



## Research paper

# Synthetic and mechanistic investigations on manganese corrole-catalyzed oxidation of sulfides with iodobenzene diacetate



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## ABSTRACT

Manganese corrole complexes catalyze the efficient oxidation of organic sulfides to sulfoxides with iodobenzene diacetate [PhI(OAc)<sub>2</sub>] as a mild oxygen source in the presence of small amounts of water. Various substituted thioanisoles can be efficiently oxidized to sulfoxides with quantitative conversions (up to 2500 TONs) and excellent selectivities for sulfoxides. The catalyst effects, including the corrole ligands and oxidation states of the central manganese, were investigated, and showed a significant impact on the catalytic sulfoxidations. The previously known high-valent manganese(V)-oxo corroles were chemically generated and kinetically studied in the oxidation of thioanisole substrates. The competition results suggested the oxidation state of manganese metal is crucial to control the nature of active oxidant forms that significantly affected their catalytic activity.

## 1. Introduction

In both nature and the laboratory, organic sulfoxides are valuable synthetic intermediates in biological systems for production of natural products, ligands for catalysis, and significant biological molecules [1–3]. Meanwhile, optically active sulfoxides play important roles in medicinal and pharmaceutical fields for the production of compounds such as antiulcer (proton pump inhibitors), antibacterial, antifungal, antihypertensive, and cardiotoxic agents, as well as psychotropics and vasodilators [4]. In addition, oxidative desulfurization is a promising method in industry to remove sulfur-containing air pollutants [5]. To date, various catalysts including metal complexes, polyoxometalates, and flavins have been reported in the literature for the catalytic oxidation of sulfides to sulfoxides commonly with H<sub>2</sub>O<sub>2</sub> or organic peroxides [6–11]. However, the use of these strong oxidants often results in oxidative degradation of the catalyst due to their oxidizing potency. Moreover, many of these methods cause the over-oxidation to sulfones, and/or involve strong oxidizing agents and highly toxic oxo-metal oxidants that have proven to be detrimental for the environment [12]. Thus, there is still a great need for design and development of more selective and greener sulfoxidation catalysts that can provide an ideal combination of excellent selectivity, high activity, broad substrate scope, and mild reaction conditions.

In recent years, advances in facile synthesis of the 19-membered macrocyclic triarylcorroles as trianionic and aromatic porphyrin-like ligands propelled seemingly increased interests in corrole chemistry, ranging from oxidation chemistry of the corresponding corrole metal complexes (metallocorroles) to biochemical and practical applications in chemistry and biology [13–16]. In particular, a large number of metallocorroles and metallocorrolazines (corrolazine = meso-*N*-substituted triazocorroles) have been prepared and exploited in a wide variety of catalytic oxidations including epoxidation, hydroxylation, aziridination, sulfoxidation, and atom transfer reactions [17–21]. For examples, Gross and coworkers reported the first example of catalytic oxidation with the iron(IV) and manganese(III) complexes of tris(pentafluorophenyl)corrole (H<sub>3</sub>TPFC) using iodobenzene (PhIO) as the sacrificial oxidant [22]. Later, biomimetic oxidations with [Mn<sup>III</sup>(TPFC)(OEt<sub>2</sub>)<sub>2</sub>] [23], albumin-conjugated manganese [24], and chromium corroles [25] were also studied by the same group of authors. Perhalogenation of the corrole macrocycle with bromine or fluorine results in increased reactivity for the corrole–manganese complexes under catalytic conditions with PhIO [26,27]. Catalytic aerobic oxidations by a fluorinated iron(IV)  $\mu$ -oxo biscorrole through a photo-disproportionation pathway was also reported [28].

One problem associated with metallocorrole catalysts is that metallocorroles are prone to oxidative degradation in the presence of

**Abbreviations:** Cor, corrole; TPC, 5,10,15-triphenylcorrole trianion; 4<sup>t</sup>Bu-TPC, 5,10,15-tris(4-tert-butylphenyl)corrole trianion; 4-NO<sub>2</sub>-TPC, 5,10,15-tris(4-nitrophenyl)corrole trianion; TPFC, 5,10,15-tripentafluorophenylcorrole trianion; TPFP, 5,10,15, 20-tetrakis(pentafluorophenyl)porphyrin dianion; PhI(OAc)<sub>2</sub>, iodobenzene diacetate; PhIO, iodosylbenzene; *m*-CPBA, *m*-chloroperoxybenzoic acid; TONs, turnover numbers; OAT, oxygen atom transfer

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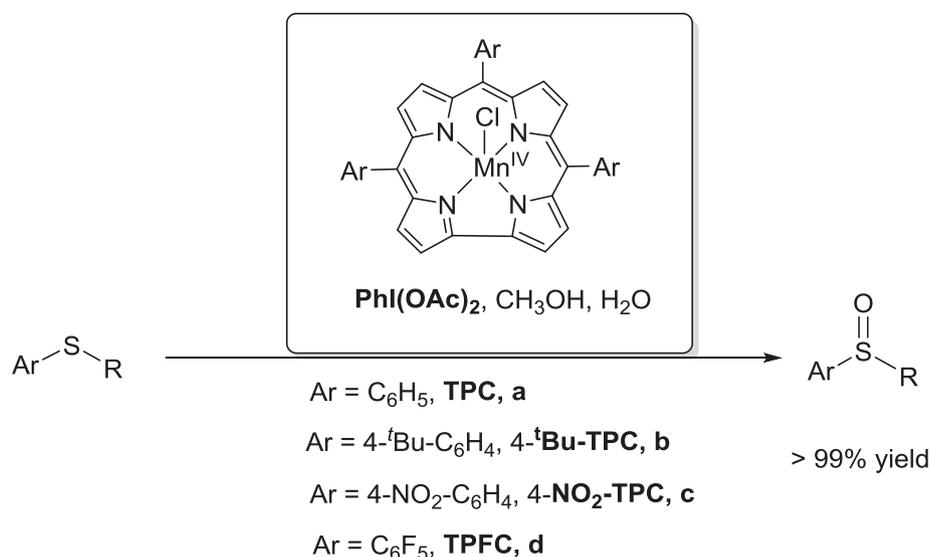
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**Scheme 1.** Catalytic sulfoxidations by manganese corroles in the presence of  $\text{PhiI(OAc)}_2$  and water.

commonly used sacrificial oxygen sources such as meta-chloroperoxybenzoic acid (*m*CPBA) and  $\text{PhIO}$ . In contrast, the less commonly used iodobenzene diacetate [ $\text{PhiI(OAc)}_2$ ] does not damage the metal catalysts nor show appreciable reactivity to the substrate under normal catalytic conditions [29,30]. Recently, our studies revealed the efficient and selective oxidations of alkenes and organic sulfides with  $\text{PhiI(OAc)}_2$  catalyzed by electron deficient iron(III) corroles [31,32]. The inherently low stability of the corrole-catalyst against degradation was significantly improved owing to the mild oxidizing power of  $\text{PhiI(OAc)}_2$ . In this work, we further explore the usefulness of  $\text{PhiI(OAc)}_2$  for the efficient and chemoselective oxidation of sulfides using a series of manganese corrole catalysts (Scheme 1). In most cases, aromatic sulfides have been successfully oxidized to the corresponding sulfoxides with quantitative conversions and excellent selectivities for sulfoxides. Furthermore, our mechanistic studies show that a low-reactivity corrole-manganese(V)-oxo intermediate, which was detected by the oxidation of the manganese(III) corrole with  $\text{PhiI(OAc)}_2$ , is not likely the sole oxidant. Instead, a more reactive and higher oxidation form oxidant, possibly corrole-manganese(VI)-oxo species, is suggested from the competition studies as the premier active oxidant for the manganese (IV) corrole-catalyzed sulfoxidation reactions.

