

Contents lists available at ScienceDirect

# Journal of Inorganic Biochemistry



journal homepage: www.elsevier.com/locate/jinorgbio

# Visible light-induced formation of corrole-manganese(V)-oxo complexes: Observation of multiple oxidation pathways



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# A R T I C L E I N F O

Article history: Received 20 April 2016 Received in revised form 2 August 2016 Accepted 4 August 2016 Available online 05 August 2016

Keywords: Manganese(V)-oxo Corroles Visible light Oxidation Kinetics

# ABSTRACT

Two manganese(V)-oxo corroles [ $Mn^{V}(Cor)O$ ] that differ in their electronic environments were produced by visible light irradiation of highly photo-labile corrole-manganese(IV) bromates. The corrole ligands under study include 5,10,15-tris(pentafluorophenyl)corrole (TPFC), and 5,10,15-triphenylcorrole (TPC). The kinetics of oxygen transfer atom (OAT) reactions with various organic reductants by these photo-generated  $Mn^{V}(Cor)O$  were also studied in CH<sub>3</sub>CN and CH<sub>2</sub>Cl<sub>2</sub> solutions.  $Mn^{V}(Cor)O$  exhibits remarkable solvent and ligand effect on its reactivity and spectral behavior. In the more electron-deficient TPFC system and in the polar solvent CH<sub>3</sub>CN,  $Mn^{V}(Cor)O$  returned  $Mn^{III}$  corrole in the end of oxidation reactions. However, in the less polar solvent CH<sub>2</sub>Cl<sub>2</sub> or in the less electron-deficient TPC system,  $Mn^{IV}$  product was formed instead of  $Mn^{III}$ . Furthermore, with the same substrates and in the same solvent, the order of reactivity of  $Mn^{V}(Cor)O$  was TPC> TPFC, which is inverted from that expected based on the electron-demand of corrole ligands. Our spectral and kinetic results in this study provide compelling evidence in favor of multiple oxidation pathways, where  $Mn^{V}(Cor)O$  may serve as direct two-electron oxidant or undergo a disproportionation reaction to form a manganese(VI)-oxo corrole as the true oxidant. The choice of pathways is strongly dependent on the nature of the solvent and the corrole ligand.

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# 1. Introduction

High-valent transition metal-oxo intermediates are of fundamental importance because of their central roles as active oxidizing species in enzymatic and synthetic catalytic oxidations [1–4]. Many transition metal catalysts have been extensively studied as models to probe the sophisticated oxygen atom transfer (OAT) mechanism as well as to invent enzyme-like oxidation catalysts [5–8]. In many cases, however, the active metal-oxo transients are still puzzling due to their high reactivities and/ or low concentrations. Moreover, a high valent metal-oxo species detected in a reaction might not be the true oxidant but a precursor to the true oxidant that is formed in small, undetectable amounts [9]. In this context, metallocorroles have garnered considerable interest in their catalytic properties because they are 19-membered analogues of metalloporphyrins, and have the capacity to access higher metal-oxo species [10-13]. Thus, a number of metallocorroles including metallocorralizines (corralizines = meso-N-substituted tetrazocorroles) [14–17] have been synthesized and explored in a wide variety of catalytic oxidations [14,18–20]. For examples, (imido)manganese(V) [21,22] and (nitrido)manganese(V/VI) corroles [23] are stable enough to be well characterized spectroscopically. In particular, the relatively stable manganese(V)-oxo corroles, abbreviated as Mn-<sup>v</sup>(Cor)O, which can be produced either by chemical oxidation or laser flash

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photolysis (LFP) methods, serve as important mechanistic probes for OAT reactions [24–26]. Nevertheless, the factors controlling their OAT reactivity with organic substrates are not fully understood, deserving further exploration [27]. For example, a well characterized Mn<sup>V</sup>-oxo corrole produced from ozone oxidation of the Mn<sup>III</sup> precursor shows no reactivity toward olefins at room temperature [19]. Similarly, the Mn<sup>V</sup>-oxo complex containing the more electron-deficient corralizine ligand is even more inert [14]. Recent studies reported by Gross and co-workers have suggested that highly electron-demanding corroles-manganese(V)-oxo species directly transfers oxygen atom, while relatively less electron-demanding corroles-managese(V)-oxo complexes undergo disproportionation reaction to generate corrole-managnese(VI)-oxo as the active oxidant [28]. In addition, a study by Yu et al. who measured the pseudo-first order rate constants of a variety of Mn<sup>V</sup>-oxo corroles reacting with alkenes in different solvents indicated that the oxygen atom transfer pathway of these metal-oxo species is solvent-dependent [29].

