Non-Heme Manganese Catalysts for On-Demand Production of Chlorine Dioxide in Water and Under Mild Conditions

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Supporting Information

ABSTRACT: Two non-heme manganese complexes are used in the catalytic formation of chlorine dioxide from chlorite under ambient temperature at pH 5.00. The catalysts afford up to 1000 turnovers per hour and remain highly active in subsequent additions of chlorite. Kinetic and spectroscopic studies revealed a MnIII(OH) species as the dominant form under catalytic conditions. A MnIII(μ-O)MnIV dinuclear species was observed by EPR spectroscopy, supporting the involvement of a putative MnIV(O) species. First-order kinetic dependence on the manganese catalyst precludes the dinuclear species as the active form of the catalyst. Quantitative kinetic modeling enabled the deduction of a mechanism that accounts for all experimental observations. The chlorine dioxide producing cycle involves formation of a putative MnIV(O), which undergoes PCET (proton coupled electron-transfer) reaction with chlorite to afford chlorine dioxide. The ClO2 product can be efficiently removed from the aqueous reaction mixture via purging with an inert gas, allowing for the preparation of pure chlorine dioxide for on-site use and further production of chlorine dioxide.

INTRODUCTION

The chlorine oxyanions (ClO₃⁻, n = 1–4) spanning oxidation states of +1 to +7 have found diverse uses from bleaching agents to oxidizers in rocket fuels. As a result of their high solubility in water and wide range of applications, water sources have been severely contaminated by these toxic anthropogenic pollutants.¹ Perchlorate (ClO₄⁻) is commonly used as an oxidant in rocket fuel, missiles, and fireworks.² Advances in perchlorate remediation with use of microbes³ as well as chemical catalysts⁴ have previously been discussed. Chlorate (ClO₃⁻) is used as an herbicide and a source of chlorine dioxide (ClO₂). Chlorite (ClO₂⁻) is primarily used as a source of ClO₂ in the pulp bleaching industry, and hypochlorite (ClO⁻) is a widely used disinfectant. Of the aforementioned chlorine-containing species, the catalytic conversion of chlorite to either dioxygen and chloride or chlorine dioxide is of great interest. The reactivity of chlorite and chlorous acid, ClO₂⁺, has been studied extensively.⁵ The reactivity of aqua transition-metal ions toward Cl⁺ has been reviewed by Fábián.⁶ Collman and Braumann have shown that metalloporphyrins catalyze the electrochemical reduction of chlorite⁷ as well as alkane oxidations with chlorite as an oxidant.⁸ The Environmental Protection Agency has recently labeled chlorite as a major water contaminant as a result of suspected health risks such as childhood anemia.⁹ Chlorite can also serve as an oxidizing or chlorinating agent when exposed to water pollutants and consequently enhance toxicity. Therefore, a method to remediate chlorite is of interest from an environmental standpoint.

The biological remediation of ClO₄⁻ occurs in three steps catalyzed by two enzymes.¹⁰ Perchlorate reductase is a molybdopterin-dependent enzyme proposed to catalyze the reduction of ClO₄⁻ to ClO₃⁻ presumably via the intermediacy of ClO₂⁻ with the production of a water molecule at each step.¹¹ Despite a favorable reduction potential, perchlorate reductase does not further reduce ClO₂⁻. Instead, chlorite is further reduced to environmentally benign chloride (Cl⁻) and dioxygen (O₂) in a reaction catalyzed by chlorite dismutase (Cld), a heme-containing enzyme.¹² This enzyme is of considerable interest since photosystem II is the only other known enzymatically catalyzed process for O=O bond formation. Dubois and co-workers have studied the mechanism of Cld and proposed that the resting FeIII-heme reacts with ClO₂⁻ to form compound I and ClO₂⁺, which quickly rebinds to give O₂ and Cl⁻.¹³ Our group has also reported on the disproportionation of chlorite mainly to chloride and chlorate.