## 2. Experimental

### 2.1. Materials and instrumentation

All commercial reagents were of the best available purity and used as supplied unless otherwise specified. Iodobenzene diacetate or (diacetoxyiodo)benzene, i.e.  $\text{PhiI(OAc)}_2$ , was purchased from Aldrich Chemical Co. and used as such. Pyrrole (98%), benzaldehyde and pentafluorobenzaldehyde from Sigma-Aldrich Chemical Company were distilled prior to use. All reactive substrates of organic sulfides for catalytic oxidations were passed through a dry column of active alumina (Grade I) before use. UV-vis spectra were recorded on an Agilent 8453 diode array spectrophotometer.  $^1\text{H}$  NMR was performed on a JEOL ECA-500 MHz spectrometer at 298 K with tetramethylsilane (TMS) as internal standard. Gas chromatograph analysis was conducted on an Agilent GC-7820A/MS-5975 equipped with a flame ionization detector (FID) using a DB-5 capillary column. The above GC-MS system is also coupled with an auto sample injector. Electrospray ionization-mass spectroscopy (ESI-MS) data was collected on an Agilent 500 LCMS ion trap system. Reactions of  $\text{Mn}^{\text{III}}(\text{Cor})$  with excess of  $\text{PhiI(OAc)}_2$  were conducted in a anaerobic methanol solution at  $23 \pm 2^\circ\text{C}$ , monitored

by the UV-vis spectrometer.

Non-metallated corroles used in this study, including 5,10,15-triphenylcorrole ( $\text{H}_3\text{TPC}$ , **a**) [14] and 5,10,15-tripentafluorophenylcorrole ( $\text{H}_3\text{TPFC}$ , **d**) [13], were prepared following the earlier reported procedures, and their characterization data ( $^1\text{H}$  NMR and UV-vis) was consistent with reported values. 5,10,15-Tris(4-tert-butylphenyl)corrole [ $\text{H}_3(4\text{-}^t\text{Bu-TPC})$ , **b**], 5,10,15-tris(4-nitrophenyl)corrole [ $\text{H}_3(4\text{-NO}_2\text{-TPC})$ , **c**] and 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin ( $\text{H}_2\text{TPFP}$ ) were purchased from Sigma-Aldrich Co and used as received. The corrole-manganese(III) dietherate complexes (**1**) were prepared as previously described [33]. In a typical procedure, a solution of  $\text{H}_3\text{TPC}$  (50 mg, 63  $\mu\text{mol}$ ) and a large excess of manganese(II) acetate (200 mg) in dry DMF under argon was heated at reflux for 30 min. Evaporation of solvent followed by column chromatography on silica gel (diethyl ether) resulted in isolation of the corresponding [ $\text{Mn}^{\text{III}}(\text{TPC})(\text{OEt}_2)_2$ ] (**1a**) in 60% yield. [ $\text{Mn}^{\text{III}}(\text{TPFP})\text{Cl}$ ] was also prepared and purified in a similar fashion. Following the known procedure [33,34], treatment of manganese(III) species **1** with tris(4-bromophenyl)ammoniumyl hexachloroantimonate gave known corrole-manganese(IV) chloride salts **2** in varied yields depending on the corrole ligands. Compounds **2** were further purified through recrystallization from  $\text{CH}_2\text{Cl}_2$ /hexane followed by column chromatography on silica gel to remove traces of the amine byproduct. All the known manganese complexes used in this study were characterized and confirmed by UV-vis spectra and ESI-MS (below), matching those previously reported [34,35].

**[Mn<sup>III</sup>(TPC)(Et<sub>2</sub>O)<sub>2</sub>] [1a]:** Yield = 70%; UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}/\text{nm}$  (relative  $\epsilon$ ): 403 (0.89), 431 (1.00), 651 (0.18); ESI-MS:  $m/z$ : 578.21 [ $\text{M}]^+$

**[Mn<sup>III</sup>(4-<sup>t</sup>Bu-TPC)(Et<sub>2</sub>O)<sub>2</sub>] [1b]:** Yield = 82%; UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}/\text{nm}$  (relative  $\epsilon$ ): 400 (0.97), 438 (1.00), 500 (0.38), 650 (0.34) ESI-MS:  $m/z$ : 746.39 [ $\text{M}]^+$

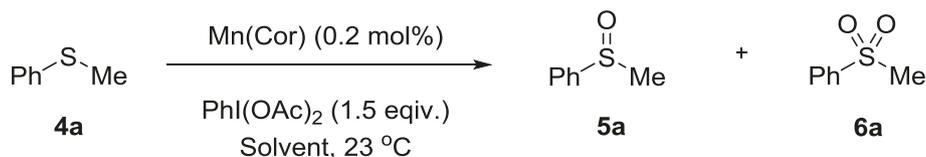
**[Mn<sup>III</sup>(4-NO<sub>2</sub>-TPC)(Et<sub>2</sub>O)<sub>2</sub>] [1c]:** Yield = 31%; UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}/\text{nm}$  (relative  $\epsilon$ ): 428 (1.00), 480 (0.99), 658 (0.40); ESI-MS:  $m/z$ : 713.10 [ $\text{M}]^+$

**[Mn<sup>III</sup>(TPFC)(Et<sub>2</sub>O)<sub>2</sub>] [1d]:** Yield = 87%. UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}/\text{nm}$  (relative  $\epsilon$ ): 400 (0.96), 415 (1.00), 469 (0.69), 598 (0.28); ESI-MS:  $m/z$ : 848.19 [ $\text{M}]^+$

**[Mn<sup>IV</sup>(TPC)Cl] [2a]:** Yield = 90%; UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}/\text{nm}$  (relative  $\epsilon$ ): 364 (0.72), 430 (1.00), 603 (0.24); ESI-MS:  $m/z$ : 578.11 [ $\text{M} - \text{Cl}]^+$ , 613.05 [ $\text{M}]^+$

**[Mn<sup>IV</sup>(4-<sup>t</sup>Bu-TPC)Cl] [2b]:** Yield = 94%; UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}/\text{nm}$  (relative  $\epsilon$ ): 366 (0.83), 440 (1.00), 605 (0.22); ESI-MS:  $m/z$ : 780.42 [ $\text{M}]^+$ , 746.39 [ $\text{M} - \text{Cl}]^+$

**Table 1**  
Catalytic oxidation of thioanisole by manganese corroles with iodobenzene diacetate.<sup>a</sup>



| Entry          | Catalyst                                      | Solvent            | H <sub>2</sub> O (μL) | Time (h) | Convsn. (%) <sup>b</sup> | Selectivity (5a:6a) <sup>b</sup> |
|----------------|---|--------------------|-----------------------|----------|--------------------------|----------------------------------|
| 1              | [Mn <sup>IV</sup> (TPC)Cl]                    | CH <sub>3</sub> OH | 0                     | 1        | 51                       | 95:05                            |
| 2              |   |                    | 5                     | 1        | 93                       | 95:05                            |
| 3              |   |                    | 18                    | 0.5      | 100                      | 96:04                            |
| 4              |   | CHCl <sub>3</sub>  | 5                     | 1        | 10                       | 90:10                            |
| 5              |   | CH <sub>3</sub> CN | 5                     | 1        | 43                       | 85:15                            |
| 6              | [Mn <sup>III</sup> (TPC)]                     | CH <sub>3</sub> OH | 18                    | 1        | 21                       | 93:07                            |
| 7              | [Mn <sup>IV</sup> (4- <sup>t</sup> Bu-TPC)Cl] | CH <sub>3</sub> OH | 18                    | 0.5      | 100                      | 96:04                            |
| 8 <sup>c</sup> |   |                    | 18                    | 2        | 100                      | 95:05                            |
| 9              | [Mn <sup>III</sup> (4- <sup>t</sup> Bu-TPC)]  | CH <sub>3</sub> OH | 18                    | 1        | 36                       | 93:07                            |
| 10             | [Mn <sup>IV</sup> (4-NO <sub>2</sub> -TPC)Cl] | CH <sub>3</sub> OH | 18                    | 1        | 80                       | 95:05                            |
| 11             | [Mn <sup>IV</sup> (TPFC)Cl]                   | CH <sub>3</sub> OH | 18                    | 1        | 80                       | 90:10                            |
| 12             | [Mn <sup>III</sup> (TPFPP)Cl]                 | CH <sub>3</sub> OH | 18                    | 1        | 54                       | 68:32                            |

<sup>a</sup> All reactions were performed in solvent (2 mL) at ca. 23 °C with a 1:1.5 M ratio of thioanisole versus PhI(OAc)<sub>2</sub> and 0.2 mol% catalyst at an initial substrate concentration of 0.25 M.

<sup>b</sup> Conversions (convn.) and product selectivity were determined by quantitative GC–MS analysis with a DB-5 capillary column on the crude reaction mixture.

<sup>c</sup> 0.04 mol% catalyst loading.

