DOI: 10.1002/ange.201005128

Chlorine Compounds

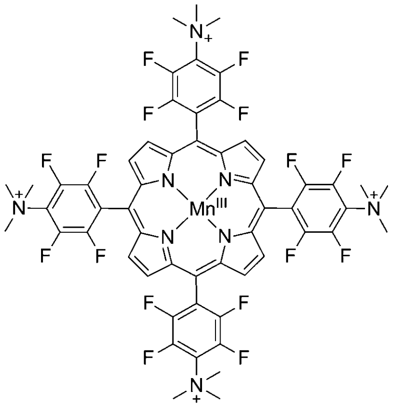
Chlorite Dismutation to Chlorine Dioxide Catalyzed by a Water-Soluble Manganese Porphyrin**

*Scott D. Hicks, Jennifer L. Petersen, Curt J. Bougher, and Mahdi M. Abu-Omar**

The oxyanions of chlorine spanning oxidation states +1 to +7 have found diverse uses. Perchlorate (ClO_4^-) is used in rocket fuel, missiles, and fireworks. Despite its strong oxidizing potential, perchlorate is quite inert in aqueous solution, and its accumulation in the environment has attracted recent attention.[1] Advances in perchlorate remediation using microbes[2] as well as chemical catalysts[3] have been discussed. Chlorate (ClO_3^-) is used as an herbicide and a source of chlorine dioxide. Chlorite (ClO_2^-) and hypochlorite (ClO^-) are used as disinfectants. Commercial production of chlorine dioxide (ClO_2) for use in pulp bleaching is from sodium chlorate reduction with methanol in the presence of sulfuric acid.[4] A smaller but growing market for chlorine dioxide is its use for water disinfection/treatment. For disinfection applications, chlorine dioxide has been made by the chlorite–hypochlorite reaction in the presence of hydrochloric acid; see for example Du Pont's Oxychlor II generator.

In the microbial removal of perchlorate, two enzymes have been identified. Perchlorate reductase, a molybdenum containing membrane-bound protein, catalyzes the reduction of perchlorate, (Cl^{VII}), to chlorite (Cl^{III}) presumabley through chlorate.[5] The second enzyme is chlorite dismutase (Cld), a heme-containing protein that transforms chlorite to chloride (Cl^-) and dioxygen (O_2). Dubois et al. have studied the mechanism of Cld and proposed a rebound pathway between Compound I (formed from the reaction of Fe^{III}–heme and chlorite) and hypochlorite to give O_2 and chloride.[6] Our group has also reported on the dismutation of chlorite under physiological pH using water-soluble iron porphyrins.[7] In these model systems, the dismutation reaction proceeds for the most part through the intermediate Compound II to give chloride and chlorate in 1:2 stiochiometry. One exception was the fluorinated [Fe(TF_4TMAP)] (TF_4TMAP = 5,10,15,20-tetrakis(tetrafluro-*N*,*N*,*N*-trimethylanilinium)porphyrinato) which afforded moderate O_2 yields.[8]

Pursuant to the above-described research we report here the preparation of the manganese analogue, [Mn(TF_4TMAP)] (Scheme 1), and its reaction catalysis under physiological pH in aqueous solution with the oxyanion chlorite. Worthy of special mention is the work of Collman and co-workers on the electrochemical reduction of chlorite catalyzed by metalloporphyrins,[9] as well as on the use of chlorite with manganese porphyrin for catalytic alkane oxidations.[10] Here we report chlorite dismutation to chlorine dioxide rather than dioxygen or chlorate. The manganese complex [Mn(TF_4TMAP)] initiates catalysis by electron-transfer (ET) followed by atom transfer. This is in sharp contrast to what has been observed previously with iron porphyrins and the enzyme chlorite dismutase.[6–8] Chlorine dioxide is produced and high-valent Mn^{IV}–oxo accumulates as chlorite is consumed until the system reaches semi-equilibrium. The ClO_2 product acts as an inhibitor due to its reaction with Mn^{III} to give the $Mn^{IV}(O)$ moiety. A mechanism that is consistent with all experimental observations is presented.