Photochemical activation of transition metal complexes to produce reactive oxidants has been known for decades [30,31]. Notably, the use of laser flash photolysis methods to generate a variety of high-valent transition metal-oxo species supported by porphyrin and corrole ligands have been well developed [27,32–36]. With photochemical production of reactive metal-oxo transients, one has access to time scales that are much shorter than the fastest mixing experiments. In addition, the kinetics of oxidation reactions by photo-generated metal-oxo species are not convoluted with the rate constants for formation of the reactive transients by reaction of the excess sacrificial oxidant with the

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low-valent metal species [35]. As our ongoing efforts to explore photochemical approaches to access high-valent metal-oxo species, we have utilized photo-induced ligand cleavage reactions to produce trans-dioxoruthenium(VI) porphyrins [37,38] as well as a putative ruthenium(V)-oxo species [39] that was also found in a photo-disproportionation of the bis-porphyrin-ruthenium(IV) µ-oxo dimer [40]. Very recently, we communicated a photo-induced entry to iron(IV)-oxo porphyrin radical cations (compound I models) or iron(IV)-oxo porphyrin (compound II models) as controlled by the electronic nature of porphyrin ligands [41]. In the present work, we report a visible light irradiation of triarylcorrole-manganese(IV) bromate complexes to form manganese(V)-oxo corroles and direct kinetic studies of their OAT reactions with organic reductants. Our kinetic and spectral results illustrate that the photo-generated manganese(V)-oxo corroles may oxidize the substrate through different oxidation pathways, depending on the nature of corrole ligand and the solvent.

# 2. Experimental

# 2.1. Materials

All commercial reagents were of the best available purity and were used as supplied unless otherwise specified. HPLC grade acetonitrile (99.93%) and methylene chloride were distilled over P<sub>2</sub>O<sub>5</sub> prior to use. Iodosylbenzene (PhIO) was purchased from the TCI America Co. and was used as obtained. Tris(4-bromophenyl)ammoniumyl hexachloroantimonate was purchased from Sigma-Aldrich Co and used as such. All reactive substrates, including all alkenes, ethylbenzene, 4-methoxythioanisole, 4-methylthioanisole, 4fluorothioanisole, 4-chlorothioanisole, thioanisole, for mixing kinetic studies were passed through a dry column of active alumina (Grade I) before use. Free corrole ligands including H<sub>3</sub>TPFC [42] and H<sub>3</sub>TPC [43] and their manganese(III) neutral complexes Mn<sup>III</sup>(TPFC) (1a) and Mn<sup>III</sup>(TPC) (1b) were prepared by literature methods and characterized by <sup>1</sup>H NMR, IR and UV-vis spectroscopies, matching those reported [19]. Treatment of manganese(III) species **1** with tris(4-bromophenyl)ammoniumyl hexachloroantimonate gave known corrole-manganese(IV) chloride salts **2** [24]. Compound **2** were further purified through recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/hexane followed by column chromatography on silica gel to remove traces of the amine by-product.

2.2. General procedure for visible light formation of manganese(V)-oxo corroles

Photo-labile compounds **3** were prepared in situ by stirring **2** with excess of Ag(BrO<sub>3</sub>) in anaerobic CH<sub>3</sub>CN, and the formation of bromate products **3** was indicated by the change of UV–vis absorption (Fig. 1). The resulting solutions **3** were used for photochemical studies immediately after preparation. (*Caution! Bromate salts of metal complexes are potentially explosive and should be handled with care*). When the solution of **3** with concentrations of ca.  $2 \times 10^{-5}$  M was irradiated with visible light at ambient temperature, the time-resolved formation of **4** was complete within 2 min as monitored by UV–visible spectroscopy. The same oxo species **4** were also produced by chemical oxidation of **1** with 5-fold excess of PhIO or PhI(OAC)<sub>2</sub> in CH<sub>3</sub>CN.