[Mn<sup>IV</sup>(4-NO<sub>2</sub>-TPC)Cl] [**2c**]: Yield = 36%; UV–vis (CH<sub>2</sub>Cl<sub>2</sub>) λ<sub>max</sub>/nm (relative ε): 363 (0.50), 424 (1.00), 602 (0.12); ESI-MS: *m/z*: 748.99 [M]<sup>+</sup>, 713.15 [M–Cl]<sup>+</sup>

[Mn<sup>IV</sup>(TPFC)Cl] [**2d**]: Yield = 89%. UV–vis (CH<sub>2</sub>Cl<sub>2</sub>) λ<sub>max</sub>/nm (relative ε): 361 (0.68), 416 (1.00), 593 (0.14); ESI-MS: *m/z*: 884.05 [M]<sup>+</sup>, 848.15 [M–Cl]<sup>+</sup>

## 2.2. General procedure for catalytic oxidations

Unless otherwise specified, all catalytic reactions were typically carried out in the presence of a small amount of H<sub>2</sub>O (15 μL) with 1 μmol of catalyst (ca. 0.2 mol%) in 2 mL of methanol containing 0.5 mmol of organic substrates. PhI(OAc)<sub>2</sub> (0.75 mmol, 1.5 equiv.) was then added to the reaction solution at 23 ± 2 °C. Aliquots of the reaction solution at constant time intervals were analyzed by GC–MS to determine the conversions, products formed, and yields. The pure products were isolated by a flash column chromatography (silica gel with CH<sub>2</sub>Cl<sub>2</sub> and hexane mixture) to give isolated yields (Table 2, entries 1 and 2). All reactions were performed at least 3 times, and the data reported represents the average of these reactions. Monitoring reaction by UV–vis spectroscopy before and after reactions indicated that no significant degradation of the manganese catalysts was found after catalytic reactions.

## 2.3. Kinetic studies

Chemical oxidation of corresponding manganese(III) complexes (**1**) with ca. 10 equivalent of PhI(OAc)<sub>2</sub> was conducted in two corrole systems, which gave the known manganese(V)-oxo corroles, i.e. [Mn<sup>V</sup>(Cor)O] (**3**). Following its formation *in situ*, oxidation reactions of **3** with excess sulfide substrate (> 100 equiv.) were conducted in a solution at 23 ± 2 °C. The approximate concentrations of the chemically-generated **3** were estimated by assuming 100% conversion of manganese(III) precursors. 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 **3**. The kinetic traces at λ<sub>max</sub> of the 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*<sub>obs</sub>. 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 sulfides were solved according to Eq. (1), where *k*<sub>0</sub> is a background rate constant found in the absence of added substrate, *k*<sub>ox</sub> 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 reported at 2σ.

$$k_{\text{obs}} = k_0 + k_{\text{ox}}[\text{Sub}] \quad (1)$$

## 2.4. Competition and Hammett correlation studies

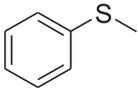
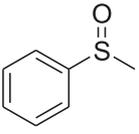
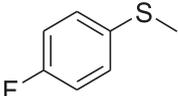
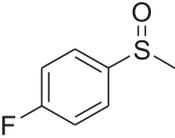
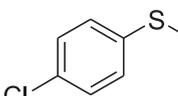
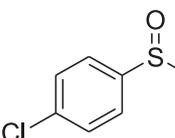
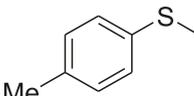
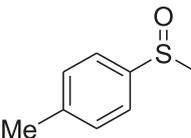
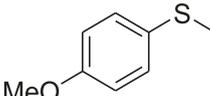
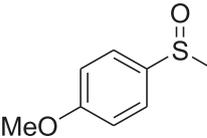
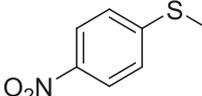
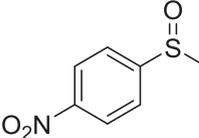
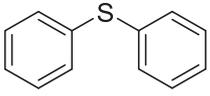
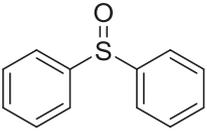
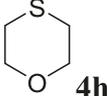
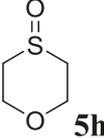
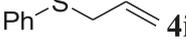
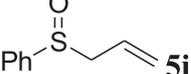
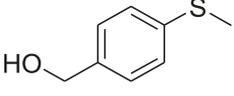
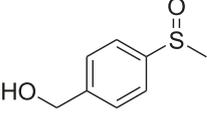
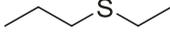
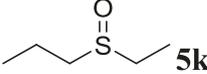
A CH<sub>3</sub>OH solution containing equal amounts of two substrates, e.g. thioanisole (0.5 mmol) and substituted thioanisoles (0.5 mmol), manganese(III) or manganese(IV) corrole catalyst (1 μmol) and an internal standard of 1,2,4-trichlorobenzene (0.1 mmol) was prepared (final volume = 2 mL). PhI(OAc)<sub>2</sub> (0.2 mmol) as the limiting reagent, was added and the mixture was stirred at ambient temperature (23 ± 2 °C) in the presence of a small amount of H<sub>2</sub>O (5 μL) for 10–20 min. Relative rate ratios for catalytic oxidations were determined by GC based on the amounts of sulfoxide products as measured against an internal standard. In this work, all the catalytic sulfoxidations proceeded with good yields (> 99%), mass balance (> 95%), and in all cases no sulfones were detected. Thus, the ratio of product formation should reasonably reflect the relative sulfide reactivity toward the corrole-manganese-catalyzed oxidations.

## 3. Results and discussion

### 3.1. Screening studies in the catalytic oxidation of thioanisole

Although the PhI(OAc)<sub>2</sub> has been used as a mild oxygen source for some time, apparently it had hitherto not been employed for manganese corrole-catalyzed sulfoxidation reactions. Thus, the usefulness of PhI(OAc)<sub>2</sub> was first evaluated in the catalytic oxidation of thioanisole

**Table 2**  
Catalytic oxidation of substituted thioanisoles by manganese(IV) corrole (**2a**) and  $\text{PhI}(\text{OAc})_2$ .<sup>a</sup>

| Entry          | Substrate   | Time (h) | Convsn. (%) <sup>b</sup> | Product   | Yields (%) <sup>b</sup> |
|----------------|---|----------|--------------------------|---|-------------------------|
| 1              |  <b>4a</b>   | 1        | 100                      |  <b>5a</b>   | 95 (92) <sup>c</sup>    |
| 2              |  <b>4b</b>   | 1        | 100                      |  <b>5b</b>   | 98 (95) <sup>c</sup>    |
| 3              |  <b>4c</b>   | 2        | 100                      |  <b>5c</b>   | 97                      |
| 4              |  <b>4d</b>   | 0.5      | 100                      |  <b>5d</b>   | 95                      |
| 5              |  <b>4e</b>   | 0.4      | 100                      |  <b>5e</b>   | 95                      |
| 6              |  <b>4f</b>  | 12       | 100                      |  <b>5f</b>  | 91                      |
| 7              |  <b>4g</b> | 4        | 100                      |  <b>5g</b> | 96                      |
| 8 <sup>d</sup> |  <b>4h</b> | 0.5      | 100                      |  <b>5h</b> | 66                      |
| 9 <sup>e</sup> |  <b>4i</b> | 24       | 100                      |  <b>5i</b> | 96                      |
| 10             |  <b>4j</b> | 1        | 100                      |  <b>5j</b> | 99                      |
| 11             |  <b>4k</b> | 6        | 15                       |  <b>5k</b> | 98                      |

<sup>a</sup> Unless otherwise specified, all reactions were performed in  $\text{CH}_3\text{OH}$  (2 mL) at ca. 23 °C with 1.5 equiv. of  $\text{PhI}(\text{OAc})_2$  (0.75 mmol), substrate (0.5 mmol), 0.2 mol% catalyst in the presence of  $\text{H}_2\text{O}$  (18  $\mu\text{L}$ ); sulfoxides and trace amounts of sulfone were detected by GC analysis of the crude reaction mixture.

<sup>b</sup> Based on the conversion of substrates and determined by quantitative GC–MS analysis with an internal standard on the crude reaction mixture after the reaction; material balance > 95%.

<sup>c</sup> Isolated yield in the parenthesis from a scaled-up reactions with 5 mmol substrate.

