

Communication

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Remarkable Acid Catalysis in Proton-Coupled Electron-Transfer Reactions of a Chromium(III)-Superoxo Complex

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Supporting Information Placeholder

ABSTRACT: Much enhanced acid catalysis was observed in oxygen atom transfer (OAT) reactions by a mononuclear nonheme Cr(III)superoxo complex, $[(Cl)(TMC)Cr^{III}(O_2)]^+$ (1), in the presence of triflic acid. In the acid-catalyzed reactions, the reactivity of 1 in OAT of thioanisole was enhanced significantly, showing more than 10⁴fold acceleration in rate. Electron transfer (ET) from electron donors to 1 also occurred only in the presence of HOTf. The enhanced reactivity of 1 by HOTf was explained by proton-coupled electron transfer (PCET) from electron donors, such as ferrocene, to 1 in light of the Marcus theory of ET. The present study reports for the first time the dramatic proton effect on the chemical properties of metal-superoxo species.

Mononuclear nonheme metal-superoxo species have been invoked as key intermediates in various biological reactions, such as in nonheme iron (e.g., isopenicillin *N* synthase, *myo*-inositol oxygenase, and cysteine dioxygenase) and copper (e.g., dopamine β -monooxygenase and peptidylglycine-*a*-amidating monooxygenase) enzymes.¹ Many metal-superoxo complexes have been successfully synthesized and characterized structurally and/or spectroscopically in biomimetic studies, and their reactivities have been explored in OAT and hydrogen atom transfer (HAT) reactions.²⁻⁵ In addition, metal-superoxo complexes have been proposed as key intermediates in superoxide reduction by biomimetic compounds of superoxide dismutases.⁶ However, chemical properties of the metal-superoxo species have been less clearly understood and still remain elusive in many aspects.

Acids play important roles in PCET reactions in biological redox reactions, such as the four-electron reduction of dioxygen in respiration and the four-electron oxidation of water in Photosystem II.⁷ The reactivity of high-valent metal-oxo complexes in OAT, HAT, and ET reactions is also markedly influenced by addition of external protons.^{8,9} However, such a proton effect has never been explored in metal-superoxo species. As our ongoing efforts in elucidating the chemical properties of metal-superoxo species and the proton effect on the reactivity of metal-oxygen intermediates, we have investigated the proton effect in oxidation reactions by metal-superoxo species. In this communication, we report a remarkable acid catalysis in the sulfoxidation of thioanisoles by a mononuclear nonheme Cr(III)-superoxo complex, $[(Cl)(TMC)Cr^{III}(O_2)]^+$ (1, TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane),⁴ with CF₃SO₃H (HOTf). We also report that ET from electron donors to

1 occurs only with HOTf and that the PCET reaction of 1 was much accelerated by protons. The mechanism of the acid-catalyzed sulfoxidation of thioanisoles by 1 is clarified by comparison with PCET from electron donors to 1. To the best of our knowledge, the present study reports the first example showing a much enhanced acid catalysis on the reactivity of metal-superoxo species in OAT and ET reactions via PCET.

The Cr(III)-superoxo complex (1) was prepared and characterized as reported previousy.^{4a} **1** was reported to react with thioanisole slowly in acetonitrile (MeCN) at 263 K with the second-order rate constant (k_{ox}) of 5.2 × 10⁻³ M⁻¹ s⁻¹.^{4b} However, the sulfoxidation of thioanisole by 1 has hardly occurred at a lower temperature (e.g., 233 K) (Figure 1a). Interestingly, upon addition of one equiv of HOTf to an MeCN solution containing 1 and thioanisole at 233 K, the absorption bands at 550 and 675 nm due to 1 disappeared, accompanied by the formation of a Cr(IV)-oxo complex, $[(Cl)(TMC)Cr^{IV}(O)]^+$ (2),^{4b} with the absorption bands at 605 nm and 960 nm (Figure 1b). The decay of 1 obeyed the first-order kinetics, and the pseudo-first-order rate constant increased linearly with increasing thioanisole concentration to give the second-order rate constant (k_{ox}) of 3.5(3) M⁻¹ s⁻¹ at 233 K (Figure S1). Although the oxidation of thioanisole by 1 occurred extremely slowly without HOTf at 233 K (vide supra), the k_{ox} value was determined to be 3.6 \times 10^{-4} $M^{\mbox{--}1}$ s^{-1} at 233 K, using large concentrations of thioanisole (Figure S2). The k_{ox} value of 1 toward thioanisole was 10⁴-fold larger with HOTf at 233 K. Product analysis of the reaction solution revealed formation of PhS(O)Me quantitatively (SI, Experimental



Figure 1. UV-visible spectral changes observed in the sulfoxidation of thioanisole (10 mM) by 1 (1.0 mM) in the (a) absence and (b) presence of HOTf (1.0 mM) in MeCN at 233 K. The insets show the time profile at 550 nm to monitor the decay of 1.

