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Chlorine Compounds

Catalytic Generation of Chlorine Dioxide from Chlorite Using a Water-Soluble Manganese Porphyrin**

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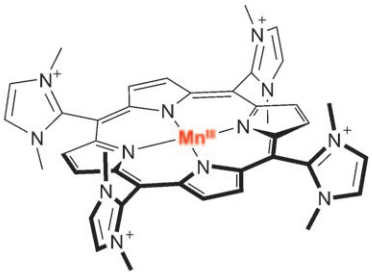
The industrial preparation of chlorine dioxide (ClO_2) is energy-intensive and fraught with health and safety issues. Furthermore, due to the instability of ClO_2 at high pressures, the gas must be generated at the point of use.[1] ClO_2 is an oxidizing agent employed as an alternative to chlorine in paper bleaching, pathogen decontamination and water treatment due to its superior antimicrobial properties and reduced tendency to produce harmful organochlorine by-products.[1] The large-scale production of ClO_2 involves the use of concentrated acids and/or externally added oxidants (such as Cl_2, H_2O_2, or hypochlorite).[2] Electrochemical methods can directly oxidize ClO_2^- to ClO_2 by a one-electron process but these require considerable input of electrical energy and may not be applicable in rural or underdeveloped areas of the world. An iron-catalyzed decomposition of ClO_2^- has been shown to afford ClO_2 (in part), but only under very acidic conditions.[3] Accordingly, these hazardous and/or costly methods must be implemented in facilities that are primarily engineered for other purposes.

Advances in chemical catalysis have numerous intrinsic advantages among the various strategies for mitigating pollution and workforce hazards in chemical practice.[4] Herein we describe an efficient, catalytic process for the generation of ClO_2 from chlorite ion (ClO_2^-) using the water-soluble manganese porphyrin tetrakis-5,10,15,20-(*N*,*N*-dimethylimidazolium) porphyrinatomanganese(III) ([Mn(TDMImP)], Scheme 1).[5] The reaction proceeds rapidly and efficiently under mild, ambient conditions. The chemistry of ClO_2^- is of current interest due to recent studies on the O_2-evolving enzyme chlorite dismutase (Cld).[6] This work adds to the understanding of the reaction of ClO_2^- with metalloporphyrins and heme proteins, in addition to presenting a green alternative to the syntheses of ClO_2 described above.



Scheme 1. Structure of [Mn(TDMImP)]. Axial ligands are water and hydroxo under the conditions used.

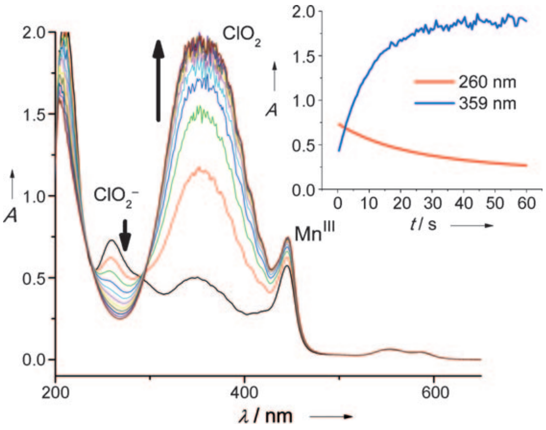


Figure 1. Time resolved UV/Vis spectra of ClO_2 (359 nm) generation when 10 μм [Mn(TDMImP)] (445 nm) is mixed with 1.9 mм $NaClO_2$ (260 nm) at pH 4.7 (100 mм acetate buffer) and $T = 25$ °C. The reaction time shown is 240 s, scanning every 10 s.

Upon adding [Mn(TDMImP)] to a freshly prepared solution of sodium chlorite at pH 4.7, a large and immediate increase in the UV absorbance at 359 nm signaled the formation of ClO_2 (Figure 1). The appearance of ClO_2 occured within seconds, concurrent with a complete loss of the absorbance at 260 nm due to ClO_2^- over 10 min. The acid-catalyzed disproportionation of ClO_2^- is sluggish above pH 3–4 and was insignificant on the time-scales studied here.[3,7] During the initial burst of reaction, about 50 equiv of ClO_2 were generated while less than half of the 190 equiv of ClO_2^- had been consumed. O_2 evolution, as monitored using a Clark electrode, was insignificant (< 2%) and could be an overestimate due to interferences from other species in solution. The only porphyrin species observed in solution during turnover was the starting Mn^{III} catalyst as evidenced by the unshifted and undiminished Soret band at 445 nm, indicating the stability of the catalyst both during and after reaction (Figure 1). Addition of a second aliquot of $NaClO_2$ to the system after reaction generate more ClO_2 in similar yield and by similar kinetics, further indicating the stability of the catalyst. Significantly, the process also proceeded efficiently when the manganese catalyst was adsorbed on montmorillonite clay (Supporting Information).