Scheme 1. Structure of [Mn(TF_4TMAP)] catalyst. The counteranion is trifluoromethane sulfonate.

Addition of 4 μM [Mn(TF_4TMAP)] to 4.0 mM chlorite solution (1000 equiv of ClO_2^-) in phosphate buffer (pH 7.0 and $\mu = 1.0\,\text{M}$) under ambient conditions (25 °C) results in rich spectral changes as shown in Figure 1. Chlorite is consumed as seen at 260 nm ($\varepsilon = 154\,\text{M}^{-1}\,\text{cm}^{-1}$), and chlorine dioxide (ClO_2) builds up at 360 nm ($\varepsilon = 1200\,\text{M}^{-1}\,\text{cm}^{-1}$). The Mn^{III} Soret band at 455 nm decreases and a new peak is observed at the edge of the ClO_2 signal at 417 nm. This signal is more pronounced at higher [Mn(TF_4TMAP)] concentration (8 μM; inset of Figure 1). The feature at 417 nm is assigned to Mn^{IV}=O based on previous literature studies[11] and independent confirmation in our laboratory from reactions of [Mn^{III}(TF_4TMAP)] with $KHSO_5$ (oxone), H_2O_2, as well as ClO^- (Supporting Information). High-valent [(TF_4TMAP)Mn^V(O)] is observed with oxygen-donor oxidants only at low temperature (0 °C) and features an intense Soret band at 427 nm.[11] The blue shift in the Soret band to

---

[*] S. D. Hicks, J. L. Petersen, C. J. Bougher, Prof. Dr. M. M. Abu-Omar
Department of Chemistry, Purdue University
560 Oval Drive, West Lafayette, IN 47906 (USA)
E-mail: mabuomar@purdue.edu

[**] This research was supported by a grant from the U.S. National Science Foundation (CHE-0749572). We thank Prof. Michael J. Zdilla for helpful discussions, and Dr. Trenton Parsell for his valuable input and help with EPR experiments.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201005128.

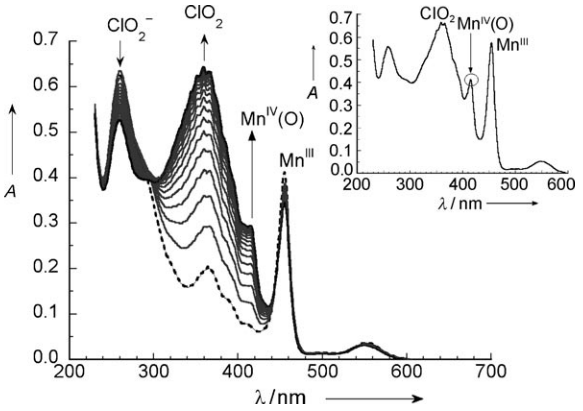


Figure 1. Repeat scan UV/Vis spectra for the dismutation of chlorite (4 mM) with [Mn(TF$_4$TMAP)] (4 μM) in phosphate buffer (pH 7.0 and $\mu = 1.0$ M) at 25 °C. Spectra aquired every 8 min. The initial spectrum is black dashed line, ending spectrum in solid black, others in gray. Inset: reaction of 4.5 mM ClO_2^- with 8 μM [Mn(TF$_4$TMAP)] after 100 min highlighting the observation of Mn^{IV}(O) at 417 nm.

417 nm observed at room temperature and with one-electron oxidants is consistent with high-valent [(Por)Mn^{IV}–oxo].[11] Groves and Spiro have recently shown that $Mn^{V}{=}O$ in porphyrin systems is the *trans*-dioxo manganese(V).[12] Herein, we will refer to it as $Mn^{V}{=}O$ for simplicity of balancing reactions when discussing the mechanism. Two important features of our reaction (Figure 1) stand out. 1) Based on the absorbance change at 360 nm (ClO_2), after 2 h 0.54 mM ClO_2 is produced (14 % yield). The reaction slows down with significant chlorite left and most of the manganese catalyst is accounted for by UV/Vis (Figure 1). Despite low kinetic conversion in the first 2 h, the reaction is catalytic and proceeds to quantitative conversion of ClO_2^- over longer times (1 day) or upon removal (purging) of the chlorine dioxide gas (Supporting Information). 2) The formation of the $Mn^{IV}{=}O$ intermediate is not instantaneous, and thus cannot be considered a steady-state intermediate. Instead, $Mn^{IV}{=}O$ increases as chlorite (260 nm) decreases and ClO_2 builds up.