Section). In addition, the oxygen source in PhS(O)Me and **2** was confirmed to be **1** by performing ¹⁸O-labeled experiments with $[(Cl)(TMC)Cr^{II}(^{18}O_2)]^+$, in which ¹⁸O was found in the PhS(¹⁸O)Me and $[(Cl)(TMC)Cr^{IV}(^{18}O)]^+$ products (Figures S3 and S4) (eq 1). It should be noted that HOTf acts as an efficient cat-

SMe + [(Cl)(TMC)Cr^{III}(O₂)]⁺

$$-S-Me + [(Cl)(TMC)CrIV(O)]^+$$
 (1)

alyst without being consumed in eq 1. It should be also noted that the absorption spectrum of 1 remained the same upon addition of HOTf (Figure S5), indicating that no protonation on the superoxo moiety in 1 occurs by $HOTf^{10}$

As shown in Figure 2 (see also Table S1), the k_{ox} value increased with increasing [HOTf], being proportional to [HOTf]² (eq 2).

$$k_{\rm ox} = k_2 [\rm HOTf]^2 \tag{2}$$

The k_{ox} values of *para*-substituted thioanisoles (X = MeO, Me, H,Cl, and Br) were determined as listed in Table S2 (see also Figures S6 and S7).

The much enhancement of the reactivity of **1** was also observed in ET from electron donors to **1** with HOTf. No ET from $[Fe^{II}(bpy)_3]^{2+}(E_{ox} = 1.06 \text{ V vs SCE})$ to **1** occurred without HOTf, as expected from E_{red} of **1** (-0.52 V vs SCE).¹¹ In the presence of HOTf, however, PCET from $[Fe^{II}(bpy)_3]^{2+}$ to **1** occurred to produce $[Fe^{III}(bpy)_3]^{3+}$ and $[(CI)(TMC)Cr^{III}(H_2O_2)]^{2+}$ (**3**), which is in equilibrium (eq 3; Figure S8),¹² as indicated by the redox titrations

$$[Fe(bpy)_3]^{2+} + [(CI)(TMC)Cr^{III}(O_2)]^+ + 2H^+ \swarrow K_{et}$$
$$[Fe(bpy)_3]^{3+} + [(CI)(TMC)Cr^{III}(H_2O_2)]^{2+} (3)$$

in Figure 3, where $[[Fe^{II}(bpy)_3]^{2+}]$ decreased with increasing [HOTf] (Figure S9). The ET equilibrium constants (K_{et}) in eq 3 were determined by global fitting of plots in Figure 3, where $K_{et} = K_{et}^{0}[H^+]^2$. The E_{red} values of **1** at various concentrations of HOTf (Figure 3, inset) were also determined from the K_{et} values (Table S3) and the E_{ox} value of $[Fe^{II}(bpy)_3]^{2+}$ using the Nernst equation (eq 4).⁸

$$E_{\rm red} = E_{\rm ox} + (2.3RT/F)\log K_{\rm et} \tag{4}$$

The dependence of E_{red} of **1** on $[\text{H}^+]$ is given by the Nernst equation (eq 5; see SI for the derivation of eq 5).⁸

$$E_{\rm red} = E_{\rm red}^0 + (2.3RT/F)\log(1 + K_{\rm red}[{\rm H}^+]^2)$$
(5)

where K_{red} is the equilibrium constant of the diprotonation in **3**. A plot of E_{red} vs log([HOTf]) is shown in Figure 3 (inset), exhibiting a linear correlation with a slope of 93 mV/log([HOTf]), which indicates that the ET reduction of **1** is accompanied by binding of two



Figure 2. Dependence of k_{ox} on [HOTf] for the sulfoxidation of *para*-MeO-thioanisole (0.50 mM) by **1** (0.50 mM) with HOTf (0–3.0 mM) at 233 K. Inset shows plot of k_{ox} vs [HOTf]².