# 2.3. Instrumentation and kinetic studies

UV–vis spectra were recorded on an Agilent 8453 diode array spectrophotometer. <sup>1</sup>H NMR was performed on a JEOL ECA-500 MHz spectrometer at 298 K with tetramethylsilane (TMS) as internal standard. Chemical shifts (ppm) are reported relative to TMS. IR spectra were obtained on a Bio-Rad FT-IR spectrometer. Kinetic measurements were performed on an Agilent 8453 diode array spectrophotometer interfaced with the Pro-K 2000 Rapid Mixing System (Applied Photophysics) by using standard 1.0-cm quartz cuvettes. Visible light was provided from a SOLA SE II light engine (Lumencor) configured with a liquid light guide. The output power can be adjusted from 6 to 120 W.

Reactions of oxo-species **4** with excess organic substrate (>100 equiv.) were conducted in a solution at  $23 \pm 2$  °C. The approximate concentrations of the photo-generated **4** were estimated by assuming 100% conversion of manganese(IV) precursors in the photochemical reactions. The rates of the reactions which represent the rates of oxo group transfer from Mn<sup>V</sup>(Cor)O to substrate were monitored by the decay of the Soret absorption band of the oxo-species **4**. The kinetic traces at  $\lambda_{max}$  of Soret band displayed good pseudo-first-order behavior for at least four half-lives, and the data was solved to give pseudo-first-order observed rate constants,  $k_{obs}$ . Plots of these values against the concentration of substrate were linear in all cases. The second-order rate constants for reactions of the oxo species with the organic substrates were solved according to Eq. (1), where  $k_0$  is a background rate constant



**Fig. 1.** Axial ligand exchange monitored by UV-visible spectroscopy: (A)  $Mn^{IV}$ (TPFC)Cl (**2a**, dashed) and  $Mn^{IV}$ (TPFC)(BrO<sub>3</sub>) (**3a**, solid) in CH<sub>3</sub>CN; (B)  $Mn^{IV}$ (TPC)Cl (**2b**, dashed) and  $Mn^{IV}$ (TPC)(BrO<sub>3</sub>) (**3b**, solid) in CH<sub>3</sub>CN; (B)  $Mn^{IV}$ (TPC)Cl (**2b**, dashed) and  $Mn^{IV}$ (TPC)(BrO<sub>3</sub>) (**3b**, solid) in CH<sub>3</sub>CN; (B)  $Mn^{IV}$ (TPC)Cl (**2b**, dashed) and  $Mn^{IV}$ (TPC)(BrO<sub>3</sub>) (**3b**, solid) in CH<sub>3</sub>CN; (B)  $Mn^{IV}$ (TPC)Cl (**2b**, dashed) and  $Mn^{IV}$ (TPC)(BrO<sub>3</sub>) (**3b**, solid) in CH<sub>3</sub>CN; (B)  $Mn^{IV}$ (TPC)Cl (**2b**, dashed) and  $Mn^{IV}$ (TPC)(BrO<sub>3</sub>) (**3b**, solid) in CH<sub>3</sub>CN; (B)  $Mn^{IV}$ (TPC)Cl (**2b**, dashed) and  $Mn^{IV}$ (TPC)(BrO<sub>3</sub>) (**3b**, solid) in CH<sub>3</sub>CN; (B)  $Mn^{IV}$ (TPC)Cl (**2b**, dashed) and  $Mn^{IV}$ (TPC)(BrO<sub>3</sub>) (**3b**, solid) in CH<sub>3</sub>CN; (B)  $Mn^{IV}$ (TPC)Cl (**2b**, dashed) and  $Mn^{IV}$ (TPC)(BrO<sub>3</sub>) (**3b**, solid) in CH<sub>3</sub>CN; (B)  $Mn^{IV}$ (TPC)(BrO<sub>3</sub>) (**3b**, solid) in CH<sub>3</sub>CN; (B) M