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under physiological pH using water-soluble iron porphyrins as catalysts. Unlike their iron analogues, manganese porphyrin complexes have been shown, independently, by us and the Groves group to catalyze chlorine dioxide formation from chlorite. Nonetheless, chlorine oxyanions ($\text{ClO}_2^-$) are the prevalent source of ClO$_2$ in every method. The majority of methods, however, involve highly corrosive conditions and harsh oxidants, which raise health and environmental/safety concerns. Of the chlorine oxys used for ClO$_2$ production, ClO$_2^-$ is the most common species due to the presence of concentrated sulfuric acid. However, the one-electron electrochemical oxidation of chlorine offers an alternative route to ClO$_2$ but requires a substantial input of energy. The primary commercial use of chlorine dioxide is as an oxidizing agent for pulp bleaching and more recently for water disinfection/treatment. Chlorine dioxide is preferred over chlorine gas ($\text{Cl}_2$) for water treatment as it exhibits superior antimicrobial activity and generates less harmful byproducts (chlorinated species or trihalomethanes). One major drawback is the instability of ClO$_2$ at high pressure, a fact that effectively prohibits its transport as a gas. Hence, on-site production of ClO$_2$ is a prerequisite for any practical application.

Our group communicated on the high reactivity of non-heme manganese–oxo complexes, $[\text{Mn}^{\text{IV}}(\text{N}4\text{Py})]^{2+}$ (Bn-TPEN = N-benzyl-N,N',N'-tris(2-pyridylmethyl)-1,2-diaminoethane) and $[\text{Mn}^{\text{IV}}(\text{N}4\text{Py})]^{2+}$ (N4Py = N,N'-bis(2-pyridylmethyl)bis(2-pyridyl)methylamine) (see Figure 1), in oxidation reactions. Herein, we provide a catalytic process for the generation of chlorine dioxide from chlorite using two non-heme manganese(II) complexes, $[\text{Mn}^{\text{II}}(\text{N}4\text{Py})]^{2+}$ and $[\text{Mn}^{\text{II}}(\text{Bn-TPEN})]^{2+}$. The reaction proceeds efficiently reaching completion within 30 min with as little as 0.10 mol % catalyst loading under ambient temperature and noncorrosive pH. The catalytic formation of chlorine dioxide is observed for both $[\text{Mn}^{\text{IV}}(\text{N}4\text{Py})]^{2+}$ and $[\text{Mn}^{\text{II}}(\text{Bn-TPEN})]^{2+}$ with second-order rate constants of 21 and 6 M$^{-1}$ s$^{-1}$, respectively. For the non-heme manganese complexes in this report, catalysis initiates via OAT (oxygen atom transfer) to generate a putative Mn$^{\text{V}}$(O) species. As chlorine dioxide is produced, a Mn$^{\text{III}}$(OH) species accumulates and the ClO$_2^-$ product acts as an inhibitor of the reaction. A comprehensive mechanism that satisfies all experimental observations is obtained from quantitative kinetics modeling.

## RESULTS

### Formation of ClO$_2$

The catalytic activity of $[\text{Mn}^{\text{III}}(\text{N}4\text{Py})]^{2+}$ and $[\text{Mn}^{\text{III}}(\text{Bn-TPEN})]^{2+}$ for ClO$_2$ production from ClO$_2^-$ was examined at 25.0 °C in 50.0 mM acetate buffer at pH 5.00. Strikingly, if the pH of the buffer is increased then the production of ClO$_2$ is halted with the disproportionation of chlorite to chloride and chlorate instead being favored. This observation suggests the process for ClO$_2$ production is proton dependent. Additionally, when the buffer composition is changed from acetate to citrate, the production of ClO$_2$ is halted suggesting that the buffer is not innocent during catalysis. The formation of ClO$_2$ was monitored following its characteristic absorption band at $\lambda_{\text{max}} = 360$ nm ($\varepsilon = 1250$ M$^{-1}$ cm$^{-1}$). The ClO$_2$ product can be extracted from the aqueous medium into diethyl ether. A typical spectrum of extracted ClO$_2$ from the catalytic reaction is shown in Figure 2a and is compared to an authentic sample of ClO$_2$. Negative mode electrospray ionization mass spectroscopy (ESI-MS) of the diethyl ether extract confirmed that ClO$_2$ (m/z 67.0) and ClO$_3$ (m/z 83.0) were formed during the reaction. Chlorite is insoluble in diethyl ether, hence the peak at 67.0 m/z is that of ClO$_2$ and not ClO$_3^-$ (Figure 2b). Dioxygen ($\text{O}_2$) was not observed in any of the reactions performed.

