

Solvent effects on the catalytic activity of manganese(III) corroles

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> **ABSTRACT:** Four Mn(III) corroles that differ in their electronic environments based on *meso*substitution by pentafluorophenyl and phenyl groups were synthesized and characterized by spectroscopic techniques. Utilization of these Mn(III) corroles for styrene oxidation using iodosylbenzene (PhIO) as oxygen source in toluene, dichloromethane (DCM), DMF, DMAc, THF and DMSO revealed a remarkable effect of solvent on the catalytic activity. Furthermore, the transformation of Mn(III) corroles into their corresponding Mn(V)-oxo corroles, and subsequent treatment with styrene also indicated that more electron-deficient Mn(V)-oxo corroles exhibit higher reactivity in toluene and DCM, while less electrondeficient Mn(V)-oxo corroles exhibit higher reactivity in DMF and DMAc. A significant difference in the observed rates of reaction suggest that the catalytic oxidation of styrene by manganese corroles may proceed through different pathways, and is strongly solvent-dependent.

KEYWORDS: manganese, corrole, Mn(V)-oxo, catalysis, solvent effect.

INTRODUCTION

Transition metal complexes of corroles have been implicated as superb catalysts in numerous chemical reactions [1-6] such as oxidation [7-10], cyclopropanation [11], hydroxylation [12], and decomposition of peroxynitrite [13, 14]. Among these catalytic reactions, manganese corroles catalyzed oxidation of organic substrates have flourished prominently in recent years [1, 8, 9, 15]. Many terminal oxidants, such as iodosylbenzene (PhIO) [9, 16, 17], *m*-chloroperbenzoic acid [18], ozone [8] and hydrogen peroxide [19] have been employed as oxygen source in the catalytic systems of manganese corroles to explore their reactivity. More recently, manganese(III) corroles catalyzed oxidation of alcohols, alkenes and alkanes by tert-butyl hydroperoxide (t-BuOOH) under mild condition has been shown to be selective and efficient [20, 21]. Although a lot of reports have focused on manganese corroles catalyzed oxidation reactions, the factors controlling their reactivity are still ambiguous.

It was found that more electron-deficient β -halogenated Mn(III) corroles such as Br₈Mn(III)(TPFC) (where TPFC = 5,10,15-trispentafluorophenyl corrole) [22] and $F_8Mn(III)(TPFC)$ [17] exhibit higher reacivity than comparatively less electron-deficient corrole Mn(III)-(TPFC) [16] in the epoxidation of alkenes. High-valent manganese-oxo corroles have been postulated as the key intermediates in a large number of manganese corroles catalyzed reactions [1, 9, 23, 24]. DFT calculations suggested that β -bromination of manganese corroles will favor oxygen atom transfer to the substrate by inducing the spin state change in its Mn(V)-oxo complex [25, 26]. The reactivity of Mn(V)-oxo corroles was observed to be greatly enhanced by axial ligation with imidazole [27, 28]. Mn(V)-oxo corrole was also suggested to undergo disproportionation to generate Mn(VI)-oxo species, which then oxidize the substrate in the oxygenation reaction [16]. Newcomb's investigations revealed the possibility of multiple active oxidants in manganese corroles catalyzed reactions [29], and has recently been found in case of manganese porphyrin catalyzed oxidation reactions [30]

The nature of solvent has long been known to play a crucial role in the oxdiation reactions [31–35], and

^oSPP full member in good standing

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Chart 1. Structures of free base corroles and their manganese complexes

has previously been reported in case of chromiumoxo corrole [36], molybdenum-oxo corrole [37] and manganese porphyrin catalyzed oxidation reactions [30, 38]. Our preliminary results showed that the rate of oxygen atom transference from manganese(V)-oxo corrole to the substrate is affected by the properties of the solvent [39]. As a part of our project on the reactivity of Mn(V)-oxo corroles, we here report the systematic investigations of the role of solvent on the catalytic oxidation of styrene by Mn(III) corroles bearing different electronic features (Chart 1) using PhIO as oxidant. The plausible mechanism for the oxidation reaction is also suggested.

