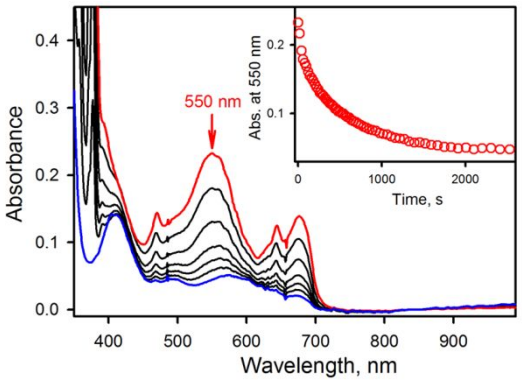


Fig. 1 UV-vis spectral changes observed in the 6-electron oxidation of anthracene (0.50 mM) by **1** (1.0 mM) in the presence of HOTf (1.0 mM) in MeCN at 233 K. The inset shows the time profile monitored at 550 nm due to the decay of **1**.

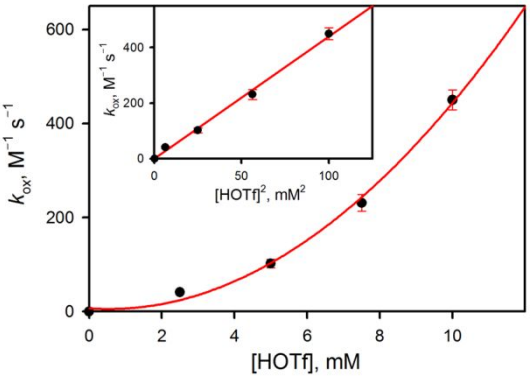


Fig. 2 Dependence of k_{ox} on [HOTf] for the oxidation of anthracene (0.50 mM) by **1** (0.50 mM) in the presence of HOTf (0–10 mM) at 233 K. Inset shows the plot of k_{ox} *vs*. [HOTf]^2.

In biomimetic studies, a Cr(III)-superoxo complex, $[(Cl)(TMC)Cr^{III}(O_2)]^+$ (**1**; TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane), was successfully synthesized and characterized spectroscopically and structurally. In addition, its reactivities towards hydrogen atom transfer (HAT), oxygen atom transfer (OAT) and hydride transfer reactions were reported as well.[14] Very recently, it was also shown that the reactivity of **1** was remarkably enhanced towards OAT reactions in the presence of triflic acid (HOTf).[11] Such a remarkable enhancement of reaction rate in OAT reaction by **1** in the presence of HOTf was explained due to the much more positive shift of one-electron reduction potential of **1** (E_{red} = 1.12 V *vs*. SCE) in the presence of HOTf (2.5 mM). As our ongoing efforts to elucidate detailed mechanistic insights of **1** into oxidation reactions, we have performed the reactivity study of **1** towards hydroxylation of aromatic compounds in the presence of HOTf. **1**, which was reported as a three-electron oxidant for the oxidation of NADH analogue,[14c] can perform six-electron oxidation of anthracene to produce anthraquinone in the presence of HOTf under stoichiometric conditions in acetonitrile (MeCN) at 233 K. The mechanism of the proton-assisted hydroxylation of anthracene and its derivatives by **1** is clarified by comparison with the proton-coupled electron-transfer (PCET) reaction of **1** with one-electron donors in light of the Marcus theory of electron transfer. Thus, we believe that the present study provides a new scope to expand the reactivity of metal-superoxo species with HOTf as a hydroxylating agent of aromatic compounds.

Notably, the oxidation of anthracene by **1** does not occur in the absence of acid (*i.e.*, HOTf) in MeCN at 233 K (Fig. S1, ESI†). However, anthracene was fully oxidized (6-electron oxidation) by two equivalents of **1** (3-electron oxidant) in the presence of two equivalents of HOTf as shown in Fig. 1 (see also Scheme 1). The stoichiometry of the reaction was confirmed by UV-vis spectral titration experiments following the decay of absorption band at λ_{max} = 550 nm due to **1** upon addition of anthracene in the presence of HOTf in MeCN at 233 K (Fig S2, ESI†).

The product analysis after the reaction was performed by ^{1}H-NMR and GC-MS measurements, resulting that anthraquinone as six-electron oxidized product of anthracene was produced (Fig. S3 for NMR and Fig. S4 for GC-MS, ESI†). The yield of anthraquinone was found to be ~100% as analyzed with ^{1}H-NMR using cyclohexane as an internal reference. The source of oxygen in the anthraquinone product was confirmed by ^{18}O-labeling experiment.