<sup>d</sup> Ring-opening products (30%) were detected by GC–MS.

<sup>e</sup> Using **2b** as catalyst in  $\text{CHCl}_3$  due to the poor solubility of the substrate in  $\text{CH}_3\text{OH}$ .

(4a) by a series of manganese corrole catalysts (**1** and **2**) that differ in oxidation states of manganese metal and in electronic environment of ligands. In order to work under homogeneous conditions and follow with GC–MS analysis, catalytic reactions were performed in different solvents at room temperature with a 0.2 mol% catalyst loading and a 1:1.5 ratio of thioanisole and  $\text{PhI}(\text{OAc})_2$ . The comprehensive screening results are compiled in Table 1. As expected, methyl phenyl sulfoxide (**5a**) and methyl phenyl sulfone (**6a**) were the only oxidized products detected by GC–MS under catalytic conditions, whereas other by-products such as the corresponding disulfide were not detected. Control experiments showed that no oxidized products were formed in the absence of either the catalyst or the  $\text{PhI}(\text{OAc})_2$ , or in the presence of  $\text{PhI}(\text{OAc})_2$  and water without catalyst. Similar to previously reported works, a small amount of water with  $\text{PhI}(\text{OAc})_2$  gave an accelerating effect in all manganese corrole-catalyzed sulfoxidations. In the absence of water, the reaction was relatively slow and 51% conversion of sulfide was observed after 1 h (entry 1 in Table 1). In contrast, the same reaction proceeded more rapidly with a small amount of  $\text{H}_2\text{O}$  (5  $\mu\text{L}$ ), and thus, 93% conversion was obtained within 1 h at ambient temperature (entry 2). Apparently, addition of 15–20  $\mu\text{L}$  of water resulted in a maximum acceleration in the rate of catalytic reaction without reducing the selectivity for sulfoxide (entry 3). According to early studies [31,36], the trace amount of water can induce the steady and slow formation of more oxidizing  $\text{PhIO}$  from the  $\text{PhI}(\text{OAc})_2$  [30], while allowing for the release of stable  $\text{HOAc}$  (detected by GC) instead of anhydride  $\text{Ac}_2\text{O}$  under anhydrous conditions, thus, resulting in a faster reaction. Additionally, water acts as the dissociation solvent and may help with removal of the axial ligand and binding of the oxygen source, in this case  $\text{PhI}(\text{OAc})_2$ , more efficiently to the metal center of the corrole catalyst [32].

Among the solvents studied, methanol was the most effective with 100% conversion and excellent selectivity for methyl phenyl sulfoxide (**5a**) (> 95% by GC) achieved in a short reaction time, which manifests the high catalytic efficiency of this oxidation. The use of other solvents such as  $\text{CHCl}_3$  or  $\text{CH}_3\text{CN}$  resulted in reduced activity as well as selectivity (Table 1, entries 4 and 5), presumably due to the low solubility of  $\text{PhI}(\text{OAc})_2$ . In this study, we found a significant catalyst effect on the sulfoxidation of **4a** in  $\text{CH}_3\text{OH}$ . Fig. 1 shows the reaction profiles for the catalytic sulfoxidation reactions of **4a** by different catalysts that differ in the corrole ligands and oxidation states of the manganese metal. For the four corrole systems studied here, the  $[\text{Mn}^{\text{IV}}(\text{TPC})\text{Cl}]$  (**2a**) and  $[\text{Mn}^{\text{IV}}(4\text{-}^i\text{Bu-TPC})\text{Cl}]$  (**2b**) without electron-deficient substituents on the corrole ligands were apparently most effective with quantitative yields

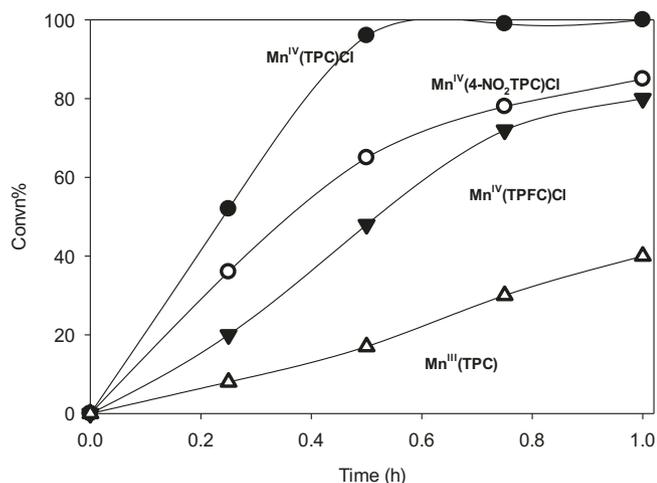


Fig. 1. Time courses of oxidation of thioanisole (0.5 mmol) with  $\text{PhI}(\text{OAc})_2$  (0.75 mmol) in  $\text{CH}_3\text{OH}$  (2 mL) at room temperature in the presence of  $\text{H}_2\text{O}$  (15  $\mu\text{L}$ ) catalyzed by different manganese corroles (1  $\mu\text{mol}$ ). Aliquots were taken at selected time intervals for product analyses with GC–MS.

and excellent selectivities achieved within 30 min (entries 3 and 7). Remarkably, the catalyst **2b** promoted the catalytic oxidation under low loadings (down to 0.04 mol% in entry 8) without loss of activity, reaching a high efficiency with up to 2500 TON. The electron-deficient catalysts  $[\text{Mn}^{\text{IV}}(4\text{-NO}_2\text{-TPC})\text{Cl}]$  (**2c**) and  $[\text{Mn}^{\text{IV}}(\text{TPFC})\text{Cl}]$  (**2d**) catalyzed the oxidations in a slower fashion compared to less electron-demand **2a** and **2b**, and a prolonged reaction time was required to obtain relatively good conversion (entries 10 and 11). This activity trend correlates well with the redox potentials recorded for different corrole ligands in which the electron-deficient groups such as F and  $\text{NO}_2$  on corrole ligands resulted in much higher oxidation potentials to access high-valent oxidation states. This observation implied that the rate-determining step in the manganese-corrole catalytic system is the oxygen atom transfer from  $\text{PhI}(\text{OAc})_2$  to generate the active oxidant (metal-oxo) and not from the proposed metal-oxo oxidant to the sulfide substrate.

Next, oxidation states of manganese catalyst have a profound impact on the catalytic activity.  $[\text{Mn}^{\text{IV}}(\text{Cor})\text{Cl}]$  proved to be much more active compared to  $\text{Mn}^{\text{III}}$  catalysts that gave much lower activities in the oxidation of thioanisole under identical conditions (entries 6 and 9). These results suggested that manganese(IV) catalysts have a faster access to form the active oxidants by  $\text{PhI}(\text{OAc})_2$ , and/or generate the more reactive oxidizing metal-oxo intermediates in comparison to the manganese(III) complexes. For comparison, one of the best-known porphyrin catalysts  $[\text{Mn}^{\text{III}}(\text{TPFPP})\text{Cl}]$  [TPFPP = tetra(pentafluorophenyl)porphyrato] performed the sulfoxidation with a much lower activity and selectivity under similar reaction conditions (entry 12).

### 3.2. Substrate scope

The promising results in Table 1 prompted us to apply the manganese corroles with the  $\text{PhI}(\text{OAc})_2$  to the catalytic sulfoxidations of various sulfides under optimized conditions. Table 2 lists the oxidized products and corresponding yields using **2a** as the catalyst. Of note, catalyst **2b** gave comparable results under similar conditions. In analogy with what we observed for **4a**, all catalytic oxidation of substituted thioanisoles proceeded with a quantitative conversion into the corresponding sulfoxides as the major identifiable products. In some cases, traces of sulfones (< 5% by GC) were detected. Significant for preparative purposes, 100% conversions and excellent yields (> 90%) in isolated products were obtained under scale-up conditions (entries 1 and 2). The excellent catalytic efficiency displayed by manganese(IV) corroles is ascribed in part to good solubility of the  $\text{PhI}(\text{OAc})_2$  in solution and the slow and steady-state formation of  $\text{PhIO}$  in the presence of small amount of water, which may dramatically improve stability of the corrole catalyst against degradation, and at same time, permit the fast access to generate the active oxidant.