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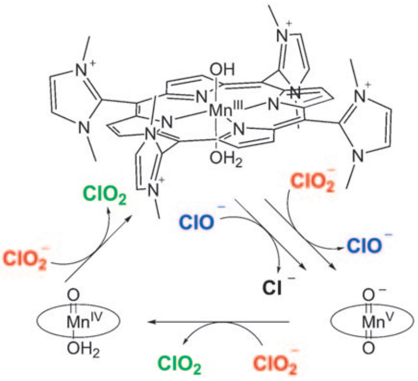
The manganese porphyrin-catalyzed appearance of ClO_2 was observed from pH 4.7–6.8 over the temperature range 5–35 °C. No ClO_2 was observed at pH 8.0 or above. When ClO_2^- was mixed rapidly with [Mn(TDMImP)] (0.5 mol %) the observed concentration of ClO_2 produced reached a plateau within two minutes (inset, Figure 1). Initial turnover frequencies at 25 °C for 2 mM ClO_2^- and 10 μM catalyst were 1.00, 1.03, and 0.47 s^{-1} at pH 4.7, 5.7, and 6.8, respectively. The ClO_2 concentration reached a maximum, and then decayed in a slower, porphyrin-mediated process that produced chlorate ion (ClO_3^-), as determined by the changes observed in the ClO_2 UV/Vis absorbance at 359 nm. The maximum concentration of ClO_2 achieved was dependent on the pH, but not the temperature, over the range 5–35 °C.



Scheme 2. Proposed mechanism for ClO_2 evolution from ClO_2^- and [Mn(TDMImP)].

To account for the decomposition of ClO_2^- and the concurrent appearance of ClO_2, we propose the mechanism shown in Scheme 2. The initial and rate-determining step in this process is oxo-transfer from ClO_2^- to Mn^{III} to generate *trans*-[(dioxo)Mn^V(TDMImP)][8] and hypochlorite ion (ClO^-). The reported ΔG for oxo-transfer from ClO_2^- is only slightly lower than that of hypobromite ion ($\Delta\Delta G^{298} = 17\,kJ\,mol^{-1}$).[9] Hypobromite is a known two-electron oxidant of [Mn^{III}(TDMImP)] and capable of rapid, reversible oxo-transfer.[5] At pH 6.8, the reduction potential for the ClO_2^-/ClO^- couple is only slightly higher than that of the $oxoMn^V/Mn^{III}$ couple ($\Delta E = -0.06\,V$), corresponding to a $K_{eq} = 10^{-2.0}$ for oxo-transfer from chlorite to Mn^{III} (Supporting Information). These thermodynamics predict that at equilibrium the >100-fold excess of chlorite should oxidize >70 % of the starting Mn^{III} to O=Mn^V=O. The intermediacy of hypochlorite generated from this step was indicated by the diagnostic chlorination of added methyl orange,[10] while sodium chlorite alone gave no detectable chlorination under these conditions (Supporting Information).

The succeeding steps of the proposed reaction scheme involve reduction of $oxoMn^V$ to Mn^{III} by two equivalents of ClO_2^-. The oxidation potential of ClO_2^- ($E° = -0.95\,V$) is close to that of NO_2^- ($E° = -1.04\,V$), which is known to reduce $oxoMn^V$ and $oxoMn^{IV}$ porphyrins readily.[11] Thus, one would predict that ClO_2^- should react with $oxoMn^V$ to generate [(oxo)Mn^{IV}(TDMImP)] and ClO_2. Furthermore, the $oxoMn^{IV}/Mn^{III}$ redox potential at pH 6.8 (Supporting Information) predicts the near-equilibrium oxidation of ClO_2^- by $oxoMn^{IV}$. Indeed, authentic [(oxo)Mn^{IV}(TDMImP)][5] was readily reduced by added chlorite ion under these reaction conditions to produce ClO_2, regenerating the manganese(III) catalyst (Supporting Information).