RESULTS AND DISCUSSION

Catalytic oxidation of styrene

Among the investigated manganese corroles (Chart 1), $\mathbf{F}_{0}\mathbf{C}$ -Mn(III) is not sufficiently stable in DCM or toluene because of its gradual oxidation into Mn(IV) corrole and may be observed by its color change from green to brown [1]. However, $\mathbf{F}_0\mathbf{C}$ -Mn(III) is relatively more stable in alkaline media. For this reason, the stock solution of $\mathbf{F}_0\mathbf{C}$ -Mn(III) might be kept in dilute ammonia atmosphere to supress its oxidation and to maintain the typical green color of manganese corroles. It may be turned brown after the addition of dilute hydrochloric acid representing a Mn(IV) corrole. Other Mn(III) corroles also show similar property, albeit it varies depending on the nature of the peripheral substituents. The most electron-deficient $\mathbf{F}_{15}\mathbf{C}$ -Mn(III) is much more stable in its +3 oxidation state and the color changes from green to brown in acidic medium is also much slower than the other Mn(III) corroles. The UV-vis spectra of the investigated manganese corroles in acidic, basic and neutral media are shown in Fig. 1. It may be concluded from Fig. 1 that $F_{15}C$ -Mn(III) remains Mn(III) in acidic medium, while the other manganese(III) corroles are partially transformed into Mn(IV) corroles. All manganese(III) corroles exhibit a wider Soret band in acidic medium and split Soret band along with the increase in the intensity of CT (charge transfer) band around 480 nm in basic medium. In order to make sure the trivalent manganese in all corrole catalysts and to guarantee their studies under the same conditions, all manganese corroles were dissolved in dichloromethane and treated with a certain amount of ammonia prior to use. The solvent was then removed under vacuum to obtain Mn(III) corrrole catalysts. The catalytic reactions were carried out in different solvents and the results are summarized in Table 1.

Under the reaction conditions employed, all the Mn(III) corroles showed good catalytic activity in toluene and DCM when using PhIO as oxidant. Styrene epoxide was the major product along with the formation of phenyl acetaldehyde and benzaldehyde. A slightly higher yield was, however, observed in DCM. The catalytic activity in toluene and DCM followed the order: $\mathbf{F}_{15}\mathbf{C}$ -Mn(III) > $\mathbf{F}_{10}\mathbf{C}$ -Mn(III) > $\mathbf{F}_{5}\mathbf{C}$ -Mn(III) > $\mathbf{F}_0\mathbf{C}$ -Mn(III). It is well-known that more electrondeficient Mn(III) porphyrin exhibits higher activity in catalytic reaction because it gives more reactive Mn(V)oxo intermediate [40]. The same was observed in case of manganese corroles where the electron-withdrawing substituents enhanced the reactivity of Mn(V)-oxo intermediate by lowering the Mn-O bond dissociation energy [41]. Benzaldehyde was found to be the major product in the catalytic oxidation of styrene by Mn(III) corrole using t-BuOOH as oxidant, indicating dioxygen



Fig. 1. The effect of acidic (dilute hydrochloric acid) and basic (ammonia) media on the UV-vis spectra of Mn(III) corroles in toluene. (a) $F_{15}C$ -Mn(III); (b) $F_{10}C$ -Mn(III); (c) F_5C -Mn(III); (d) F_0C -Mn(III)

involved free radical mechanism [20]. When the catalytic reactions were carried out in argon atmosphere, the yield of benzadehyde was significantly lowered (Table 1, see yields in parentheses), confirming the role of dioxygen in the catatlytic reaction under aerobic conditions. As styrene epoxide was the main product in toluene and DCM, oxygen atom transfer (OAT) reaction between Mn(V)-oxo corrole and substrate should be the main pathway that controls the catalytic reaction. Notably, the less electron-deficient Mn(III) corroles, F5C-Mn(III) and $\mathbf{F}_0\mathbf{C}$ -Mn(III), gave higher yields of bezaldehyde. This implies that when the Mn(V)-oxo corrole intermediate is less reactive, radical pathway plays more significant role in the catatlytic system under aerobic conditions. The different yields of styrene epoxide in toluene and DCM also indicate that the reactivity of Mn(V)-oxo corrole is correlated with the nature of the solvent.