As evident in Table 2, the reactivity of thioanisoles was affected by the electronic effects of the substituents on the aromatic rings of **4a–f**. For examples, 4-methoxythioanisole (**4e**) resulted in the fastest reaction among all substrates studied (entry 5). On the contrary, the oxidation of 4-nitrothioanisole (**4f**) proceeded slowest and required much longer reaction time (12 h) to reach the complete conversion (entry 6). This can be ascribed to the reduced nucleophilicity of sulfide due to the electron-withdrawing substituents on the substrate. In addition, the relative rates ( $k_{\text{rel}}$ ) for the catalytic oxidation of several substituted thioanisoles (Y-thioanisole, Y = 4-MeO, 4-Me, 4-F, 4-Cl and 4- $\text{NO}_2$ ) were evaluated by monitoring the formation of sulfoxides by GC (see the Experimental Section). Fig. 2 depicts a linear correlation ( $R = 0.92$ ) of  $\log k_{\text{rel}}$  [ $k_{\text{rel}} = k(\text{Y-thioanisole})/k(\text{thioanisole})$ ] versus Hammett  $\sigma^+$  substituent constant in the competitive oxidation by  $[\text{Mn}^{\text{IV}}(\text{TPC})\text{Cl}]$  catalyst. The slope ( $\rho^+$ ) of the plot is  $-1.75$ , suggesting a single mechanism with involvement of an electrophilic oxidant, most likely a corrole-manganese-oxo intermediate. Furthermore, negative  $\rho^+$  value also indicates the transition states for rate-limiting steps involve positive charge development. Similar negative values were also found for

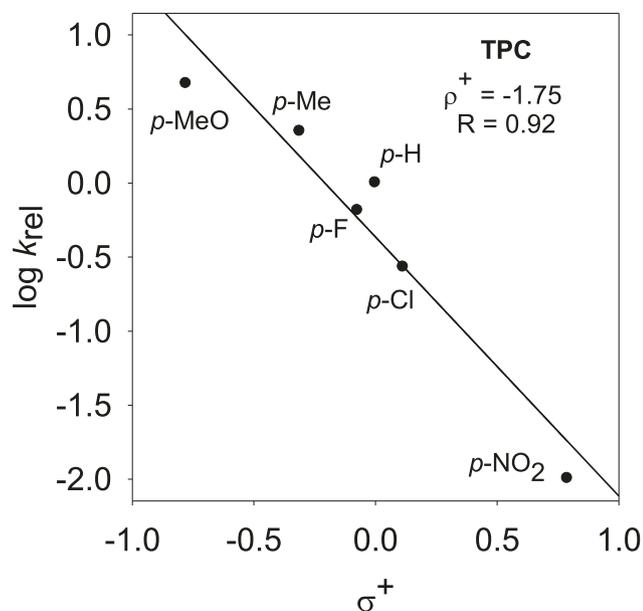


Fig. 2. Hammett correlation studies ( $\log(k_{rel})$  vs  $\sigma^+$ ) for  $[\text{Mn}^{\text{IV}}(\text{TPC})\text{Cl}]$  (**2a**) catalyzed sulfoxidation of thioanisole and substituted thioanisoles by  $\text{PhiI}(\text{OAc})_2$  in  $\text{CH}_3\text{OH}$  at  $23 \pm 2^\circ\text{C}$ .

the sulfide oxidations with the corrole-manganese(V)-oxo species with halogen-substituted ligand ( $\rho^+ = -1.06$  to  $-1.34$ ), [37] iron(IV) corrole catalysts ( $\rho^+ = -0.85$  to  $-0.98$ ), and inorganic and organic hydroperoxides ( $\rho^+ = -0.65$  to  $-1.90$ ).

Sulfoxidation of diphenyl sulfide **4g** was also found to be relatively slow (entry 7), possibly due to the steric effect of two bulky phenyl groups making it harder to access the oxidizing intermediate for the oxo transfer reaction. In this study, the seemingly large and rigid substrate dibenzothiophene was shown to be inert toward this catalytic system (data not shown) that might be ascribed to sterics. Its efficacy for sulfoxidation was further demonstrated in the oxidation of allylic sulfide **4i** (entry 9). In many oxidants such as peroxy acids,  $\text{NaIO}_4$ , and traditional catalytic systems, the oxidation of sulfides is often interfered by the presence of electron-rich double bonds. With catalyst **2b** and  $\text{Phi}(\text{OAc})_2$  in the presence of  $\text{H}_2\text{O}$ , we found that no epoxidation took place and only sulfoxide **4i** was obtained in a quantitative yield even with slower reaction rate (entry 9). Similarly, the presence of the hydroxyl group did not disturb the selective oxidation of sulfide and no alcohol oxidation was observed (entry 10). Surprisingly, the oxidation of alkyl sulfide (**2j**) proceeded much slower and only 15% conversion was obtained after 6 h (entry 11), presumably owing in part to its reduced nucleophilicity and poor solubility in  $\text{CH}_3\text{OH}$ .

### 3.3. Kinetic studies

The synthetic value of the new catalytic system presented above is indisputable, but mechanistic understanding of the complex OAT processes is important for the design of still more effective and selective oxidants. High-valent metal-oxo corroles have been proposed as the key intermediates in many metallocorrole-catalyzed reactions [32,38,39]. Of note, the possible generation of the reactive manganese(V)-oxo corroles (**3**) was reported in previous studies [23,27,37]. To this end, we conducted the chemical oxidation of  $\text{Mn}^{\text{III}}(\text{Cor})$  by  $\text{Phi}(\text{OAc})_2$  in  $\text{CH}_3\text{OH}$  in the absence of sulfides to probe the nature of the active oxidizing intermediate. In metal-oxo chemistry, one typically can expect that the formed metal-oxo intermediates may behave differently due to the different electronic environments of the ligands.

As shown in Fig. 3A, addition of 10 equivalents of  $\text{Phi}(\text{OAc})_2$  resulted in a fast conversion of  $[\text{Mn}^{\text{III}}(\text{TPC})(\text{OEt}_2)_2]$  to a known manganese(V)-oxo **3a**, i.e.  $[\text{Mn}^{\text{V}}(\text{TPC})\text{O}]$ , which displays distinct Soret

bands, matching the spectra reported previously from ozone, *m*-CPBA or photochemical oxidation reactions [35,37,40]. In a fashion similar to that described for the generation of **3a**, the highly electron-deficient  $[\text{Mn}^{\text{V}}(\text{TPFC})\text{O}]$  (**3d**) was also formed with a slightly slower rate than that of **3a** due to the expected higher oxidation potential of TPFC system (Fig. 3B). It is worth noting that using the same procedure by reacting  $[\text{Mn}^{\text{IV}}(\text{Cor})\text{Cl}]$  with  $\text{Phi}(\text{OAc})_2$  did not give the corresponding  $[\text{Mn}^{\text{V}}(\text{Cor})\text{O}]$  intermediates among all corrole systems studied here.