H⁺ ions in **3**, agreeing with $2 \times (2.3RT/F)$ at 233 K = 93 mV/log([HOTf]) (eq 5). The *E*_{red} value of **1** is positively shifted from -0.52 V vs SCE without HOTf to 1.12 V vs SCE with HOTf (2.5 mM), because the ET reduction of **1** occurs at the ligand center to produce **3**¹¹ in which two protons are bound.

The diprotonation in **3** in the presence of HOTf is also supported by the kinetic measurements (vide infra). The PCET rate constants from $[Fe^{II}(bpy)_3]^{2+}$ to **1** were determined by monitoring the decrease in absorbance at 520 nm due to $[Fe^{II}(bpy)_3]^{2+}$ (Table S4 and Figure S10). The second-order rate constants (k_{et}) increased with increasing [HOTf], being proportional to $[HOTf]^2$ (Table S5 and Figure S11), as observed in the sulfoxidation of *para*-MeO-thioanisole by **1** with HOTf (eq 2; Figure 2).

Rate constants of ET from ferrocene derivatives to **1** were also determined (Table S4 and Figures S12 and S13). From the spectral titration experiments, the ET stoichiometry was established as given by eq 3, where ET from Fc to **1** occurs with the 1:1 stoichiometry and two protons are required for the PCET reaction (Figure S14). The formation of Cr^{III} -species was confirmed with cold-spray ionization mass spectrometer and EPR (Figure S15). The yield of **3** was determined to be 86(5)% by the iodometric titration (Figure S16).

The deuterium kinetic isotope effect (KIE) was also examined by comparing the $k_{\rm et}$ value of ET from 1,1'-dibromoferrocene to **1** with HOTf (2.5 mM) and that with DOTf (2.5 mM) (Figure S17). The KIE value observed for the PCET reaction was 0.85. Such an inverse KIE in the PCET reaction with HOTf vs DOTf was also reported for PCET from toluene to an iron(IV)-oxo complex with HOTf vs DOTf, showing sharp contrast to the large KIE (31) in concerted PCET from toluene and toluene- d_8 to an iron(IV)-oxo complex without acid.¹³

The rate constants (k_{et}) of ET from the one-electron donors to **1** are also evaluated in light of the Marcus theory of adiabatic ET as given by eq 6,

$$k_{\rm et} = Z \exp\left[-(\lambda/4)(1 + \Delta G/\lambda)^2/k_{\rm B}T\right]$$
(6)

where Z is the frequency factor that is taken as $10^{11} \text{ M}^{-1} \text{ s}^{-1}$, (= $k_{\text{B}} TK/h$; k_{B} is the Boltzmann constant, T is the absolute temperature, K is the formation constant of the precursor complex, and h is the Planck constant), ΔG_{et} is the ET free energy change, and λ is the ET reorganization energy.¹⁴ The driving force dependence of k_{et} is shown in Figure 4, where log k_{et} values of ET from electron donors to **1** with HOTf (2.5 mM) at 233 K are plotted against the driving force ($-\Delta G_{\text{et}}$) of PCET. The $-\Delta G_{\text{et}}$ values were determined from E_{ox} of electron donors and E_{red} of **1** with HOTf, as given by eq 7,



Figure 3. Spectroscopic redox titrations at 520 nm for the decrease in $[[Fe^{II}(bpy)_3]^{2+}]$ as a function of the initial concentration of **1** added to an MeCN solution of $[Fe^{II}(bpy)_3]^{2+}$ and HOTf (blue circles, 1.5 mM; black circles, 2.5 mM; red circles, 3.0 mM) at 233 K. Inset shows the dependence of E_{red} of **1** on log([HOTf]).

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

(7)

where *e* is the elementary charge. The $-\Delta G_{\rm et}$ dependence of $k_{\rm et}$ of PCET from ferrocene derivatives to **1** with HOTf (2.5 mM) is well fitted by using the Marcus equation (eq 6) with the best fit λ value of 2.32 eV, whereas the $k_{\rm et}$ values of PCET from $[{\rm Fe^{II}L_3}]^{2+}$ to **1** are fitted using the somewhat smaller λ value of 1.93 eV due to the smaller reorganization energy of the electron-self exchange between $[{\rm Fe^{II}L_1}]^{2+}$ and $[{\rm Fe^{II}L_1}^{3+}$, as compared with that between Fc and Fc⁺.¹⁵