The kinetics of catalytic dismutation was followed at 260 nm (ClO_2^-) and 360 nm (ClO_2) (Supporting Information). While the time profiles at 260 nm fit exponential decay to a first approximation, they certainly exhibit much more rich and complex kinetics. Furthermore, the absorbance at 260 nm also has contribution from the hypochlorite ion (ClO^-), which is formed during the course of the reaction (see below). As mentioned, approximately 0.54 mM of ClO_2 is formed in the first 2 h of reaction. However, the absorbance at 260 nm continues to decrease slowly. The kinetics of ClO_2 formation at 360 nm follows first-order behavior more closely, but again only for the first 2 h. Much longer times show slow gradual decrease in the signal at 360 nm.

Analysis of the reaction mixture after around 2 h by ion chromatography revealed that chlorine-containing species in solution are left over ClO_2^- and Cl^-. At higher conversion of chlorite, the only chlorine containing product beside ClO_2 is chloride. $Mn^{V}{=}O$ is stable in solution only at low temperature (0 °C) and at 25 °C oxygen-donor substrates such as oxone and ClO^- give $Mn^{IV}{=}O$ as a result of comproportionation. Therefore, we investigated the reaction of [Mn(TF$_4$TMAP)] with ClO_2^- under stoichiometric condition at pH 10.5 (borate buffer) and 0 °C. Under these conditions $Mn^{V}{=}O$ is stable (Supporting Information).[11] Nevertheless, only $Mn^{IV}{=}O$ was observed (Figure 2).

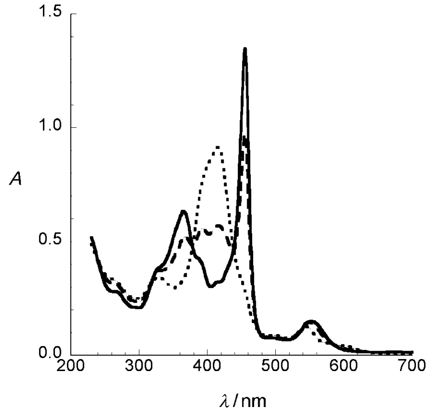
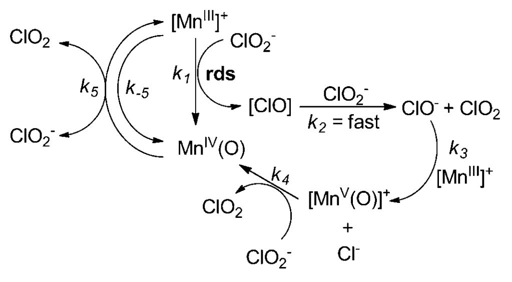


Figure 2. Spectral changes for the reaction of [Mn(TF$_4$TMAP)] (14 μM) and ClO_2^- (2 equiv) in borate buffer (pH 10.5 and $\mu = 25$ mM) at 0 °C. Solid line is starting [Mn^{III}(TF$_4$TMAP)], dashed upon mixing, and dotted after 40 min. Final spectrum is that of Mn^{IV}(O).[11]