The catalytic reactions in basic solvents (DMF and DMAc) were drastically different from those in toluene and DCM as expected. In addition to the decrease in the yield of styrene epoxide and total conversion, the product distribution was also significantly different. In DMF, styrene epoxide and benzadehyde were observed

the major product, while phenylacetaldehyde could not be detected. The less electron-deficient Mn(III) corroles gave higher yields of styrene epoxide and higher total yields, that is, the most electron-rich $\mathbf{F}_0\mathbf{C}$ -Mn(III) exhibited the highest catalytic activity [1]. The reactivity of manganese corroles in basic solvents followed the order: $\mathbf{F}_{15}\mathbf{C}$ -Mn(III) < $\mathbf{F}_{10}\mathbf{C}$ -Mn(III) < $\mathbf{F}_{5}\mathbf{C}$ -Mn(III) < $\mathbf{F}_0\mathbf{C}$ -Mn(III). This order is totally reversed compared with the same catalytic reaction in toluene and DCM. This may be due to the fact that disproportionation of Mn(V)-oxo corroles to Mn(VI)-oxo corrole is strongly favored in electron-rich corrole $\mathbf{F}_0\mathbf{C}$ -Mn(III) [1, 29, 42], and high-valent Mn(VI)-oxo corrole may be involved as active intermediate in this case. Interestingly, the reaction in DMAc favored benzaldehyde rather than styrene epoxide and only traces of phenyl acetaldehyde could be observed. The yield of benzaldehyde in DMAc was sharply decreased from 30.6% under aerobic conditions to 2.7% under anaerobic conditions (Table 1, see yields in parentheses), indicating the involvement of dioxygen. All the investigated Mn(III) corroles exhibited similar catalytic activity towards epoxide in DMAc (Table 1). The difference in the catalytic behavior of

Solvent	Catalyst	Yield, % ^b				
		Benzaldehyde	Phenyl acetaldehyde	Styrene oxide	Total	
Toluene ^c	F ₁₅ C -Mn	7.9 (6.9)	10.9 (15.8)	51.4 (47.0)	70.2 (69.7)	
	$\mathbf{F}_{10}\mathbf{C}$ -Mn	11.0 (7.8)	12.1 (16.1)	45.1 (44.7)	68.2 (68.6)	
	F ₅ C -Mn	17.5 (8.4)	6.1 (11.7)	38.2 (41.7)	61.8 (61.8)	
	$\mathbf{F}_0\mathbf{C}$ -Mn	14.2 (12.2)	2.9 (4.7)	21.2 (18.1)	38.3 (35.0)	
DCM	$\mathbf{F}_{15}\mathbf{C}$ -Mn	4.4	22.3	59.5	86.2	
	$\mathbf{F}_{10}\mathbf{C}$ -Mn	2.7	25.2	55.1	83.0	
	F ₅ C -Mn	19.8	10.2	42.3	72.4	
	$\mathbf{F}_0\mathbf{C}$ -Mn	25.6	7.3	39.1	72.0	
DMF	$\mathbf{F}_{15}\mathbf{C}$ -Mn	11.7	0	16.7	28.4	
	$\mathbf{F}_{10}\mathbf{C}$ -Mn	11.6	0	20.9	32.5	
	F ₅ C -Mn	12.7	0	24.1	36.8	
	$\mathbf{F}_{0}\mathbf{C}$ -Mn	22.2	0	25.3	47.5	
DMAc ^c	$\mathbf{F}_{15}\mathbf{C}$ -Mn	25.9 (11.4)	1.6 (1.5)	9.7 (11.8)	37.2 (24.7)	
	$\mathbf{F}_{10}\mathbf{C}$ -Mn	20.8 (8.7)	4.2 (3.1)	14.8 (13.1)	39.8 (24.9)	
	F ₅ C -Mn	27.1 (5.7)	2.0 (1.2)	10.9 (14.4)	40.0 (21.3)	
	$\mathbf{F}_{0}\mathbf{C}$ -Mn	30.6 (2.7)	0.9 (0.8)	11.2 (12.0)	42.7 (15.5)	
THF	$\mathbf{F}_{15}\mathbf{C}$ -Mn	11.0	2.1	3.9	17.0	
	$\mathbf{F}_{10}\mathbf{C}$ -Mn	11.2	1.7	4.4	17.3	
	F ₅ C -Mn	12.0	1.4	4.8	18.2	
	$\mathbf{F}_{0}\mathbf{C}$ -Mn	17.3	1.3	8.4	27.0	
DMSO	$\mathbf{F}_{15}\mathbf{C}$ -Mn	6.0	0	1.4	7.4	
	$\mathbf{F}_{10}\mathbf{C}$ -Mn	2.7	0	0	2.7	
	F ₅ C -Mn	0.9	0	0	0.9	
	$\mathbf{F}_{0}\mathbf{C}$ -Mn	0.6	0	0	0.6	