When the product obtained in the oxidation of anthracene by **1**-$^{16}O_2$ ($[(Cl)(TMC)Cr^{III}(^{16}O_2)]^+$) in the presence of HOTf in MeCN at 233 K was compared with that obtained in the oxidation of anthracene by **1**-$^{18}O_2$ ($[(Cl)(TMC)Cr^{III}(^{18}O_2)]^+$) in the presence of HOTf, peak at *m/z* = 208 for anthraquinone-^{16}O,^{16}O in GC-MS spectrum shifted to *m/z* = 212 for anthraquinone-^{18}O,^{18}O (Fig. S4 for GC-MS, ESI†), indicating that two oxygen atoms in anthraquinone originated from **1**. In addition, product analysis by CSI-MS and EPR measurements revealed that chromium(III) complex, $[Cr^{III}(TMC)]^{3+}$ (**2**), was produced as the final inorganic product (Fig. S5, ESI†).

The kinetic measurements of the anthracene oxidation by **1** were performed by following the decay of absorbance at 550 nm due to **1** in the presence of HOTf (2.5 mM) in MeCN at 233 K. The decay rate of **1** in the oxidation of anthracene by **1** is given by eqn (1). According to the stoichiometry of the six-electron oxidation of anthracene by **1** (Scheme 1), the initial concentrations of **1**. ($[Cr^{III}(O_2)]_0$) and anthracene ($[An]_0$) are given by eqns (2) and (3), respectively. Then, eqn (1) is rewritten by eqn (4).

$$-d[Cr^{III}(O_2)]/dt = k_{ox}[Cr^{III}(O_2)][An] \quad (1)$$

$$[Cr^{III}(O_2)]_0 = [Cr^{III}(O_2)] + [Cr^{III}] \quad (2)$$

$$[An]_0 = [An] + 2[Cr^{III}] \quad (3)$$

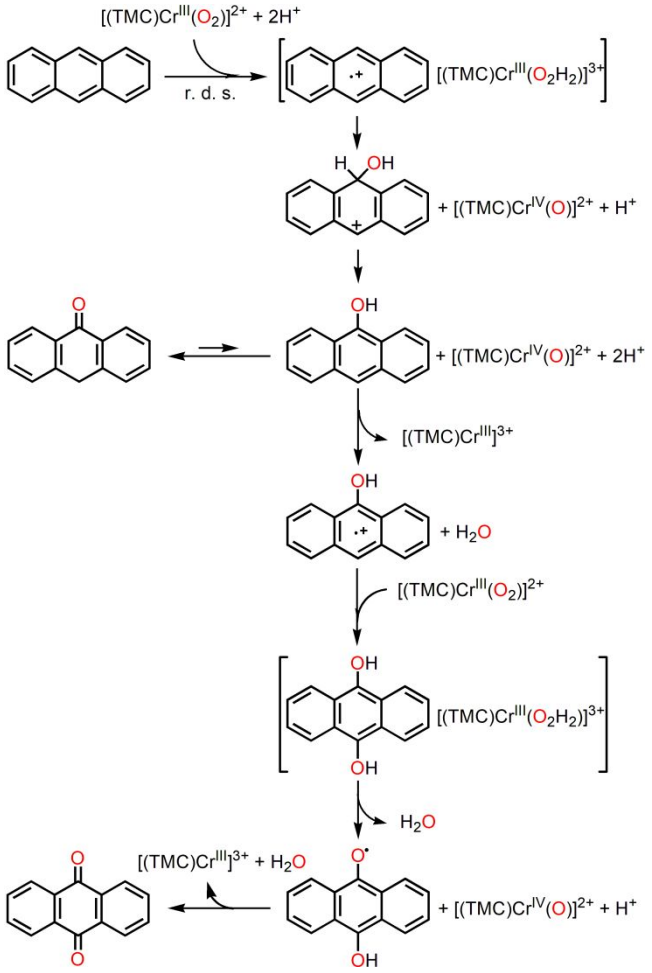
$$-d[Cr^{III}(O_2)]/dt = k_{ox}[Cr^{III}(O_2)]([An]_0 - 2[Cr^{III}(O_2)]_0 + 2[Cr^{III}(O_2)]) \quad (4)$$

Solving the differential eqn (4) with eqns (2) and (3) gives eqn (5)

$$\log[x/(C + 2x)] = -(C/2.3)k_{ox}t + \log[x_0/(C + 2x_0)] \quad (5)$$

where $x = [Cr^{III}(O_2)]$, $x_0 = [Cr^{III}(O_2)]_0$, $C = [An]_0 - 2[Cr^{III}(O_2)]_0$, $x_0/(C + 2x_0) = 1$. Thus, plot of $\log[x/(C + 2x)]$ *vs*. *t* gives a straight line that passes through zero with slope = $-(C/2.3)k_{ox}$, where C is $-x_0$. The k_{ox} value of the oxidation of anthracene by **1** in the presence of HOTf (2.5 mM) in MeCN at 233 K was determined by using eqn (5) to be 41(4) M^{-1} s^{-1} (Fig. S6 and Table S1, ESI†).