**Scheme 1.** Photochemical formation of corrole-manganese(V)-oxo complexes by visible light irradiation of manganese(IV) bromates.

found in the absence of added substrate,  $k_{ox}$  is the second-order rate constant for reaction with the substrate, and [Sub] is the concentration of substrate. All second-order rate constants are averages of 2–3 determinations consisting of 3 independent kinetic measurements. Errors in the rate constants were weighted and are at  $2\sigma$ .

$$k_{obs} = k_0 + k_{ox}[Sub] \tag{1}$$

# 3. Results and discussions

#### 3.1. Visible light formation of corrole-manganese(V)-oxo complexes

As shown in Scheme 1, two manganese(III) corroles (1) with different electronic environments were comparatively studied in this work. Mn<sup>III</sup>(TPFC) (1a) and Mn<sup>III</sup>(TPC) (1b) were both known and synthesized according to the reported procedure [19,27]. As noticed in early reports [13,44], compound 1a is significantly stable in solutions; however, in CH<sub>2</sub>Cl<sub>2</sub> the less electron-deficient 1b can be oxidized into Mn<sup>IV</sup> corrole. Oxidation of the neutral triarylcorrole–manganese(III) species 1 with tris(4-bromophenyl)ammoniumyl hexachloroantimonate gave the corrole–manganese(IV) chloride salts 2 [24]. Facile exchange of the counterions in 2 with excess amount of Ag(BrO<sub>3</sub>) gave the corresponding bromate salts 3, and its formation was indicated by the UV–vis spectra. These species 3 were highly photo-labile and attempts to isolate and spectroscopically characterize 3 more fully were not successful. Thus, they were prepared in situ and immediately used for photochemical reactions after preparation.

Irradiation of bromate complex 3 in anaerobic CH<sub>3</sub>CN with visible light from a SOLA engine (output power 60 W) resulted in formation of corrole-manganese(V)-oxo species in two different systems, i.e. the electron-deficient 4a (Fig. 2A), and the non-electron-deficient 4b (Fig. 2B). By considering the electrophilic nature of the corrolemanganese(V)-oxo species, one can expect that the order of apparent stability is TPFC < TPC. These time-resolved UV-vis absorption spectra show decay of photo-labile precursors (3) and growth of the oxo products (4) with clean isosbestic points at specific wavelengths labeled in Fig. 2. As evident, the species 4a displayed split Soret bands that are distinct with a stronger blue-shifted band. In comparison to 4a, the absorption spectrum of the less electron-deficient 4b was similar in shape, but with a significantly weaker blueshifted Soret band shown as a shoulder. Of note, the spectra of visible light-generated 4a and 4b matched those reported previously from ozone or PhIO oxidation of corresponding manganese(III) precursors 1 (see Fig. S1 in the Supplementary material) [19,25]. The formation of 4a by photochemical oxidation was also observed with a slower rate compared to that of **4b**. In the TPFC system, the oxidation of  $Mn^{IV}$  species **3a** from the highly electron-deficient corrole is apparently not favored in view of the expected high oxidation potential. On the contrary, the TPC system has the less electron-withdrawing aryl groups on the corrole ring; as thermodynamically favored; the 3b undergoes photo-oxidation to form 4b more readily.

Laser flash photolysis (355 nm) of corrole-Mn<sup>IV</sup>(ClO<sub>3</sub>) complexes gave Mn(V)-oxo species by homolytic cleavage of an O-Cl bond [27]. Photolysis of porphyrin- $Ru^{IV}(XO_3)_2$  (X = Cl and Br) complexes was also reported to produce trans-dioxoruthenium(VI) species through analogous homolytic cleavage of the O-X bond [37,38]. Clearly, visible light irradiation of bromates 3 represents the same homolysis manifold that results in one-electron photo-oxidation to afford corrolemanganese(V)-oxo species 4. Of note, we found that photochemical cleavages of the bromate complexes were considerably more efficient and faster than cleavages of chlorate complexes (see Fig. S2 in the Supplementary material). Control experiments showed that no species 4 was formed in the absence of light. As expected, using more intensive visible light (ca. 120 W) resulted in about four times faster formation of 4a under same conditions. However, significant photo-degradation was found for 4b with high intensity light. The use of other solvents such as CH<sub>2</sub>Cl<sub>2</sub> or EtOAc also gave similar results. However, no oxo formation was observed when CH<sub>3</sub>OH or THF was used. Presumably, the weakly binding bromate or chlorate counterions were displaced by these coordinating solvents.