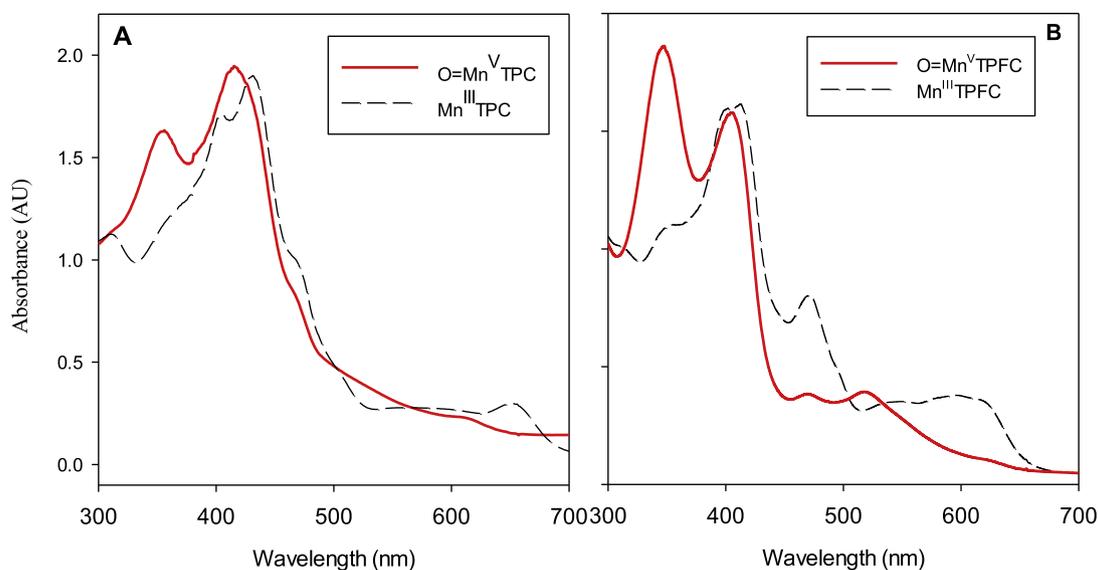
In the presence of organic substrates, the time-resolved spectra show the clean conversion of **3a** to regenerate the  $\text{Mn}^{\text{IV}}$  species that was characterized by its known  $\lambda_{\text{max}}$  at 430 nm (Fig. 4A). Again, this observation is in accord with previous photochemical studies of **3a** [35,40]. In kinetic studies, we monitored the absorbance in the Soret band region at 350 nm, which decreased over the course of reaction without overlap with other peaks (Fig. 3B). The traces were fit to single-exponential decays, as expected for reactions under pseudo-first-order conditions. Plots of  $k_{\text{obs}}$  versus concentration of thioanisole as the substrate typically gave straight lines with near-zero intercepts (Inset in Fig. 4B). In contrast, the reaction of more electron-deficient **3d** with thioanisole in  $\text{CH}_3\text{OH}$  regenerated a  $\text{Mn}^{\text{III}}$  product only, and there was no evidence for the accumulation of any  $\text{Mn}^{\text{IV}}$  species during the reaction course (Fig. 5). As indicated in previous reports [37,40], this reaction sequence is consistent with a direct two-electron reduction from  $\text{Mn}^{\text{V}}$  to  $\text{Mn}^{\text{III}}$ . Regardless of the complexity of the decay reactions in different corrole systems, the kinetics of the reactions of **3a** and **3d** with thioanisoles followed a simple second-order rate law. We measured the kinetics in four sets of studies for several substrates with three independent kinetic runs, and the second-order rate constants are listed in Table 3. Noticeably, the kinetic data of **3a** in this work from the chemically generated method were comparable with the literature reported  $k_{\text{ox}}$  for the same oxidant produced from photochemical generation [40].

In addition to decaying back to  $\text{Mn}^{\text{IV}}$  species, the second-order rate constants determined from pseudo-first-order kinetic studies for reactions of **3a** with thioanisoles are apparently greater in comparison with those of more electron-deficient species **3d** with same reductants (Table 3). Typically, the reactivity of the electrophilic high-valent metal-oxo species is increased with the more electron-deficient ligands. When the rates of **3a** and **3d** are compared, however, the reactivity order is inverted with the system of less electron demand, i.e. the TPC complex **3a** reacting faster with any given substrate than the more electron-deficient TPFC **3d**. According to the previously proposed mechanistic model [40], these kinetic results can be rationalized by disproportionation of **3a** to give  $\text{Mn}^{\text{IV}}$  corrole and a more reactive corrole-manganese(VI)-oxo cationic species as the predominant oxidant, which transfers an oxygen atom to organic sulfides and generates another equivalent of the  $\text{Mn}^{\text{IV}}$  species. In the more electron-deficient TPFC system,  $\text{Mn}^{\text{V}}$ -oxo corrole is the electrophilic oxidant which directly oxidized sulfides to form the  $\text{Mn}^{\text{III}}$  product in the end of reaction as we observed in Fig. 5.

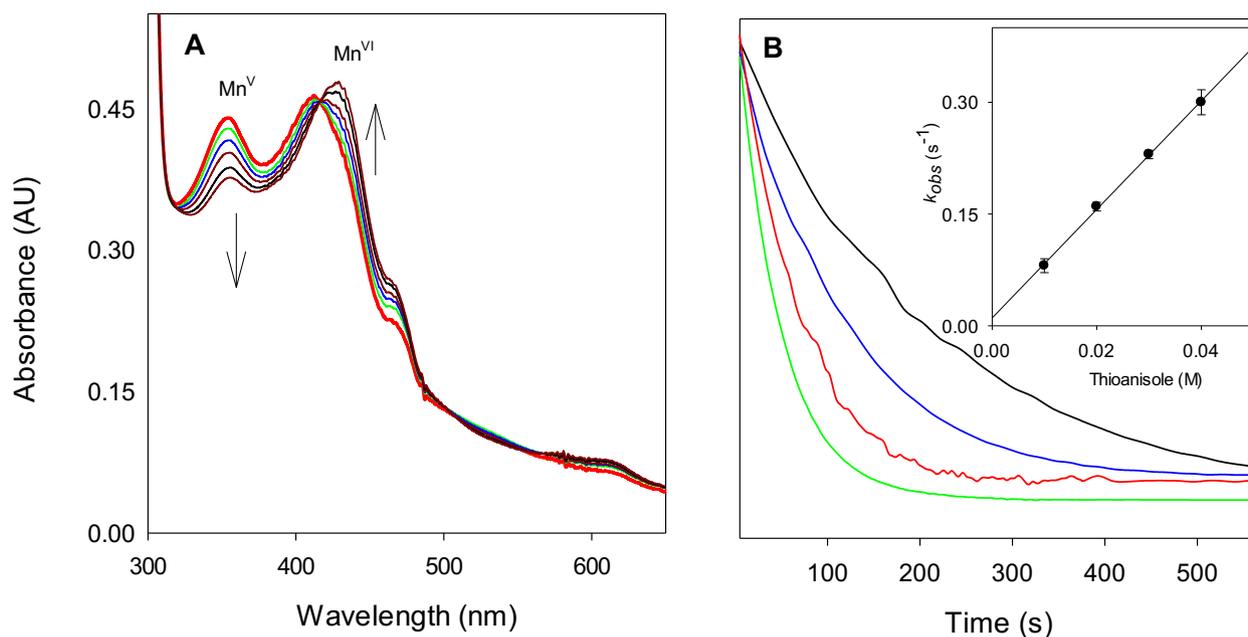
### 3.4. Competition studies

One objective of our studies is to identify the active oxidants during catalytic turnover conditions with these manganese corrole catalysts, which could lead to better control of the catalytic oxidation reactions, especially in terms of selectivities. In a typical catalytic reaction, however, the concentrations of active oxidants do not build up to detectable concentrations. Moreover, as our kinetic studies of porphyrin-manganese(IV)-oxo species [41], corrole-manganese(V)-oxo species [35], and porphyrin-iron(IV)-oxo species [42] indicate, a high-valent metal-oxo species detected in a reaction might not be the true oxidant in the system.

To evaluate whether the directly observed manganese(V)-oxo species **3** in the above kinetic studies is also the active oxidant under catalytic turnover conditions, the competitive sulfoxidation reactions



**Fig. 3.** UV-vis spectra for chemically generated oxo-species (A)  $[\text{Mn}^{\text{V}}(\text{TPC})\text{O}]$  (**3a**, solid red) from reaction of  $[\text{Mn}^{\text{III}}(\text{TPC})(\text{OEt}_2)_2]$  (dash black); (B)  $[\text{Mn}^{\text{V}}(\text{TPFC})\text{O}]$  (**3d**, solid red) from reaction of  $[\text{Mn}^{\text{III}}(\text{TPFC})(\text{OEt}_2)_2]$  (dash black) with excess  $\text{PhI}(\text{OAc})_2$  (10 equiv.) in  $\text{CH}_3\text{OH}$  solutions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 4.** (A) Time-resolved spectra for the reaction of **3a** with thioanisole (20 mM) over 5 min (cycle time = 50 s per spectrum) in  $\text{CH}_3\text{OH}$  at 23 °C. (B) Kinetic traces monitored at  $\lambda_{\text{max}} = 350$  nm in the presence of 0.01 M (black), 0.02 M (blue), 0.03 M (red) and 0.04 M (green) thioanisole. Inset shows plot of the observed pseudo-first-order rate constants versus the concentration of thioanisole. The standard deviations were at 2  $\sigma$ . (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

catalyzed by manganese(III) corroles (**1**) and chloro-manganese(IV) corroles (**2**) with  $\text{PhI}(\text{OAc})_2$  as the sacrificial oxygen source were conducted as described in the experimental section. In competition studies, a limiting amount of sacrificial oxidant was used to keep the conversion less than 20%. The amounts of oxidation products formed were determined by GC analysis. Each sulfide substrate was oxidized to the corresponding sulfoxide in nearly quantitative yield based on the oxidant consumed without forming the over-oxidation product sulfone. Thus, the rate of sulfoxide formation should reasonably reflect the thioanisole reactivity toward the manganese corrole-catalyzed oxidations.