When anthracene was replaced by deuterated anthracene (anthracene-d_{10}), no kinetic isotope effect (KIE) was observed (Fig. S6, ESI†), suggesting that no C-H bond cleavage is involved in the rate-determining step. The reactivity of **1** towards oxidation of anthracene was further investigated varying HOTf concentration (Fig. S7, ESI†). The k_{ox} value of the oxidation of anthracene by **1** increased



Scheme 2. Plausible reaction mechanism.

with an increase in HOTf concentration (Fig. S8 and Table S1, ESI†), exhibiting second-order dependence with respect to HOTf concentration as shown in Fig. 2 [eqn (6)].[15]

$$k_{ox} = k_2[\text{HOTf}]^2 \quad (6)$$

Based on the results described above, the plausible mechanism of aromatic hydroxylation of anthracene by **1** in the presence of HOTf in MeCN at 233 K is shown in Scheme 2, where six-electron oxidation of anthracene by **1** in the presence of HOTf proceeds through the rate determining initial electron transfer from anthracene to **1** to produce anthracene radical cation and $[Cr^{III}(TMC)(O_2H_2)]^{3+}$. Although the intermediates after the rate-determining step (r. d. s.) cannot be observed, the initial electron-transfer step may be followed by further oxidation of anthracene radical cation to generate 9-hydroxyanthracene and $[Cr^{IV}(TMC)(O)]^{2+}$ with the elimination of two protons. 9-Hydroxyanthracene is known to be tautomerized to anthrone,[16] which is further oxidized by an electron transfer to the generated $[Cr^{IV}(TMC)(O)]^{2+}$ in the presence of two protons to produce 9-hydroxyanthracene radical cation and a $[Cr^{III}(TMC)]^{3+}$ species.[17] Further electron transfer takes place from 9-hydroxyanthracene radical cation to another molecule of **1** in the presence of water to generate 9,10-dihydroxyanthracene and $[Cr^{III}(TMC)(O_2H_2)]^{3+}$. In the final step, anthraquinone is produced by stepwise electron transfer and

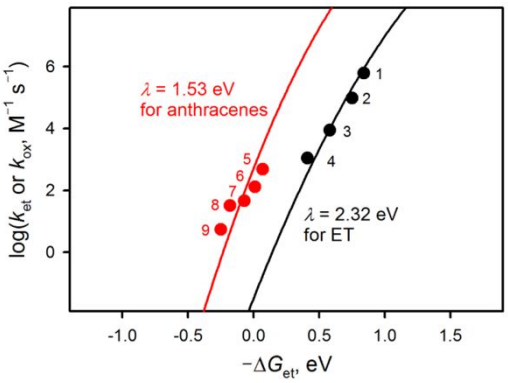


Fig. 3 Driving force ($-\Delta G_{et}$) dependence of rate constants (log k_{et} or log k_{ox}) of electron transfer from ferrocene derivatives (black circles; (1) 1,1′-dimethylferrocene, (2) ferrocene, (3) bromoferrocene, (4) 1,1′-dibromoferrocene) and from anthracene derivatives (red circles; (5) 9,10-dimethylanthracene, (6) 9-methylanthracene, (7) anthracene (8) 9-bromoanthracene and (9) 9-anthracenecarboxaldehyde) to **1** in the presence of HOTf (2.5 mM) at 233 K. The red and black lines are Marcus lines calculated with λ values of 1.53 and 2.32 eV, respectively.

proton transfer from 9,10-dihydroxyanthracene to $[Cr^{III}(TMC)(O_2H_2)]^{3+}$ to finally produce **2**, accompanied by the elimination of water.

The kinetic measurements for the oxidation of 9-substituted anthracene derivatives (XAn), such as 9-methylanthracene, 9-bromoanthracene and 9-anthracenecarboxaldehyde, were also examined in the presence of HOTf (2.5 mM) in MeCN at 233 K. According to the stoichiometry of the four-electron oxidation of XAn by **1** (3-electron oxidant), the kinetic equations are derived to determine the second-order rate constant (k_{ox}) (see Experimental Section in ESI†; Determination of k_{ox} value for the four-electron oxidation of substrate by 3-electron oxidant). The k_{ox} values of the four-electron oxidation of XAn by **1** were determined by using eqn (S5) in ESI† (see also Fig. S10 and Table S2, ESI†).

The kinetic measurements for the oxidation of 9,10-dimethylanthracene were also performed in the presence of HOTf (2.5 mM) in MeCN at 233 K. The second-order rate constants (k_{ox}) for the two-electron oxidation of 9,10-dimethylanthracene by **1** (3-electron oxidant) was determined by using eqn (S10) in ESI† (see Experimental Section in ESI†; Determination of k_{ox} value for the two-electron oxidation of substrate by 3-electron oxidant; Fig. S11 and Table S2, ESI†).