### Products Analysis by Ion Chromatography (IC)

Ion chromatography was used to identify and quantify chlorine-containing anionic products. IC was performed on reaction mixtures upon maximum yield/concentration of ClO$_2$, confirming that the majority of the chlorite reactant was consumed and both Cl$^-$ and ClO$_3^-$ were also formed. When the concentration of chlorite or catalyst was increased, more chlorate was formed. Longer reaction times led to the complete decomposition of chlorite, while the concentration of chlorine dioxide remained relatively constant. The exact yields of anions of selected reaction conditions are summarized in Table 1. Ion chromatograms and exact yields of anions for all reactions are provided in the Supporting Information (Figures S2–S24 and Tables S1–S5).
Table 1. Results for the Catalytic Conversion of Chlorite to Chlorine Dioxide in 50.0 mM Acetate Buffer (pH 5.00)\textsuperscript{a}

<table>
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<tr>
<th>catalyst</th>
<th>[cat]/,\mu M</th>
<th>[ClO\textsubscript{2}\textsuperscript{−}]\textsubscript{0}</th>
<th>[ClO\textsubscript{2}\textsuperscript{−}]\textsubscript{t}</th>
<th>[Cl\textsuperscript{−}]</th>
<th>[ClO\textsubscript{3}\textsuperscript{−}]</th>
<th>[ClO\textsubscript{2}]</th>
<th>% ClO\textsubscript{2}\textsuperscript{b}</th>
<th>% ox. equiv.\textsuperscript{c}</th>
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<tr>
<td>Mn(N4Py)</td>
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<td>10.0</td>
<td>4.24</td>
<td>2.24</td>
<td>1.79</td>
<td>1.68</td>
<td>29</td>
<td>22</td>
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<tr>
<td>Mn(N4Py)</td>
<td>10.0</td>
<td>4.00</td>
<td>1.10</td>
<td>1.10</td>
<td>0.88</td>
<td>0.91</td>
<td>31</td>
<td>20</td>
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<tr>
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<tr>
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<td>0.47</td>
<td>0.04</td>
<td>35</td>
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\textsuperscript{a}All concentrations are mM unless otherwise stated. Chlorine dioxide concentrations were quantified by using UV-vis spectroscopy on the reaction mixture. Ion chromatography was used to quantify the concentrations of other chlorine-containing species. Ion chromatograms were performed at 1 h unless otherwise stated. \textsuperscript{b}Percentage calculated by using the final concentration of chlorine dioxide divided by the concentration of reacted chlorite. \textsuperscript{c}Percentage of oxidizing equivalence unaccounted for by chlorine-containing species. \textsuperscript{d}Ion chromatogram taken at maximum ClO\textsubscript{2} formation.

Reactivity of Chlorine Dioxide with Manganese(II) and Manganese(III) Complexes. To test how the product affects the reaction, ClO\textsubscript{2} was collected in acetate buffer (pH 5.00) from a separate reaction and the reactivity of both catalysts with ClO\textsubscript{2} was examined. The reaction of ClO\textsubscript{2} with precatalyst, manganese(II) species, resulted in a slower decrease in absorption for ClO\textsubscript{2} at 260 nm (ε\textsuperscript{a} = 154 M\textsuperscript{−1} cm\textsuperscript{−1}); however, both catalysts have a maximum absorption at this wavelength. Furthermore, the absorption of the catalyst increases as Mn\textsuperscript{III}(OH) accumulates over the course of the reaction. Therefore, the reaction kinetics were studied following the formation of ClO\textsubscript{2} at 360 nm albeit the Mn\textsuperscript{III}(OH) form of the catalyst also absorbs in this region but with minimal contribution due to its low extinction coefficient. While the time profiles at 360 nm (ClO\textsubscript{2}) fit a single exponential equation to a first approximation, the time profiles exhibit features of more complex kinetics (see Figures 4 and 5).