**Fig. 2.** (A) Time-resolved formation spectra of **4a** (red line) following irradiation of **3a** ( $7.0 \times 10^{-6}$  M) over 80 s with visible light in anaerobic CH<sub>3</sub>CN solution at 23 °C; (B) Spectra of **4b** (red line) following irradiation of **3b** ( $8.0 \times 10^{-6}$  M) over 30 s with visible light. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 3. Time-resolved spectra of 4a reacting (A) in CH<sub>3</sub>CN with cyclohexene (0.5 M) over 1000s. Inset shows kinetic traces for decay of 4a (348 nm) and formation of Mn<sup>III</sup> (465 nm). (B) In CH<sub>2</sub>Cl<sub>2</sub> with cyclohexene (0.5 M) over 300 s. Inset shows kinetic traces for decay of 4a (346 nm) and formation of Mn<sup>IV</sup> (430 nm).

# 3.2. Kinetic and spectral studies

Oxidation kinetics of photo-generated oxo species 4 with alkenes, activated hydrocarbon, and thioanisoles were investigated. In kinetic studies, solutions containing the oxo 4 were mixed with solutions containing large excesses of organic substrate, and pseudo-first-order rate constants for decay of the manganese(V)-oxo species were measured spectroscopically. Early report indicates the rates of reactions of corrole-manganese(V)-oxo species were dependent on its concentration [27]. Thus, we produced transients 4 in a similar concentration of approximate 2.  $0 \times 10^{-5}$  M for all kinetic studies. Fig. 3 shows the UV-vis spectra changes of 4a in the presence of organic substrate in different solvents. Fig. 3A shows the clean conversion of 4a in CH<sub>3</sub>CN to regenerate the Mn<sup>III</sup> species with a distinct peak at 465 nm. The decrease in absorbance at 348 nm corresponding to the decay of 4a was accompanied by an isosbestic growth at 465 nm characteristic formation of Mn<sup>III</sup> species (inset in Fig. 3A). The traces were fit to single-exponential decay, as expected for reactions under pseudo-first-order conditions. When CH<sub>2</sub>Cl<sub>2</sub> was used as the solvent instead of CH<sub>3</sub>CN, Fig. 3B shows that the species 4a regenerated a Mn<sup>IV</sup> species which was characterized by its known  $\lambda_{max}$  at 430 nm. This observation is in accord with previous LFP studies of 4a, which was also found to give Mn<sup>IV</sup> species in CH<sub>2</sub>Cl<sub>2</sub> solutions after the reaction [27]. In contrast, in both solvents reactions of the less electron-deficient **4b** returned Mn<sup>IV</sup> species only and there was no evidence for accumulation of any Mn<sup>III</sup>(TPC) during the reaction(See Fig. S3 in the Supplementary material). It is worth to point out that the formation of the Mn<sup>IV</sup> species in these reactions does not implicate one-electron reactions because the decay reactions are relatively slow.

Although the decay reactions of species 4 were complex in different solvents and corrole systems, apparent pseudo-first-order decay rate constants for 4 increased linearly as a function of substrate concentration (Fig. 4), thus permitting calculation of apparent second-order rate constants  $(k_{ox})$  for various substrates (Table 1). The trend of the  $k_{ox}$ values in Table 1 clearly parallels the substrate reactivity; for examples, organic sulfides are about 3 or 4 orders of magnitude more reactive than alkenes or ethylbenzene with the same oxo species. Of note, the  $k_{ox}$ values for cyclohexene are in good agreement with the values for oxidant 4a produced from the chemical oxidation method. For the parasubstituted thioanisoles (Y-thioanisoles; Y = 4-MeO, 4-Me, 4-F, and 4-Cl), we observed a significant substituent dependence on the second-order rate constants, as reflected in the Hammett plot shown Fig. 4B. A linear correlation (R = 0.99) of  $\log k_{rel} [k_{rel} = k(para-Y$ thioanisole)/k(thioanisole)] versus Hammett  $\sigma^+$  substituent constant [45] gave the slope ( $\rho^+$ ) of the plot as  $-1.34 \pm 0.18$ , which reflects the degree of positive charge development on the styrene in the transition states for the oxo transfer reactions. Similar values were also found with species 4a generated by the chemical method in different solvent (EtOAc) [28]. The Hammett correlation results strongly suggest that the observed manganese(V)-oxo species is likely to be the active oxidant which transfers an oxygen atom to thioanisoles through an electrophilic mechanism.