^a The molar ratio of substrate/PhIO/catalyst was 1000:100:1. ^b Yields based on the amount of oxidant used. ^c Yields in parentheses were got in argon atmosphere.

manganese corroles in DMF and DMAc still needs further exploration.

Manganese(III) corroles exhibited very little catalytic activity in THF and DMSO because of the susceptible oxidation of these solvents in the presence of oxidizing agents. It was found that PhIO can significantly oxidize DMSO but slightly oxidize THF in 3 h. However, in the presence of manganese(III) corrole, THF and DMSO were remarkably oxidized by PhIO within 15 min. Obviously, Mn(III) corroles could not efficiently catalyze the epoxidation of styrene in THF and DMSO due to the involvement of the solvent oxidation.

Kinetics of the reaction between Mn(V)-oxo corroles and styrene

High-valent metal-oxo species have been extensively studied in terms of their generation, stability and substrate

reactivity [43–46]. To get insights into manganese corroles catalyzed reactions, we decided to extend our investigations on the kinetics between Mn(V)-oxo corroles and styrene in different solvents (DCM, toluene, DMF, and DMAc). THF and DMSO could not be used as solvents for kinetic studies due to their possible self-oxidation. The manganese corrole solution ($\sim 3 \times 10^{-5}$ M) was treated with PhIO for about 5 min followed by flash chromatography on basic alumina to give Mn(V)-oxo corrole [17].

Owing to the limited stability of Mn(V)-oxo corroles in solution [1], the self-decay process of Mn(V)-oxo corroles may easily be traced by UV-vis spectroscopy. In DMF and DMAc, all Mn(V)-oxo corroles gradually turned to Mn(III) corroles, while in toluene and DCM only more electron-deficient F_{15} C-Mn(V)-oxo and F_{10} C-Mn(V)-oxo returned to their corresponding Mn(III) corroles during the self-decay process. In contrast, F_5 C-Mn(V)-oxo and F_0 C-Mn(V)-oxo could not return to their corresponding Mn(III) corroles completely due to their gradual oxidation to Mn(IV) corrole species as indicated by their UV-vis spectra. Figures 2 and 3 show the UV-vis spectral changes of four Mn(V)-oxo corroles in toluene and DMF, respectively. It can be seen that less electron-deficient $\mathbf{F}_{5}\mathbf{C}$ -Mn(V)-oxo and $\mathbf{F}_{0}\mathbf{C}$ -Mn(V)-oxo exhibit different self-decay pattern in DMF and toluene compared with the more electron-deficient $\mathbf{F}_{15}\mathbf{C}$ -Mn(V)oxo and $\mathbf{F}_{10}\mathbf{C}$ -Mn(V)-oxo. The kinetics of the self-decay of Mn(V)-oxo corroles was monitored by the absorption at left arm of the Soret-band. The decay was accelerated remarkably in the presence of large excess of styrene (Fig. 4), showing that Mn(V)-oxo corroles are reactive towards styrene substrate. The self-decay rate constants were calculated by the exponential fit of the kinetic curves and the data is summarized in Table 2. Interestingly, two different orders of self-decay rate constants were found in all these solvents. In toluene and DCM, the self-decay rate constants decrease with the decreasing electrondeficient nature of Mn(V)-oxo corrole *i.e.* $k_{F15C-Mn(V)-oxo} >$ $k_{F10C-Mn(V)-oxo} > k_{F5C-Mn(V)-oxo} > k_{F0C-Mn(V)-oxo}$, while in DMF and DMAc the order of self-decay rate constants was reversed *i.e.* $k_{\text{F15C-Mn(V)-oxo}} < k_{\text{F10C-Mn(V)-oxo}} < k_{\text{F5C-Mn(V)-oxo}} < k_{\text{F0C-Mn(V)-oxo}}$. As the self-decay rate constants reflect the reactivity of Mn(V)-oxo corroles, therefore, it may be concluded that the OAT reaction between Mn(V)-oxo corroles and substrates is affected significantly by the nature of the solvent used.