![Image](326x141.png)

Figure 3. Examination of product inhibition by reacting ClO\textsubscript{2} with the manganese catalysts, [Mn\textsuperscript{II}(N4Py)]\textsuperscript{2+} and [Mn\textsuperscript{II}(Bn-TPEN)]\textsuperscript{2+}. The dashed red spectrum is the starting catalyst. UV-vis scans at 2, 7, 12, 180, and 360 s. (a) The reaction of [Mn\textsuperscript{II}(N4Py)]\textsuperscript{2+} (500 \, \mu M) and chlorine dioxide (1.15 mM) results in the rapid disappearance of ClO\textsubscript{2} and the appearance of a Mn\textsuperscript{III}(OH) species for both manganese complexes. (b) [Mn\textsuperscript{II}(N4Py)]\textsuperscript{2+} was more reactive toward ClO\textsubscript{2} in comparison to [Mn\textsuperscript{II}(Bn-TPEN)]\textsuperscript{2+} as shown in Figure 3. The reaction of ClO\textsubscript{2} with the resting state form of the catalyst, manganese(III) species, resulted in a slower decrease in absorption for ClO\textsubscript{2} relative to starting with Mn\textsuperscript{II}(OH\textsubscript{2}) (Figures S25 and S26, Supporting Information). This observation implies that the decomposition of ClO\textsubscript{2} is dependent on the oxidation state of the catalyst.

Absorption Spectroscopy and Kinetics. The consumption of chlorite can be monitored by the decrease in absorbance at 260 nm (ε = 154 M\textsuperscript{−1} cm\textsuperscript{−1}); however, both catalysts have a maximum absorption at this wavelength. Furthermore, the absorption of the catalyst increases as Mn\textsuperscript{III}(OH) accumulates over the course of the reaction. Therefore, the reaction kinetics were studied following the formation of ClO\textsubscript{2} at 360 nm albeit the Mn\textsuperscript{III}(OH) form of the catalyst also absorbs in this region but with minimal contribution due to its low extinction coefficient. While the time profiles at 360 nm (ClO\textsubscript{2}) fit a single exponential equation to a first approximation, the time profiles exhibit features of more complex kinetics (see Figures 4 and 5).

![Image](562x251.png)

Figure 4. Kinetics of ClO\textsubscript{2} formation with use of [Mn\textsuperscript{II}(N4Py)]\textsuperscript{2+} as a catalyst. (a) UV-vis spectral changes of the reaction for 40 min. Initial catalyst (dashed), first and last scan (solid), others gray. Conditions: [Mn\textsuperscript{II}(N4Py)] = 10.0 \, \mu M; [ClO\textsubscript{2}\textsuperscript{−}] = 4.05 mM. (b) Changes in concentration of ClO\textsubscript{2} versus time. Solid lines represent kinetic modeling fits. Conditions: [Mn\textsuperscript{II}(N4Py)]\textsubscript{0} = 10.0 \, \mu M; [ClO\textsubscript{2}\textsuperscript{−}] = 9.85, 7.37, 6.00, 4.14, 1.95 mM (top to bottom).

Ion chromatography confirms that the majority of the chlorite is consumed (except for starting with high chlorite concentration of 10.0 mM) when the maximum concentration of ClO\textsubscript{2} is reached.