Fig. 4. (A) Plots of the observed rate constants ( $k_{obs}$ ) versus the concentration of *para*-substituted thioanisoles; (B) Hammett plot for oxidations of *para*-substituted thioanisoles with 4a in CH<sub>3</sub>CN.

#### Table 1

Apparent second-order rate constants  $(k_{ox})$  for reactions of photo-generated corrolemanganese(V)-oxo species<sup>a</sup>.

Oxo	Substrate	$k_{\rm ox}({\rm M}^{-1}{\rm s}^{-1})$	
		CH <sub>3</sub> CN	CH <sub>2</sub> Cl <sub>2</sub>
4a 4b	Cyclohexene Cyclohexene <sup>b</sup> cis-Cyclooctene PhEt Styrene PhSMe p-MeO-PhSMe p-F-PhSMe p-Cl-PhSMe Cyclohexene cis-Cyclooctene PhEt PhSMe p-MeO-PhSMe p-F-PhSMe	$\begin{array}{c} (3.4\pm0.2)\times10^{-3}\\ (3.9\pm0.4)\times10^{-3}\\ (2.9\pm0.2)\times10^{-3}\\ (1.4\pm0.1)\times10^{-4}\\ (3.0\pm0.1)\times10^{-3}\\ 4.9\pm0.4\\ 62.0\pm0.7\\ 22.0\pm0.6\\ 6.7\pm0.5\\ 3.6\pm0.3\\ (10.0\pm1.0)\times10^{-2}\\ (5.0\pm0.6)\times10^{-2}\\ (2.1\pm0.3)\times10^{-3}\\ 6.0\pm0.8\\ 85.5\pm2.4\\ 24.8\pm1.5 \end{array}$	$\begin{array}{c} (1.6\pm0.2)\times10^{-2}\\ (1.5\pm0.1)\times10^{-2}\\ (11.0\pm0.9)\times10^{-3}\\ (2.7\pm0.3)\times10^{-4} \end{array}$

 $^a~$  In CH<sub>3</sub>CN or CH<sub>2</sub>Cl<sub>2</sub> with a concentration of 2.0  $\times$  10 $^{-5}$  M at 23  $\pm$  2 °C. The values are average of 3 runs with 2 $\sigma$  standard deviation.

<sup>b</sup> From **4a** generated by chemical oxidation of **1a** [25].

#### 3.3. Mechanistic consideration for multiple oxidation pathways

One of the noteworthy aspects of the manganese(V)-oxo kinetics is the fact that a remarkable solvent effect on the reactivity and spectral behavior of **4a** was observed. In addition to decaying back to Mn<sup>IV</sup> corrole in CH<sub>2</sub>Cl<sub>2</sub> solution, 4a exhibited higher reactivity in CH<sub>2</sub>Cl<sub>2</sub> than that in CH<sub>3</sub>CN with same substrates. Owing to the electrophilic nature of high-valent metal-oxo species, one typically observes that more electron-withdrawing ligands give more reactive metal-oxo derivatives. For the two corrole systems studied here, however, the reactivity order is inverted with the system of less electron demand, i.e. the triphenylcorrole complex 4b apparently reacting faster with any given substrate than the more electron-deficient 4a. These kinetic results strongly support the previously proposed mechanistic model involving disproportionation of 4 to give Mn<sup>IV</sup> corrole and a more reactive corrolemanganese(VI)-oxo cationic species (5) as the predominant oxidants in these systems [19,27,28]. Importantly, the report of a well-characterized corrole-manganese(VI)-nitrido species suggests that such high oxidation state manganese species are accessible [23]. In practice, the concentration of 5 might be too small to permit observation, and the major species observed spectroscopically is still 4. If complexes 5 are the actual oxidants, then the equilibrium reactions for formation of these species should be more favorable for the ligand that has the less electron demand. Accordingly, the observed kinetics could reflect the populations of species 5 controlled by the disproportionation equilibrium constant which should be larger for the TPC ligand [27]. The mechanistic model is similar to that proposed for reactions of neutral porphyrin-manganese(IV)-oxo species, where the actual oxidants in