To have a quantitative evaluation of the solvent effect on the OAT reaction, *pseudo*-first order reaction rate constants (k_{obs} , Table 2) of Mn(V)-oxo corroles and styrene were measured in different solvents (molar ratio: Mn(V)-oxo/styrene = 1/1000), and the corresponding bar-graph is shown in Fig. 5. The orders of *pseudo*-first-order reaction rates and self-decay rate constants in different solvents are the same. It may be concluded that in DCM and toluene, more electron-deficient Mn(V)-oxo corrole exhibits the higher reactivity, while in DMF and DMAc more electron-rich Mn(V)-oxo corrole exhibits the higher reactivity. Such a reversed reactivity order may be rationalized by the disproportionation of Mn(V)-oxo corrole into high valent Mn(VI)-oxo corrole in



Fig. 2. UV-vis spectral changes of manganese(V)-oxo corroles ($\sim 3 \times 10^{-5}$ M) in toluene: F_{15} C-Mn(V)-oxo (a), F_{10} C-Mn(V)-oxo (b), F_5 C-Mn(V)-oxo (c) and F_0 C-Mn(V)-oxo (d)



Fig. 3. UV-vis spectral changes of manganese(V)-oxo corroles ($\sim 3 \times 10^{-5}$ M) in DMF: **F**₁₅**C**-Mn(V)-oxo (a), **F**₁₀**C**-Mn(V)-oxo (b), **F**₅**C**-Mn(V)-oxo (c) and **F**₀**C**-Mn(V)-oxo (d)



Fig. 4. Kinetic curves for the reaction of $F_{15}C-Mn(V)$ -oxo and large excess of styrene in toluene (a) and DMF (b) (25.0 ± 0.1 °C)

DMF and DMAc. In such a case, the more electron-rich Mn(V)-oxo corrole exhibits a higher reactivity due to its easier disproportionation [1, 16]. These kinetic evidences suggest that Mn(VI)-oxo corrole may be a possible active

intermediate in manganese corroles catalyzed reactions, as proposed by Gross *et al.* [16], and also support the idea of multiple active oxidants proposed by Newcomb *et al.* [29].

Solvent		$k/k_{\rm obs}~(10^{-4}~{ m s}^{-1})$					
		$\mathbf{F}_{15}\mathbf{C}$ -Mn(V)-oxo	$\mathbf{F}_{10}\mathbf{C}$ -Mn(V)-oxo	$\mathbf{F}_{5}\mathbf{C}$ -Mn(V)-oxo	$\mathbf{F}_0\mathbf{C}$ -Mn(V)-oxo		
Toluene	Self-decay	9.5084	8.0568	6.9426	5.7977		
	styrene	24.2069	17.4945	16.1225	11.5829		
DCM	Self-decay	17.3646	12.6631	5.1967	2.4992		
	styrene	29.2546	24.9920	19.5378	5.7962		
DMF	Self-decay	6.7986	9.3212	11.2855	14.2537		
	styrene	9.5995	13.2886	16.6463	18.7270		
DMAc	Self-decay	2.2067	7.2884	13.4097	23.2774		
	styrene	12.3047	20.7339	28.6217	39.0235		

Table 2. Self-decay rate constants (*k*) and *pseudo*-first-order reaction rate constants (k_{obs}) of Mn(V)-oxo corroles with styrene in different solvents at 25.0 ± 0.1 °C^{a,b}

^a The reaction was monitored by the absorption at left arm of the Soret band. ^b The decay rate constants were calculated by the exponential fit of the kinetic curve.



Fig. 5. Self-decay and *pseudo*-first-order reaction rate constants of Mn(V)-oxo corroles with styrene in different solvents at 25.0 ± 0.1 °C

Mechanistic consideration

By comparing the catalytic activity and the rate constants of manganese corrole derivatives, we suggest that catalytic oxidation reaction of styrene by Mn(III) corroles may proceed *via* three pathways in different solvents as shown in Scheme 1 (path 1-3).