![Image](562x251.png)

Figure 5. Kinetics of ClO\textsubscript{2} formation with use of [Mn\textsuperscript{II}(Bn-TPEN)]\textsuperscript{2+} as a catalyst. (a) UV-vis spectral changes of the reaction for 1 h. Initial catalyst (dashed), first and last scan (solid), others gray. Conditions: [Mn\textsuperscript{II}(Bn-TPEN)]\textsubscript{0} = 50.0 \, \mu M; [ClO\textsubscript{2}\textsuperscript{−}] = 4.00 mM. (b) Change in concentration of ClO\textsubscript{2} versus time. Solid lines represent kinetic modeling fits. Conditions: [Mn\textsuperscript{II}(Bn-TPEN)]\textsubscript{0} = 50.0 \, \mu M; [ClO\textsubscript{2}\textsuperscript{−}] = 9.99, 7.93, 5.99, 4.02, 2.09 mM (top to bottom).
The kinetics for [MnII(N4Py)]^{2+} and [MnII(Bn-TPEN)]^{2+} were examined. When a solution of chlorite (2.00–10.00 mM) was monitored in the presence of [MnII(N4Py)]^{2+} (10.0 μM), an induction period was observed before the appearance of ClO2. This induction period ranged from 5 to 300 s, depending on the initial catalyst concentration. When a solution of chlorite (2.00–10.00 mM) was monitored in the presence of [MnII(Bn-TPEN)]^{2+} (50.0 μM), an induction period was not observed and ClO2 followed approximately first-order kinetics. A 5-fold increase in the concentration of [MnII(Bn-TPEN)]^{2+} was necessary to achieve comparable reaction times as a result of its lower reactivity (Figures 4b and 5b).

Preliminary inspection of the data shows dependence on [ClO2]− and [Mn]. While the rate of reaction increases linearly with respect to [Mn] (Figures S11a and S21a, Supporting Information), the dependence on [ClO2]−, the limiting reagent, is more complex (Figures S11b and S21b, Supporting Information). Furthermore, the amount of ClO2 produced is lower reactivity (Figures 4b and 5b).

Multiple Additions of ClO2−. The reactivity of both catalysts upon multiple additions of chlorite was examined. ClO2− (4.00 mM) was reacted with [MnII(N4Py)]^{2+} (10.0 μM) or [MnII(Bn-TPEN)]^{2+} (50.0 μM). Upon reaching the maximum concentration of ClO2, the mixture was purged with argon gas for 5 min to remove the ClO2 product. A second aliquot of ClO2− (4.00 mM) was added to the catalyst solution and the kinetics of ClO2 formation was monitored. A decrease in the observed rate was observed for both catalysts, [MnII(N4Py)]^{2+} with a 40% decrease while [MnII(Bn-TPEN)]^{2+} had a 66% decrease, as a result of catalyst deactivation (Figure 6).

Time-Dependent Product Distribution. To further elucidate the mechanism for chlorine dioxide formation, the concentrations of all chlorine-containing species were analyzed at 10-min intervals by ion chromatography (ClO2−, Cl−, ClO3−) and UV–vis spectroscopy (ClO2). As expected, the reaction products chlorite, chlorate, and chlorine dioxide are produced as chlorite is consumed (Figure 7). Chlorine dioxide reaches a plateau within 30 min while the concentration of both chloride and chlorate continues to increase over time.

Electron Paramagnetic Resonance (EPR). EPR spectroscopy was used to identify the change in oxidation state of the manganese catalysts. Both ClO2− (4.00 mM) and ClO2 (1.00 mM) were reacted independently with [MnII(N4Py)]^{2+} (500 μM) and [MnII(Bn-TPEN)]^{2+} (500 μM) in acetate buffer (pH 5.0). Figure 8 shows the EPR spectra for [MnII(N4Py)]^{2+} and its reaction with ClO2− and ClO2. The reactions with chlorite were allowed to continue for 1 h, purged of ClO2 with use of argon, and frozen. The same procedure was carried out for the reactions with ClO2, except the reaction time was only 20 min. In these reactions, the characteristic signal for MnII is not observed and a feature that can be assigned to a MnIII(μ-O)MnIV dinuclear complex emerges. Both catalysts gave identical EPR spectra under reaction conditions. The EPR spectra for [MnII(Bn-TPEN)]^{2+} can be found in the Supporting Information (Figure S1). MnIII(S = 2) and MnII(S = 1 or 0) would not be observable in perpendicular mode EPR.
Catalytic oxidation of ClO$_2^-$ to ClO$_2$ by two water-soluble non-heme manganese complexes has been studied at 25.0 °C and pH 5.00. To our knowledge, this is the first example of manganese non-heme catalysts that catalyze this conversion. Good yields of ClO$_2$ were observed in less than 1 h with use of as little as 0.10 mol % [Mn$^{III}$(N4Py)]$^{2+}$ and 0.50 mol % [Mn$^{III}$(Bn-TPEN)]$^{2+}$. These catalyst loadings correspond to turnover frequencies (TOF) defined as [ClO$_2$] produced per mole of catalyst loading per hour, of 1000 and 200 h$^{-1}$, respectively. Since the production of ClO$_2$ in situ and on-site is important for industrial applications, these non-heme manganese catalysts offer a convenient route to ClO$_2$ production under reasonably mild and noncorrosive conditions with use of an earth-abundant metal and readily available ligands.