The hypochlorite ion produced in the initial step would also be expected to oxidize [Mn^{III}(TDMImP)] as shown in Scheme 2. This stoichiometry predicts that 5 equiv of ClO_2^- would be dismutated to 4 equiv of ClO_2 and 1 equiv of Cl^- in this process. The observed unchanged oxidation state of the catalyst during turnover (Figure 1) requires that any change in the Mn^{III}–porphyrin oxidation state be slow relative to Mn^{III}-regenerating reactions. Since ClO^- is a fast oxidant of Mn^{III},[11,12] the oxidation of Mn^{III} by ClO_2^- must be the rate-determing step of the overall catalytic cycle.

Notably, the related *N*-methyl-2-pyridyl (TM2PyP) and 4-pyridyl (TM4PyP) manganese porphyrins were not efficient caytalysts of this process. At neutral pH, the previously reported reduction potenials for the $oxoMn^V/Mn^{III}$ couple are lowest for TDMImP by >60 mV.[5] Therefore, the imidazolium porphyrin should be oxidized most readily by ClO_2^-, which is consistent with oxo-transfer from ClO_2^- being the rate-determining step, as well as TDMImP being the optimal catalyst.

At pH 8.0 the reaction of ClO_2^- and [Mn^{III}(TDMImP)] produced the O=Mn^{IV} porphyrin, characterized by its broadened and slightly blue-shifted Soret band.[5] No ClO_2 was detected under these conditions. According to the Nernst relationships, ClO_2^- should able to oxidize Mn^{III} fully to Mn^V under basic conditions and Mn^V should be reduced readily to Mn^{IV} by ClO_2^-. However, the catalytic cycle in Scheme 2 would then stall at the Mn^{IV} oxidation state because the O=Mn^{IV} compound cannot efficiently oxidize ClO_2^- and return to the resting Mn^{III} state at this pH. Indeed, we found that [(oxo)Mn^{IV}(TDMImP)] was not reduced by chlorite at high pH.

ClO_2 gas generated from the catalytic decomposition of ClO_2^- could be removed by efficient sparging of a reaction vessel charged with pH 6.8 phosphate buffer, ClO_2^-, and the catalyst. This effluent was bubbled through chilled, distilled water, which took on the characteristic color of dilute aqueous ClO_2 and could be confirmed by UV/Vis spectroscopy. The ClO_2 collected in this way was titrated with added iodide. Iodide is readily oxidized to I_2 by ClO_2,[13] which could then be quantified by titrimetry (Supporting Information). Using this procedure, 46.6 μmol of ClO_2 were recovered from a 25 °C reaction of 98.4 μmol of $NaClO_2$ with 0.1 μmol [Mn(TDMImP)] (60 % yield, ca. 500 turnovers).

The various reactions of ClO_2^- with metalloporphyrins reported to date are highly diverse in terms of intermediates and products. Accordingly, it is instructive to compare the reactivity reported here with that of other systems, both enzymatic and synthetic. Most notably, a water-soluble synthetic iron porphyrin that generates O_2 from ClO_2^- has been reported as a biomimic of the heme protein Cld.[14] However, two other iron porphyrins were shown to dismutate ClO_2^- directly to chlorate (ClO_3^-) and chloride (Cl^-) with no observation of O_2.[14b] Collman and Brauman, who used ClO_2^- with a synthetic manganese porphyrin catalyst in oxidations of cyclohexane, also observed O_2 evolution in non-aqueous media.[15] The heme-thiolate enzyme chloroperoxidase transiently generates ClO_2 from ClO_2^-, ultimately producing a mixture of ClO_3^-, Cl^-, and O_2 through undetermined mechanisms.[16] By contrast, a recent mechanistic study of ClO_2^- decomposition by horseradish peroxidase (HRP) has shown that ClO_2^- acts as both oxidant and reducing agent in a peroxidase cycle that generates ClO_2, but not ClO_3^-.[17] The present study represents the only known fast generation of ClO_2 from a synthetic porphyrin system.