If the ratio of products in the competitive oxidation reaction is the same as the ratio of absolute rate constants, then one can infer that the

same oxo species is active under catalytic and single-turnover conditions. For example, it was found that the ratio of rate constants for reaction of TPFC-manganese(V)-oxo species **3d** with organic sulfides is similar to the ratio of products found in competitive catalytic oxidations (Table 4). Differences in inherent reactivities of the thioanisoles obviously influence the ratio of products, but the close match between the ratios of absolute rate constants and the ratios of products from the competition experiment strongly suggests that species manganese(V)-oxo **3d** was likely the active oxidant in the catalytic oxidation reactions by  $\text{Mn}^{\text{III}}(\text{TPFC})$  with  $\text{PhI}(\text{OAc})_2$ , consistent with the previous report [37].

The situation with manganese(IV) catalysts is quite different. Table 4 also lists some results from competition studies with

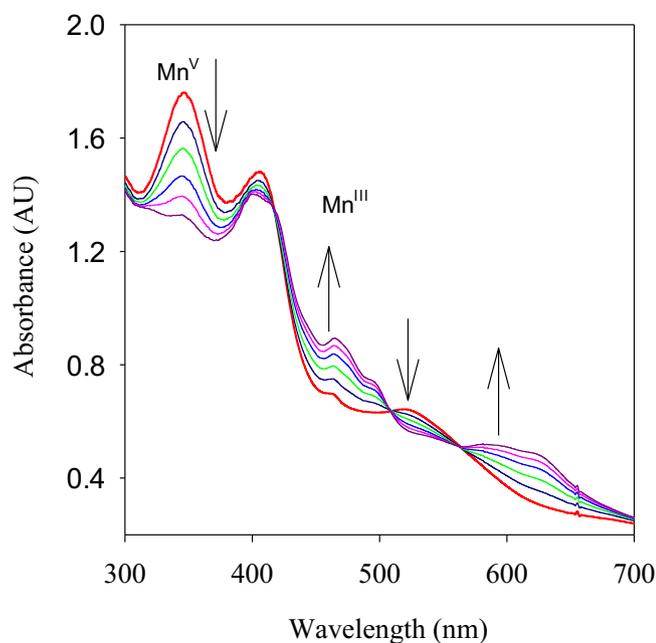


Fig. 5. Time-resolved spectra for the reaction of **3d** ( $2.0 \times 10^{-5}$  M) with thioanisole (20 mM) over 6 min (cycle time = 60 s per spectrum) in  $\text{CH}_3\text{OH}$  at  $23^\circ\text{C}$ .

**Table 3**  
Second-order rate constants for reactions of corrole-manganese(V)-oxo species.<sup>a</sup>

| Entry | Substrate                        | Rate constant ( $\text{M}^{-1} \text{s}^{-1}$ ) |                  |                 |
|-------|----------------------------------|---|------------------|-----------------|
|       |                                  | 3a <sup>b</sup>                                 | 3a <sup>c</sup>  | 3d <sup>b</sup> |
| 1     | PhSCH <sub>3</sub>               | $7.9 \pm 0.3$                                   | $6.0 \pm 0.8$    | $5.3 \pm 0.1$   |
| 2     | <i>p</i> -F-PhSCH <sub>3</sub>   | $25.8 \pm 2.6$                                  | $24.8 \pm 1.5$   | $7.0 \pm 0.4$   |
| 3     | <i>p</i> -Cl-PhSCH <sub>3</sub>  | $12.0 \pm 0.9$                                  | –                | $3.5 \pm 0.2$   |
| 4     | <i>p</i> -MeO-PhSCH <sub>3</sub> | $91.0 \pm 5.1$                                  | $85.5 \pm 2.4^b$ | $62.0 \pm 5.7$  |

<sup>a</sup> In  $\text{CH}_3\text{OH}$  at  $23 \pm 2^\circ\text{C}$ . The values are average of 2–3 runs with 2σ standard deviation.

<sup>b</sup> Formed by  $\text{PhI}(\text{OAc})_2$  (ca. 10 equiv.) oxidation in this work.

<sup>c</sup> Photo-generated in  $\text{CH}_3\text{CN}$  from Ref. [41].

**Table 4**  
Relative rate constants from kinetic studies and competitive catalytic studies.<sup>a</sup>

| Catalyst                              | Substrates                | Method                       | $k_{\text{rel}}^b$ |
|---------------------------------------|---------------------------|------------------------------|--------------------|
| [Mn <sup>III</sup> (TPFC)] <b>1d</b>  | <i>p</i> -F-PhSMe/PhSMe   | Kinetic results <sup>c</sup> | 1.32               |
|                                       |                           | PhI(OAc) <sub>2</sub>        | 1.35               |
|                                       | <i>p</i> -Cl-PhSMe/PhSMe  | Kinetic results <sup>c</sup> | 0.66               |
|                                       |                           | PhI(OAc) <sub>2</sub>        | 0.70               |
| [Mn <sup>IV</sup> (TPC)Cl] <b>2a</b>  | <i>p</i> -F-PhSMe/PhSMe   | Kinetic results <sup>c</sup> | 3.30               |
|                                       |                           | PhI(OAc) <sub>2</sub>        | 0.62               |
|                                       | <i>p</i> -MeO-PhSMe/PhSMe | Kinetic results <sup>c</sup> | 11.52              |
|                                       |                           | PhI(OAc) <sub>2</sub>        | 4.55               |
| [Mn <sup>IV</sup> (TPFC)Cl] <b>2d</b> | <i>p</i> -F-PhSMe/PhSMe   | Kinetic results <sup>c</sup> | 1.32               |
|                                       |                           | PhI(OAc) <sub>2</sub>        | 0.95               |
|                                       | <i>p</i> -MeO-PhSMe/PhSMe | Kinetic results <sup>c</sup> | 11.70              |
|                                       |                           | PhI(OAc) <sub>2</sub>        | 4.76               |

<sup>a</sup> Equal amounts of two substrates, e.g. thioanisole (0.25 mmol) and substituted thioanisole (0.25 mmol), catalyst (1 μmol), H<sub>2</sub>O (5 μL), and PhI(OAc)<sub>2</sub> (0.1 mmol) in  $\text{CH}_3\text{OH}$  (2 mL) was stirred for ca. 20–30 min at  $23 \pm 2^\circ\text{C}$ .

<sup>b</sup> Relative ratios of absolute rate constants from kinetic results and competitive oxidations at ambient temperature.

<sup>c</sup> Kinetic results were calculated based on data collected in the Table 3 of this work.

[Mn<sup>IV</sup>(TPC)Cl] (**2a**) and [Mn<sup>IV</sup>(TPFC)Cl] (**2d**) catalysts and the ratios of absolute rate constants for reactions of the same substrates with the observed manganese(V)-oxo transient **3a** and **3d**. As evidenced in Table 4, the ratios of absolute rate constants found in direct kinetic studies differed substantially from the oxidation ratios for competition oxidation reactions of the two substrates in both systems studied here. Substantially different behavior is particularly apparent for oxidations of para-fluorothioanisole and thioanisole, in which case the absolute rate constant for oxidation of para-fluorothioanisole by **3a** is greater than that for oxidation of thioanisole by the same oxo species, but para-fluorothioanisole is oxidized faster than thioanisole in competition studies with manganese(IV) corrole as the catalyst. One obvious explanation for this behavior is that a manganese(V)-oxo species is unlikely to serve as the active oxidant under catalytic conditions with PhI(OAc)<sub>2</sub>. Furthermore, the ratios of rate constants for oxidations by **3a** or **3d** are much larger than the observed product ratios from competition studies, suggesting that the manganese(V)-oxo corrole is less reactive (higher selectivity) than the species formed in the catalytic reactions. Thus, the competition studies might explain that catalytic oxidation reactions catalyzed by [Mn<sup>IV</sup>(Cor)Cl] were much more efficient than those by the [Mn<sup>III</sup>(Cor)(OEt<sub>2</sub>)<sub>2</sub>] catalyst (Table 1 and Fig. 1). Reaction of the corrole-manganese(IV) catalysts with the sacrificial oxidant PhI(OAc)<sub>2</sub> possibly give a more reactive manganese(VI)-oxo species that is the major oxidant of the sulfide substrate, even though the definitive detection and assignment of the elusive oxidant needs to be spectroscopically characterized in the future studies.