Several manganese(III) porphyrin complexes have been examined for the catalytic formation of chlorine dioxide independently by our group and that of Groves. The initial step for the heme complexes is oxygen atom transfer from chlorite to [Mn$^{III}$] via either heterolytic or homolytic Cl–O bond cleavage of chlorite. Homolytic Cl–O bond cleavage results in a Mn$^{IV}$(O) complex while heterolytic cleavage results in a Mn$^{V}$(O) cationic species. A proposed mechanism for the catalytic conversion of ClO$_2^-$ to ClO$_2$ for manganese porphyrin catalysts is given in Scheme 1.

Scheme 1. General Mechanism for the Conversion of ClO$_2^-$ to ClO$_2$ with Use of Water-Soluble Manganese Porphyrin Catalysts

In contrast to the previously described manganese porphyrin systems, our non-heme catalysts described herein are present in the +2 oxidation state and are 5-coordinate. Over the course of the reaction, the Mn$^{II}$(OH)$_2$ species is fully consumed giving rise to higher oxidation states of the manganese complexes as evident by UV–vis (Figure 3) and EPR spectroscopy (Figure 8). The relatively low stability of the Mn$^{IV}$(O) species supported by N4Py and Bn-TPEN ligation in water solution suggests that this species does not accumulate at sufficient concentrations to be detected. These observations are in contrast to manganese porphyrin complexes where the precatalyst, [Mn$^{III}$]$^+$, remains the dominant form of the catalyst with Mn$^{III}$(O) and [Mn$^{IV}$(O)]$^+$ species being proposed intermediates in the catalytic cycle. Another stark difference is the observed induction period when using [Mn$^{II}$(N4Py)]$^{2+}$ as a catalyst. The induction period indicates slower formation of the active species in comparison to [Mn$^{III}$(Bn-TPEN)]$^{2+}$ as a result of lower catalyst loading. The dominant observable form of the catalyst under catalysis is a Mn$^{III}$(OH) species (UV–vis 440 and 560 nm). This complex has been prepared independently for the Bn-TPEN ligand. The Mn$^{IV}$(O) is expected to exhibit an absorption band at higher wavelength (ca. 1040 nm); furthermore, Mn$^{III}$(OH) is also responsible for the increase in absorption at 260 nm (Figure 3). These observations as well as proposed reaction steps (Scheme 2) were used to predict the concentrations of these manganese species over the course of the reaction by using a mathematical model as shown in Figure 9.