The rate constants of proton assisted hydroxylation of anthracene and its derivatives by **1** is then compared with the rate constants of outer-sphere electron-transfer reactions as explained by the Marcus theory of electron transfer [eqn (7)],[18]

$$k_{et} = Z\exp[-(\lambda/4)(1 + \Delta G_{et}/\lambda)^2/(k_B T)] \quad (7)$$

where Z is the collision frequency which is normally taken as 1×10^{11} M^{-1} s^{-1}, which corresponds to $k_B TK/h$ (k_B is the Boltzmann constant, T is the absolute temperature, K (= ~0.020 M^{-1})[18] is the formation constant of the precursor complex, and h is the Planck constant), λ is the reorganization energy of electron transfer and ΔG_{et} is the free energy change of electron transfer. The driving force ($-\Delta G_{et}$) values were determined from the difference between the one-electron oxidation potentials (E_{ox}) of electron donors and the one-electron

reduction potential of **1** (E_{red} = 1.12 V *vs.* SCE) in the presence of HOTf (2.5 mM), as given by eqn (8), where *e* is the elementary charge.

$$-\Delta G_{et} = e(E_{red} - E_{ox}) \quad (8)$$

The driving force dependence of logarithm of the rate constants of outer-sphere electron transfer (k_{et}) from one-electron donors (*i.e.*, ferrocene derivatives) to **1** in the presence of HOTf (2.5 mM) in MeCN at 233 K is shown in Figure 3 (black circles), where the log k_{et} values[11] are plotted against the $-\Delta G_{et}$ values. The driving force dependence of k_{et} is well fitted by the black line in Figure 3 using eqn (7) with the λ value of 2.32 eV.[11] The rate constants of electron transfer from anthracene derivatives (k_{ox}) to **1** are also plotted against $-\Delta G_{et}$ values in Figure 3 (red circles), where the driving force dependence of k_{ox} is fitted with somewhat smaller reorganization energy of λ = 1.53 eV (red line in Fig. 3). The smaller λ value for the case of anthracene derivatives in the Marcus plot compared with that of outer-sphere electron transfer from one-electron donors (*i.e.*, ferrocene derivatives) to **1** may be accounted by much faster electron exchange between 9,10-dimethylanthracene and 9,10-dimethylanthracene radical cation (5.0×10^8 M^{-1} s^{-1})[18a] compared to that between ferrocene and ferrocenium cation (5.3×10^6 M^{-1} s^{-1}) in MeCN[18b] and small bond reorganization energy of anthracene derivatives, which are delocalized π-compounds.[12c]

In conclusion, aromatic hydroxylation of anthracene by **1** has been made possible in the presence of HOTf to produce anthraquinone, which is the fully oxidized (six-electron oxidation) product of anthracene. The reaction proceeds *via* the rate-determining PCET from anthracene to **1**, followed by the subsequent fast oxidation reactions all the way to anthraquinone. In addition, no KIE (*i.e.*, KIE = 1) also suggests no involvement of C-H bond cleavage in the rate-determining step, which is PCET. The rates of PCET from anthracene derivatives to **1** were evaluated in comparison with the outer-sphere electron-transfer reactions from one-electron donors to **1** in the presence of HOTf in light of the Marcus theory of electron transfer. This study provides valuable mechanistic insight into the hydroxylation of aromatic substrates by metal-superoxo species *via* the rate-limiting PCET process.

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17 It should be noted that, in the oxidation of anthracene by $[Cr^{IV}(TMC)(O)]^{2+}$ in the presence of HOTf at 233K, almost no reaction occurred (see Fig. S9, ESI†), indicating that Cr(III)-superoxo complex (**1**) is the actual reactive intermediate for the oxidation of anthracene.

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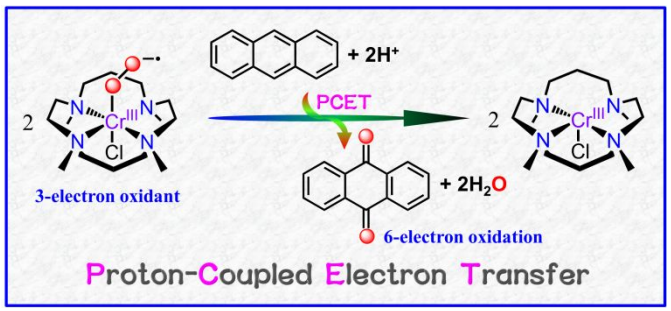
Table of Contents Graphic



Aromatic hydroxylation of anthracene by a mononuclear nonheme Cr(III)-superoxo complex proceeds *via* the rate-determining proton-coupled electron transfer, followed by fast further oxidation to anthraquinone.