#### 4. Conclusion

In conclusion, we have demonstrated that the corrole-manganese complexes effectively catalyzed the oxidation of aryl sulfides into sulfoxides with PhI(OAc)<sub>2</sub> in the presence of a small amount of water. On the basis of catalyst effects, the corrole ligands and the oxidation states of manganese metal played important roles in the catalytic sulfoxidations, in which manganese(IV) catalysts containing non-electron deficient ligands were found to be more effective than electron-deficient manganese(III) corroles. The readily soluble and mild oxidative nature of PhI(OAc)<sub>2</sub> overcame the limitations for corrole-manganese catalysts, which exhibited high activity due to the improved stability against catalyst degradation. The previously known manganese(V)-oxo corroles were produced by chemical oxidations in mixing experiments and their kinetic data with thioanisoles were accumulated in this work. The competition studies have suggested the different oxidant forms might be involved under catalytic turnover conditions. The corrole-manganese(V)-oxo intermediates observed in the kinetic studies appear to be involved as the active oxidants when manganese(III) catalysts were employed, since the product ratios in catalytic reactions closely matched the ratios of rate constants from the kinetic studies. However, a more reactive oxidant, possibly manganese(VI)-oxo derivatives might be the oxidants in the manganese(IV) corrole-catalyzed sulfoxidation reactions. Further studies to define synthetic applications and detect the oxidizing transient species are underway in our laboratory.

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#### References

- [1] C.M. Carreno, *Chem. Rev.* 95 (1995) 1717–1760.
- [2] B.M. Trost, M. Rao, *Angew. Chem., Int. Ed.* 54 (2015) 5026–5043.
- [3] S. Otocka, M. Kwiatkowska, L. Madalinska, P. Kielbasinski, *Chem. Rev.* 117 (2017)

- 4147–4181.
- [4] S. Caron, R.W. Dugger, S.G. Ruggeri, J.A. Ragan, D.H.B. Ripin, *Chem. Rev.* 106 (2006) 2943–2989.
- [5] E. Ito, J.A.R. van Veen, *Catal. Today* 116 (2006) 446–460.
- [6] R. Noyori, M. Aoki, K. Sato, *Chem. Commun.* (2003) 1977–1986.
- [7] J.E. Baeckvall, *Modern Oxidation Methods*, Wiley-VCH Verlag, Weinheim, 2004.
- [8] C. Bolm, F. Bienewald, *Angew. Chem., Int. Ed.* 34 (1996) 2640–2642.
- [9] H. Egami, T. Katsuki, *J. Am. Chem. Soc.* 129 (2007) 8940–8941.
- [10] K. Kamata, T. Hirano, N. Mizuno, *Chem. Commun.* (2009) 3958–3960.
- [11] Y. Arakawa, K. Yamanomoto, H. Kita, K. Minagawa, M. Tanaka, N. Haraguchi, S. Itsuno, Y. Imada, *Chem. Sci.* 8 (2017) 5468–5475.
- [12] P. Kowalski, K. Mitka, K. Ossowska, Z. Kolarska, *Tetrahedron* 61 (2005) 1933–1953.
- [13] Z. Gross, N. Galili, L. Simkhovich, I. Saltsman, M. Botoshansky, D. Blaeser, R. Boese, I. Goldberg, *Org. Lett.* 1 (1999) 599–602.
- [14] B. Koszarna, D.T. Gryko, *J. Org. Chem.* 71 (2006) 3707–3717.
- [15] I. Aviv, Z. Gross, *Chem. Commun.* (2007) 1987–1999.
- [16] R.D. Teo, J.Y. Hwang, J. Termini, Z. Gross, H.B. Gray, *Chem. Rev.* 117 (2017) 2711–2729.
- [17] Z. Gross, H.B. Gray, *Adv. Syn. Catal.* 346 (2004) 165–170.
- [18] A.J. McGown, Y.M. Badiei, P. Leeladee, K.A. Prokop, S. Debeer, D.P. Goldberg, Synthesis and reactivity of high-valent transition metal corroles and corrolazines, in: K.M. Kadish, K.M. Smith, R. Guilard (Eds.), *Handbook of Porphyrin Science*, World Scientific Press, 2011.
- [19] H.-Y. Liu, M.H.R. Mahmood, S.-X. Qiu, C.K. Chang, *Coord. Chem. Rev.* 257 (2013) 1306–1333.
- [20] H.M. Neu, R.A.G. Baglia, D.P. Acc, *Chem. Res.* 48 (2015) 2754–2764.
- [21] R.A. Baglia, J.P.T. Zaragoza, D.P. Goldberg, *Chem. Rev.* 117 (2017) 13320–13352.
- [22] Z. Gross, L. Simkhovich, N. Galili, *Chem. Commun.* (1999) 599–600.
- [23] Z. Gross, G. Golubkov, L. Simkhovich, *Angew. Chem. Int. Ed. Engl.* 39 (2000) 4045–4047.
- [24] A. Mahammed, Z. Gross, *J. Am. Chem. Soc.* 127 (2005) 2883–2887.
- [25] A. Mahammed, H.B. Gray, A.E. Meier-Callahan, Z. Gross, *J. Am. Chem. Soc.* 125 (2003) 1162–1163.
- [26] G. Golubkov, J. Bendix, H.B. Gray, A. Mahammed, I. Goldberg, A.J. DiBilio, Z. Gross, *Angew. Chem., Int. Ed.* 40 (2001) 2132–2134.
- [27] H.Y. Liu, T.S. Lai, L.L. Yeung, C.K. Chang, *Org. Lett.* 5 (2003) 617–620.
- [28] R. Zhang, E. Vanover, T.-H. Chen, H. Thompson, *Appl. Catal., A* 465 (2013) 95–100.
- [29] W. Adam, S. Hajra, M. Herderich, C.R. Saha-Moller, *Org. Lett.* 2 (2000) 2773–2776.
- [30] J.H. In, S.E. Park, R. Song, W. Nam, *Inorg. Chim. Acta* 343 (2003) 373–376.
- [31] T.-H. Chen, K.-W. Kwong, A. Carver, W.L. Luo, R. Zhang, *Appl. Catal., A* 497 (2015) 121–126.
- [32] T.H. Chen, K.W. Kwong, N.G. Lee, D. Ranburger, R. Zhang, *Inorg. Chem. Acta* 451 (2016) 65–72.
- [33] L. Simkhovich, A. Mahammed, I. Goldberg, Z. Gross, *Chem. Eur. J.* 7 (2001) 1041–1055.
- [34] L. Simkhovich, I. Goldberg, Z. Gross, *Inorg. Chem.* 41 (2002) 5433–5439.
- [35] R. Zhang, D.N. Harischandra, M. Newcomb, *Chem. Eur. J.* 11 (2005) 5713–5720.
- [36] K.W. Kwong, T.H. Chen, W. Luo, H. Jedd, R. Zhang, *Inorg. Chim. Acta* 430 (2015) 176–183.
- [37] A. Kumar, I. Goldberg, M. Botoshansky, Y. Buchman, Z. Gross, *J. Am. Chem. Soc.* 132 (2010) 15233–15245.
- [38] D.N. Harischandra, R. Zhang, M. Newcomb, *J. Am. Chem. Soc.* 127 (2005) 13776–13777.
- [39] D.N. Harischandra, G. Lowery, R. Zhang, M. Newcomb, *Org. Lett.* 11 (2009) 2089–2092.
- [40] K.W. Kwong, N.F. Lee, D. Ranburg, J. Malone, R. Zhang, *J. Inorg. Biochem.* 163 (2016) 39–44.
- [41] R. Zhang, J.H. Horner, M. Newcomb, *J. Am. Chem. Soc.* 127 (2005) 6573–6582.
- [42] N.-F. Lee, D. Patel, H.Y. Liu, R. Zhang, *J. Inorg. Biochem.* 183 (2018) 58–65.