Even though not observed directly, the putative Mn$^{IV}$(O) and its participation is substantiated by the observation in the EPR spectra of a Mn$^{III}$(µ-O)Mn$^{IV}$ dinuclear species. The first-order dependence on [Mn] effectively rules out this dinuclear species as the active form of the catalyst, which would afford second-order kinetic dependence on catalyst. All of these observations are consistent with activation of the precatalyst via an OAT reaction with ClO$_2^-$ forming Mn$^{IV}$(O) and ClO$_2^-$ (eq 1) to enter the proposed catalytic cycle in Scheme 2. The hypochlorite formed does not rebound with the newly formed manganese–oxo species to form dioxygen but instead quickly reacts with excess chloride to form chloride and chlorine dioxide (eq 7) with reaction kinetics provided in Figure S43. Supporting Information. The high-valent manganese–oxo species then has three fates: (1) react via a PCET reaction with chloride to give ClO$_2$ and Mn$^{III}$(OH) (eq 2), (2) react via an OAT reaction with chloride to form chlorate and precatalyst (eq 3), or (3) reacting with the dominant form of the catalyst, Mn$^{III}$(OH), to form the dinuclear Mn$^{III}$(µ-O)Mn$^{IV}$ species. The first pathway produces chlorine dioxide, which involves protonation of the oxo ligand on Mn$^{IV}$ and hence accounts for the observed pH dependence for ClO$_2$ production. The second pathway results in the formation of chlorate and precatalyst, which quickly reacts with chlorine dioxide (eq 4) to form Mn$^{III}$(OH) thus re-entering the catalytic cycle. The chlorate that is formed does not react with either of the catalysts under the conditions used. The dominant species, Mn$^{III}$(OH), reacts with chloride in the presence of protons via homolytic Cl–O bond cleavage to form [ClO$_2$] and regenerate the Mn$^{IV}$(O) species (eq 5). This proposal has precedence in the iron heme systems based on DFT calculations. The [ClO$_2$] radical byproduct is known to react with chloride to make ClO$^-$ and ClO$_2$. Also, reactions with ClO$_2$ to give [ClO$_3$O$_2$]$_x$, which disproportionates in water to HOCl, ClO$_3$–, and H$^+$. However, in our proposed reaction mechanism the [ClO$_2$] species reacts with the buffer (acetate) to form chloride and peracetic acid (eq 8). To account for the apparent slow
An induction period was not observed for \([\text{Mn}^{II}(\text{Bn-TPEN})]^2+\) precatalyst with chlorite is slow relative to subsequent reactions. The rate constant constants, obtained from mathematical modeling, for the ligand oxidation or metal dissociation is included (eq 6). Rate as other species, the deactivation reaction assumed to be either down and eventual cessation of the production of ClO2 as well results in a 2:1:1 equivalence of Cl\(^{-}\):ClO\(^2\) and ClO\(^3\)^{−}. The resulting balanced equation reactions.25

<table>
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<th>catalyst</th>
<th>(k_1)</th>
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<th>(k_3)</th>
<th>(k_4)</th>
<th>(k_5)</th>
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All rate constants are in M\(^{-1}\)s\(^{-1}\) unless otherwise stated. See Scheme 2, eqs 1–7, for reaction steps. In eq 7, the reaction is 1st order in [ClO\(^2\)\(^−\)] and 2/3 order in [ClO\(^3\)^{−}]. Determination of reaction order is described in the Supporting Information.

The mathematical model accurately predicts the induction period observed for \([\text{Mn}^{II}(\text{N4Py})]^2+\) where the reaction of precatalyst with chlorite is slow relative to subsequent reactions. An induction period was not observed for \([\text{Mn}^{II}(\text{Bn-TPEN})]^2+\) as a result of higher catalyst loading. The model also predicts that the reactivity of chlorite with \(\text{Mn}^{II}(\text{OH})\) \((k_4)\) is slower than that of \(\text{Mn}^{IV}(\text{O})\) \((k_5)\) supporting the observation that \(\text{Mn}^{III}(\text{OH})\) is the dominant form during catalysis. The disappearance of the characteristic \(\text{Mn}^{II}(\text{OH}_2)\) signal by EPR spectroscopy suggests that the precatalyst, if regenerated, is quickly converted to higher oxidation state species. According to the mathematical model the assumption that precatalyst is generated but quickly converted is validated by the observed product inhibition.