Scheme 2. Two oxidation pathways of corrole-manganese(V)-oxo species controlled by the nature of ligands and solvents. The parallelogram represents a corrole structure and subs stands for organic substrates.

the systems apparently are cationic porphyrin–manganese(V)-oxo species formed in disproportionation equilibria [9].

In view of the above significant decaying spectra and the rate constants of photo-generated species 4, we propose that the oxidation of organic substrates by corrole-manganese(V)-oxo corroles may proceed via two different pathways as shown in Scheme 2. In the more electrondeficient corrole system and in the polar solvent CH<sub>3</sub>CN, the active oxidizing specie is Mn<sup>V</sup>-oxo corrole, and the dominant pathway is the electrophilic reaction between Mn<sup>V</sup>-oxo corrole and substrate (Scheme 2, path a). In this situation, Mn<sup>III</sup> corrole was observed in the end of reaction. When the less polar solvent CH<sub>2</sub>Cl<sub>2</sub> and/or the less electron-deficient system were involved, the direct OAT process becomes progressively less favorable and the disproportionation reaction of species **4** (path b) to form Mn<sup>VI</sup>-oxo (**5**) as the active oxidant gains dominance. As outlined in Scheme 2, photo-disproportionation of 4 gives the highly reactive manganese(VI)-oxo 5 in addition to one molecule of a Mn<sup>IV</sup> product; oxidation of an organic reductant by **5** gives a second molecule of Mn<sup>IV</sup> product. During the course of the reaction, the proposed Mn<sup>VI</sup>-oxo **5** was not accumulated to be detected because it reacts much faster than it is formed. This mechanism provided a rationalization for the inverted reactivity patterns for **4** as well as the final Mn<sup>IV</sup> product formation observed during the course of reactions. It is worth noting that remarkable solvent and ligand effects on the participation of multiple active oxidants were previously known in heme- and nonheme-manganese(III) catalyzed oxidation reactions [46,47].

#### 4. Conclusions

In conclusion, we report here a new photochemical entry to produce and study high-valent corrole-manganese(V)-oxo derivatives by visible light irradiation of the corresponding manganese(IV) bromate complexes. The photochemistry is ascribed to the homolytic cleavage of the O—Br bond in the bromate ligand that results in an one-electron oxidation of the manganese (IV) to generate the manganese(V)-oxo species. We have observed the remarkable effect of the nature of the corrole ligand and the solvent on oxidation pathways of these high-valent corrole-metal-oxo intermediates. Our kinetic and spectral findings in this work provide compelling evidence to support multiple oxidation pathways of biomimetic corrole-Mn<sup>V</sup>-oxo species. A thorough investigation of solvent effects on the reactivities of various manganese(V)-oxo corroles derived from different electron-rich and electron-poor substituents are currently underway in our laboratory.

#### Abbreviations

CorcorroleTPFC5,10,15-tripentafluorophenylcorrole trianionTPC5,10,15-triphenylcorrole trianionPhIOiodosylbenzeneLFPlaser flash photolysisOAToxygen atom transfer

#### Acknowledgments

We greatly acknowledge the National Science Foundation (CHE 1464886) and Kentucky NSF EPSCoR program (REG 2015) for support of this research. K. W. Kwong is grateful to the Graduate School of WKU for a Graduate Student Research Fellowship (GSRF). D. Ranburger and J. Malone are thankful to the WKU Office of Research for awarding internal FUSE grants.

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.jinorgbio.2016.08.004.

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