The reduction of Mn^{III} to Mn^{II} by chlorite is thermodynamically unfavorable. However, subsequent steps can carry the reaction to completion as has been proposed for the iron(III) catalyzed decomposition of chlorite in acidic aqueous medium.[13] In the iron(III) aqua system a complex kinetic model has been proposed involving ClO_2, Cl_2, and Cl^{II} as intermediates in electron-transfer reactions that are reminiscent of Fenton-type chemistry. Any mechanism proposed for our reaction must be consistent with the observations described above and the redox potentials of the partners involved. In particular, the reaction slows down while the catalyst is still not degraded and accounted for, and secondly high-valent $Mn^{IV}{=}O$ (Soret 417 nm) forms concurrent with ClO_2 formation and ClO_2^- consumption. We propose the sequence of reactions shown in Scheme 2. We refer to the manganese(III) porphyrin [Mn(TF$_4$TMAP)] as $[Mn^{III}]^+$ and the manganese(V) dioxo complex[12] as $[Mn^{V}(O)]^+$. Chlorite decomposition initiates through electron-transfer reaction with Mn^{III} to give Mn^{IV}(O) and ClO (Cl^{II} species). The latter



Scheme 2. Mechanism for chlorite dismutation catalyzed by [Mn(TF$_4$TMAP)].

has been discussed in reactions leading to ozone depletion,[14] observed in pulse radiolysis experiments,[15] and proposed in the iron-catalyzed decomposition of chlorite in aqueous medium.[13] ClO reacts with ClO_2^- rapidly to give ClO_2 and hypochlorite (ClO^-). The hypochlorite byproduct reacts with Mn^{III} to give Cl^- and Mn^V–oxo. This reaction has been demonstrated independently.[11] $[Mn^V(O)]^+$ undergoes ET with ClO_2^- to give ClO_2 and $Mn^{IV}(O)$. The potential for ClO_2^- oxidation to ClO_2 is -1.071 V, and at pH 7.0 the potential for an analogous Mn^V–oxo to $Mn^{IV}(O)$ is 1.44 V.[16] Therefore, this reaction is thermodynamically favorable and essentially irreversible ($K_{\mathrm{Mn^V/ClO_2^-}} \approx 10^6$). $Mn^{IV}(O)$ is also presumed to react through ET with ClO_2^- to afford ClO_2 and $Mn^{III}–O^-$, which reverts to Mn^{III} through rapid protonation of the oxo group. The reduction potential for $Mn^{IV}(O)$ to Mn^{III} at pH 7.0 based on an analogous porphyrin system is 1.08 V.[16] Therefore, the reaction between $Mn^{IV}(O)$ and ClO_2^- is an equilibrium with $K_{\mathrm{Mn^{IV}/ClO_2^-}} \approx 1.5$. Hence, as ClO_2 accumulates $Mn^{IV}(O)$ builds up and the reaction is inhibited. The rate-determining step is essentially the reaction of Mn^{III} and ClO_2^- and in combination with the reactions in Scheme 2 accounts for most of the catalysis. As ClO_2 and $Mn^{IV}(O)$ build up, a semi-equilibrium is reached and product inhibition is observed. Indeed when ClO_2 is removed by purging the reaction with an inert gas (N_2 for example), chlorite decomposition resumes and quantitative conversion to ClO_2 and Cl^- is observed.

Kinetic simulations of Scheme 2 with $k_1 = 2$, $k_2 = \text{fast}$ ($\geq 10^5$), $k_3 = 20$, $k_4 = 1000$, $k_5 = 100$, $k_{-5} = 60\,\mathrm{M^{-1}\,s^{-1}}$, and protonation of $Mn^{III}–O^-$ being instantaneous provide reasonable agreement with observed concentration changes. The relative rates rather than absolute values of the reactions of Mn^V- and Mn^{IV}–oxo determine how much ClO_2 is formed and the relative ratios of Mn^{III} and Mn^{IV}–oxo in solution. For example, the simulation predicts no accumulation of $Mn^V(O)$ and after around 2 h, 10% of the starting Mn^{III} is present as $Mn^{IV}(O)$, which is in good agreement with experiment.