A word is in order here regarding the overall stoichiometry of the reaction. The precatalyst enters the catalytic cycle by converting chlorite to hypochlorite via OAT (eq 1), which then reacts with chlorite to produce 2:1 equivalence of ClO\(^2\):Cl\(^−\) (eq 7). Subsequent formation of ClO\(^2\)_2Cl\(^−\) for the outer cycle shown in Scheme 2. The inner reaction pathway results in a 1:1 equivalence of ClO\(^3\)^{−}:Cl\(^−\). The resulting balanced equation products comes to 5.76 mM, accounting for nearly all the chlorite conversion, the net oxidation state equivalent of the products is +13.43, leaving ca. 22% of the reactants oxidizing equivalents not accounted for. We probed for potential water oxidation by looking to see if O\(_2\) is produced. The result was negative, no O\(_2\) was observed. That limits the possibilities to the oxidation of the buffer. This theory is supported by the halt in ClO\(^2\) formation when the buffer composition was changed from acetate to citrate with the same buffer capacity and pH. However, we were unable to detect acetate oxidation products in our system by mass spectrometry. It is noted that acetate buffer is frequently used in studying kinetics of ClO\(^2\) reactions.

Multiple additions of ClO\(^3\)^{−} for both catalysts were conducted to determine whether the catalysts were still active for the catalytic formation of ClO\(^2\). Both manganese catalysts remained active for the production of ClO\(^2\); however, slower reaction rates were observed with relatively comparable yields of ClO\(^2\). This can be attributed to the relatively robust nature of the ligands and their manganese complexes under oxidizing conditions allowing for the observed high turnover numbers (TON) for ClO\(^2\) formation of 2160 and 560 for \([\text{Mn}^{II}(\text{N4Py})]^2+\) and \([\text{Mn}^{II}(\text{Bn-TPEN})]^2+\), respectively. These turnover numbers result from three successive additions of chlorite with a mild decrease in ClO\(^2\) yield suggesting that even higher turnovers can be obtained.

## CONCLUSIONS

Two non-heme coordination complexes of manganese, \([\text{Mn}^{II}(\text{N4Py})]^2+\) and \([\text{Mn}^{II}(\text{Bn-TPEN})]^2+\), catalyze the formation of chlorine dioxide from chlorite under ambient temperature at pH 5.00. The catalysts are robust and stable.
enough to afford 1000 turnovers per hour and still remain active in subsequent additions of chlorite. Kinetic and spectroscopic studies revealed that a MnIII(OH) species is the dominant form of the catalyst under reaction conditions. However, a MnIII(μ-O)MnIV dinuclear species is observed by EPR spectroscopy, which supports the involvement of a putative MnV(IV) species. The first-order kinetic dependence on the manganese catalyst precludes the MnIII(μ-O)MnIV dinuclear species as the active form of the catalyst. Based on quantitative kinetic modeling, a mechanism has been put forth to explain the experimental observations (Scheme 2). The chlorine dioxide producing cycle involves formation of a MnV(IV)(O) species, which undergoes PCET reactions with chlorine to afford ClO2. The proposed mechanism differs from that of the manganese porphyrin systems as a result of the difference in the ligand coordination to the metal as well as the starting oxidation state. While the chlorine mass balance is excellent and the converted chlorite can be fully accounted for by the experimentally observed stoichiometric ratios of products. Nevertheless, the ClO2 product can be efficiently removed from the aqueous reaction mixture via purging with an inert gas. These manganese non-heme catalysts offer a new method for the preparation of pure chlorine dioxide for on-site use, and further production of ClO2. They also circumvent the need to use the higher molecular weight, more expensive, and more elaborate manganese non-heme catalysts o...

**ASSOCIATED CONTENT**

4 Supporting Information

The synthesis and characterization of [MnII(N4Py)]2+ and [MnII(Bn-TPEN)]2+ complexes; ion chromatograms for all of the reactions performed; EPR spectroscopy of [MnII(Bn-TPEN)]2+ and the reactions with chlorite and chlorine dioxide; the reactions performed; EPR spectroscopy of [MnII(Bn-TPEN)]2+ and higher molecular weight, more expensive, and more elaborate manganese porphyrin systems as a result of the di...

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Notes

The authors declare no competing financial interest.

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