The plot of log k_{ox} for the acid-catalyzed sulfoxidation of thioanisole derivatives by **1** with HOTf (2.5 mM) at 233 K vs $-\Delta G_{et}$ is also fitted by using eq 6 with the significantly smaller λ value of 1.30 eV (red line in Figure 4). The much larger k_{ox} values than those expected from outer-sphere ET may result from the much larger *K* values of the precursor complexes, because the stronger interaction of **1** is expected with organic substrates as compared with that of $[Fe^{II}L_3]^{2+}$ (vide infra).¹⁴

The dependence of $k_{\rm f}$ of the oxidation of thioanisole (S) by **1** with HOTf (1.0 and 2.5 mM) on [S] at 233 K exhibits a saturation behavior (Figure S18), as expressed by eq 8, resulting from the formation of the precursor complex (K) prior to ET ($k_{\rm ET}$). The $k_{\rm ET}$ and K values are obtained from the intercept and the slope of the linear plot of $k_{\rm f}^{-1}$ vs [S]⁻¹ (eq 8).

$$k_{\rm f}^{-1} = (k_{\rm ET}K)^{-1} [S]^{-1} + k_{\rm ET}^{-1}$$
(8)

The average *K* value in Figure S18 is determined to be 76(4) M^{-1} , which is much larger than the value (0.021 M^{-1} at 233 K) normally used for outer-sphere ET. The difference in the log *K* values between thioanisole and $[Fe^{II}L_3]^{2+}$ is 3.5, which agrees with the observed difference (3.5) between the log k_{ox} value of thioanisole (no. 11, red line) and the log k_{et} value (blue line) in Figure 4. Such an agreement indicates that the acid-catalyzed sulfoxidation of thioanisole by 1 proceeds via rate-determining PCET from thioanisole to 1 through the precursor complex with $[(Cl)(TMC)Cr^{III}(O_2)]^{+}$ - $(H^+)_2$,¹⁶ followed by the O–O bond cleavage by thioanisole radical cation to produce the sulfoxide and the $Cr^{IV}(O)$ complex via the O⁻⁻ transfer and releasing two protons (Scheme 1). The ET reactivity of 1 binding two protons are consumed or produced in the overall reaction.



Figure 4. The $-\Delta G_{et}$ dependence of log k_{et} or log k_{ox} of PCET from ferrocene derivatives [(1) 1,1'-dimethylferrocene, (2) ferrocene, (3) bromoferrocene, (4) 1,1'-dibromoferrocene], [Fe^{II}L₃]²⁺ complexes [(5) [Fe^{II}(Me₂bpy)₃]²⁺, (6) [Fe^{II}(Ph₂phen)₃]²⁺, (7) [Fe^{II}(bpy)₃]²⁺, (8) [Fe^{II}(phen)₃]²⁺] and thioanisole derivatives [(9) *para*-MeO-thioanisole, (10) *para*-Me-thioanisole, (11) thioanisole, (12) *para*-Cl-thioanisole, (13) *para*-Br-thioanisole] to 1 with HOTf (2.5 mM) at 233 K. The red, blue, and black lines are Marcus lines calculated with λ values of 1.30, 1.93, and 2.32 eV, respectively.

Scheme 1. Proposed Mechanism of the Acid-Catalyzed Sulfoxidation of *p*-Methoxythioanisole by 1



In conclusion, a remarkable acid catalysis was observed in the sulfoxidation of thioanisole by a Cr(III)-superoxo complex (1) with HOTf, which proceeds through the rate-determining PCET from thioanisoles to 1. The driving force dependence of k_{et} of PCET from electron donors to 1 with HOTf was well evaluated in light of the Marcus theory of ET, providing valuable insights into the acid catalysis in the oxidation of substrates by metal-superoxo species through PCET.

ASSOCIATED CONTENT

Supporting Information.

Experimental details, Tables S1 – S6, and Figures S1 – S18. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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- (12) The spectroscopic titrations in Figure 3 fit with eq 3, where H_2O_2 is bound to the Cr^{III} complex. If H_2O_2 is bound to the Cr^{III} complex, the addition of H_2O_2 would result in no change in the equilibrium (eq 3) as confirmed in Figure S8 (SI).
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- (16) If one-step OAT from thioanisoles to $[(Cl)(TMC)Cr^{II}(O_2)]^+$ - $(H^+)_2$ is the rate-determining step, the k_{ox} values would be much larger than those expected from the Marcus line in Figure 4, because any interaction required for one-step OAT would be much larger than that for ET.

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