The proposed mechanism for ClO_2 generation by [Mn(TDMImP)] is intriguing for its pronounced differences to the mechanism proposed for Cld and the iron porphyrin Cld-mimics.[6,14] In Cld, the Cld-mimic iron porphyrin, and [Mn(TDMImP)], ClO_2^- acts as a two-electron oxo-transfer agent, producing an equivalent of ClO^- and either an oxoiron^{IV} porphyrin cation radical[6,14] or dioxoMn^V. In the case of Cld and the iron mimic, the newly formed ClO^- appears to react with Compound I to form an oxygen–oxygen bond, leading to the release of O_2, although the precise mechanism is not known. However, the results presented here suggest that ClO^- initially produced from the oxidation of [Mn^{III}(TDMImP)] by ClO_2^- does not react with the newly formed dioxoMn^V species, but instead diffuses away to oxidize a second Mn^{III} site. The overall process and the outcome are similar to the reaction of manganese(III) porphyrins with peroxynitrite, which produces oxoMn^{IV} and NO_2.[18] The nucleophilic addition of ClO^- to the ferryl oxygen of a heme-protein Compound I suggested for Cld is strikingly similar to the previously observed oxygenation of bromide and chloride by electrophilic oxoMn^V.[5,19] Also, O–O bond formation has been observed for an oxoMn^V corrole.[20] Yet it appears that [(dioxo)Mn^V(TDMImP)] prefers an outer-sphere electron transfer from ClO_2^- to afford ClO_2 over an O–O bond-forming inner sphere reaction with ClO^-. Clearly, further efforts are needed to discern the nature of the observed selectivity among these reaction channels.

In summary, the facile, [Mn(TDMImP)]-catalyzed generation of chlorine dioxide reported here offers a green alternative to the other commonly employed routes of ClO_2 preparation. This new method can be carried out in an aqueous system at near-neutral pH under ambient pressure and temperature. In addition, the use of [Mn(TDMImP)] as a catalyst avoids the necessity of auxiliary oxidizers or acids, since the reaction is self-initiating. We have shown that the produced ClO_2 gas can be removed from the reaction vessel using a simple apparatus and used to oxidize a substrate in 60% yield. The heterogeneous version of this process would adapt well to flow or cartridge systems for water purification and would facilitate removal and recycling of the catalyst. In keeping with the tenets of green chemistry,[4] this new method reduces the risks of generating ClO_2 by removing the hazards (e.g. concentrated strong acids, large quantities of oxidizers) rather than simply limiting the exposure to such hazards.

Experimental Section

Reagents: Sodium chlorite was obtained from Aldrich as $>80\%$ technical grade and recrystallized twice from ethanol/water ($>95\%$ final).[21] Dilute chlorite solutions (0.5–10.0 mM) were standardized spectrophotometrically ($\varepsilon_{260\,nm} = 154\ cm^{-1}M^{-1}$).[22] Buffers were prepared fresh each day using either acetic acid/sodium acetate (pH 4.7, 5.7) or potassium phosphate (monobasic)/potassium phosphate (dibasic) (pH 6.8, 8.0) and pH-adjusting no more than 0.1 units using perchloric acid or sodium hydroxide. [Mn^{III}(TDMImP)] was synthesized as the chloride salt using reported procedures.[5]

UV/Vis spectroscopic measurements were taken using a Hewlett–Packard 8453 diode array spectrophotometer equipped with a temperature-controlled cell housing, VWR 1140 thermostat bath, and a Hi-Tech SFA Rapid Kinetics Accessory.

Reactions of ClO_2^- with [Mn^{III}(TDMImP)] were studied using traditional UV/Vis spectroscopy and rapid mixing. Solutions of [Mn^{III}(TDMImP)] and ClO_2^- were prepared in buffered solutions and mixed 1:1. Final concentrations for reactions were obtained by dividing the initial concentrations by two. The cell holder and mixing accessory were allowed to equilibrate to each temperature for 30 min.

Aliquots of ClO_2^- and [Mn^{III}(TDMImP)] stock solutions were added to 10 mL of 100 mM buffer in a test tube with side arm and immediately sealed using a rubber stopper outfitted with a fritted sparging tube. The reaction mixture was sparged with He during the course of the reaction through another fritted bubbler into a second test tube containing 20–40 mL of aqueous 200 mM KI. The reaction was allowed to run for 20 min, at which point the trapping solution was transferred to a flask and titrated with 0.05 M sodium thiosulfate to a colorless endpoint (using a starch indicator). To the colorless solution, approximately 5 mL of concentrated H_2SO_4 was added to liberate more I_2. This solution was titrated again. The number of moles of ClO_2 transferred during the sparging was determined by dividing the number of moles of thiosulfate used in the second titration by 4. By subtracting the number of moles of ClO_2 calculated from the number of moles of thiosulfate used in the first titration and dividing the total number by 2, the number of moles of Cl_2 transferred was determined.

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