We have reported herein on the dismutation of chlorite catalyzed by the fluorinated water-soluble manganese porphyrin $[Mn(TF_4TMAP)]$. In contrast to the iron(III) $[Fe(TF_4TMAP)]$-catalyzed reaction, dioxygen is not produced. Instead, ClO_2 is formed and Mn^{IV}–oxo accumulates concurrent with ClO_2^- consumption. The reaction comes to semi-equilibrium at moderate chlorite conversion due to product (ClO_2) inhibition. The reaction can be shifted to give quantitative product by removal of the ClO_2 gas. Scheme 2 presents a series of reactions that account for all of the experimental observations and is consistent with thermodynamic considerations. Our findings present another pathway for chlorite dismutation catalyzed by manganese porphyrin in which ET initiates the catalysis followed by atom-transfer reactions. Our results parallel many of the observations noted for iron(III) and mercury(II)-mediated chlorite decomposition in aqueous medium through redox chemistry.[13,17]

Experimental Section

All reactions were carried out in deionized water obtained from a Millipore Milli-Q Academic TC water purification system. Phosphate buffers were prepared by dissolving mono- and dibasic sodium phosphate. 5,10,15,20-Tetrakis(pentafluorophenyl)porphyrin was purchased from Scientific Frontier. Sodium chlorite was purchased from Sigma and purified by crystallization. The purity was confirmed by ion chromatography and UV/Vis. Chlorite samples even after crystallization contained a few percent chloride and less than 2% chlorate. Potassium monopersulfate ($KHSO_5$ or oxone) was obtained from Acros Organic Chemicals. UV/Vis spectra and kinetics were recorded on a Shimadzu UV-2501PC scanning spectrophotometer equipped with a temperature control cell holder. Ion chromatography was performed on a Dionex DX-500 Liquid Chromatography System equipped with a Dionex LC25 Chromatography Oven, a Dionex ED40 Electrochemical Detector, and a Dionex Ion-Pac AS9-HC ion exchange column. 9 mM Na_2CO_3 was used as eluant. Chromatography calibration standards were prepared in the 0.5–60 mM concentration range. Peaks were identified by comparison to standard samples, and quantified by comparison of the integrals of the signals to standard curves for the corresponding ion. Retention times and peak identities were as follows: chlorite, 4.48 min; chloride, 5.23 min; and chlorate, 7.4 min. ESI mass spectra were obtained using a Finnigan LTQ Linear Ion Trap Mass spectrometer in positive ion mode. Sample was introduced by direct infusion from a syringe pump. $(TF_4DMAP)H_2$ or $(T(p\text{-}Me_2N)F_4PP)H_2$ was synthesized following a literature procedure.[18] The complexes $[Mn(TF_4DMAP)]$ and $[Mn(TF_4TMAP)]$ were prepared according to modified literature methods for their iron counterparts as detailed below.[19] The anion for $[Mn(TF_4TMAP)]$ was triflate.

Synthesis of $[Mn(TF_4DMAP)]$: $[Mn(TF_4DMAP)]$ was prepared by refluxing 200 mg (0.17 mmol) of $(T(p\text{-}Me_2N)F_4PP)H_2$ and 435 mg (1.7 mmol) of $Mn(OAc)_2 \cdot 4\,H_2O$ in DMF for 12 h under N_2 atmosphere. Solvent was removed under reduced pressure and the resulting brown-yellow solid was chromatographed (neutral alumina) with benzene as eluant. UV/Vis data [λ, nm] acetonitrile 365, 474, 575, 606; MS (ESI), *m*/*z* 1127.

Synthesis of $[Mn^{III}(TF_4TMAP)](CF_3SO_3)_5$. $[Mn(TF_4TMAP)]$ was prepared by reacting 100 mg (0.08 mmol) of $[Mn(TF_4DMAP)]$ and 200 μL of trifluoromethanesulfonate stirred in trimethyl phosphate at 60 °C for 12 h under N_2 atmosphere. An immediate color change was observed, brown to red. Methanol (1 mL) was added to destroy any unreacted methyl trifluoromethanesulfonate. A red precipitate was collected after slowly adding the reaction mixture to rapidly stirred diethyl ether. The product was crystallized by vapor diffusion of acetonitrile and diethyl ether. UV/Vis data [λ, nm] 373, 464, 556.

EPR spectra were recorded on a Bruker ESP 300E EPR spectrometer equipped with an HP 5350B microwave frequency counter, an Oxford ITC4 temperature controller, and a VC40 gas flow controller (for liquid He).

Received: August 16, 2010
Revised: September 29, 2010

Keywords: chlorine dioxide · chlorite dismutation · electron transfer · manganese · porphyrinoids

---

[1] *Perchlorate, Environmental Occurrence, Interactions and Treatment* (Eds.: B. Gu, J. D. Coates), Springer, New York, **2006**, p. 411.

[2] J. D. Coates, L. A. Achenbach in *Perchlorate, Environmental Occurrence, Interactions and Treatment* (Eds.: B. Gu, J. D. Coates), Springer, New York, **2006**, pp. 279–291.

[3] a) M. M. Abu-Omar, *Chem. Commun.* **2003**, 2102–2111; b) K. D. Hurley, Y. X. Zhang, J. R. Shapley, *J. Am. Chem. Soc.* **2009**, *131*, 14172–14173.
[4] Chlorine Oxides and Chlorine Oxygen Acids: H. Vogt, J. Balej, J. E. Bennett, P. Wintzer, S. A. Sheikh, P. Gallone, S. Vasudevan, K. Pelin in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, **2010**, p. 55.
[5] J. D. Coates, L. A. Achenbach, *Nat. Rev. Microbiol.* **2004**, *2*, 569–580.
[6] a) B. R. Streit, J. L. DuBois, *Biochemistry* **2008**, *47*, 5271–5280; b) A. Q. Lee, B. R. Streit, M. J. Zdilla, M. M. Abu-Omar, J. L. DuBois, *Proc. Natl. Acad. Sci. USA* **2008**, *105*, 15654–15659.
[7] M. J. Zdilla, A. Q. Lee, M. M. Abu-Omar, *Inorg. Chem.* **2009**, *48*, 2260–2268.
[8] M. J. Zdilla, A. Q. Lee, M. M. Abu-Omar, *Angew. Chem.* **2008**, *120*, 7811–7814; *Angew. Chem. Int. Ed.* **2008**, *47*, 7697–7700.
[9] J. P. Collman, R. Boulatov, C. J. Sunderland, I. M. Shiryaeva, K. E. Berg, *J. Am. Chem. Soc.* **2002**, *124*, 10670–10671.
[10] L. M. Slaughter, J. P. Collman, T. A. Eberspacher, J. I. Brauman, *Inorg. Chem.* **2004**, *43*, 5198–5204.
[11] W. Nam, I. Kim, M. H. Lim, H. J. Choi, J. S. Lee, H. G. Jang, *Chem. Eur. J.* **2002**, *8*, 2067.
[12] N. Jin, M. Ibrahim, T. G. Spiro, J. T. Groves, *J. Am. Chem. Soc.* **2007**, *129*, 12416–12417.
[13] a) I. Fábian, G. Gordon, *Inorg. Chem.* **1992**, *31*, 2144–2150; b) I. Fábian, R. van Eldik, *Inorg. Chem.* **1993**, *32*, 3339–3342; c) I. Fábian, *Coord. Chem. Rev.* **2001**, *216–217*, 449–472.
[14] S. Du, J. S. Francisco, G. K. Schenter, B. C. Garrett, *J. Am. Chem. Soc.* **2009**, *131*, 14778–14785.
[15] G. V. Buxton, M. S. Subhani, *J. Chem. Soc. Faraday Trans. 1* **1972**, *68*, 947–957.
[16] D. Lahaye, J. T. Groves, *J. Inorg. Biochem.* **2007**, *101*, 1786.
[17] a) L. A. Lednicky, D. M. Stanbury, *J. Am. Chem. Soc.* **1983**, *105*, 3098–3101; b) M. G. Ondrus, G. Gordon, *Inorg. Chem.* **1972**, *11*, 985–989; c) B. Z. Shakhashiri, G. Gordon, *J. Am. Chem. Soc.* **1969**, *91*, 1103–1107.
[18] K. M. Kadish, C. Araullo-McAdams, B. C. Han, M. M. Franzen, *J. Am. Chem. Soc.* **1990**, *112*, 8364–8368.
[19] T. La, R. Richards, G. M. Miskelly, *Inorg. Chem.* **1994**, *33*, 3159–3163.