In toluene and DCM, the active specie is Mn(V)-oxo corrole, and the dominant pathway is the electrophilic reaction between Mn(V)-oxo corrole and styrene (Scheme 1, path 1). In this situation, more electron-deficient Mn(III) corroles exhibit a higher activity. In DMF and DMAc, the

active specie is mainly Mn(VI)-oxo corrole generated from Mn(V)-oxo complex by disproportionation reaction. The catalytic oxidation reaction proceeds through path 3 (Scheme 1), and the more effective catalyst is electronrich Mn(III) corrole whose Mn(V)-oxo complex easily generates Mn(VI)-oxo cation [29]. In all the investigated solvents, benzaldehyde is formed *via* dioxygen involved free-radical mechanism (Scheme 1, path 2). This pathway is favored in DMAc and is remarkably suppressed under anaerobic conditions.

EXPERIMENTAL

Reagents

All the solvents, toluene, dichloromethane (DCM), *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMAc), tetrahydrofuran (THF) and dimethyl sulfoxide (DMSO), as well as the standard samples of the reaction products and internal standard (chlorobenzene) were purchased from Sinopharm Chemical Reagent Co. Ltd. and dried prior to use. Commercial analytical grade styrene (Aladdin) was passed through silica gel column prior to use and the purity was tested by GC analysis.

Apparatus

Electronic absorption measurements were performed on a Blue Star B UV-vis spectrophotometer connected with a thermostat at 25.0 ± 0.1 °C. Mass spectra (MS) were recorded on a VG ZAB-HS mass spectrometer (EI, 70 eV). The product analysis was done by a gas chromatograph (Echrom A90) equipped with an Agilent HP-5 capillary column coupled with an FID detector.



Scheme 1. Proposed mechanism for oxidation reactions catalyzed by manganese corroles in different types of solvents ([O] = PhIO and subs = stryene)

Procedure

The catalytic reaction was carried out in six solvents. The mixture of catalyst (1 μ mol), styrene (1 mmol) and PhIO (0.1 mmol) in 2 mL of each solvent was stirred for 3.5 h at room temperature. After periodic time interval, a certain amount of internal standard was added to this reaction mixture and the aliquot was injected into a preheated GC. The identification and quantification of the products were done from the response factors of standard product sample.

Kinetic studies were carried out in quartz cuvette with PTFE septa. The freshly synthesized Mn(V)-oxo corrole solution ($\sim 3 \times 10^{-5}$ M) was taken in the cuvette and placed immediately in a thermostat cell holder in a UV-vis spectrophotometer. The absorbance data was collected over the range of 300–800 nm at 5-sec interval. Each measurement was repeated three times at 25.0 ± 0.1 °C.

Synthesis

Free base corroles (Chart 1) were prepared according to the previously reported methods [8, 47–49].

Preparation of Mn(III) corroles. All Mn(III) corroles (Chart 1) were prepared by refluxing the mixture of corresponding free base corrole and Mn(OAc)₂·4H₂O (molar ratio: 1:10) in methanol for 2 h, and the products were purified by chromatography on silica gel using dichloromethane as eluent [16, 17]. The yields of all Mn(III) corroles were above 90%. **Manganese(III) 5,10,15-tris(pentafluorophenyl) corrole, F**₁₅**C-Mn(III).** UV-vis (CH₂Cl₂): λ_{max} , nm (log ε) 308 (4.32), 397 (4.53), 414 (4.55), 593 (4.00). MS (ESI): m/z (%) 848.2 ([M]⁺, 100). **Manganese(III)** **5,15-bis(pentafluorophenyl)-10-(phenyl) corrole, F**₁₀**C-Mn(III).** UV-vis (CH₂Cl₂): λ_{max} , nm (log ε) 308 (4.38), 402 (4.51), 418 (4.50), 581 (4.04), 620 (4.00). MS (ESI): *m/z* (%) 758.3 ([M]⁺, 100). **Manganese(III) 5,15-bis(phenyl)-10-(pentafluorophenyl) corrole, F₅C-Mn(III).** UV-vis (CH₂Cl₂): λ_{max} , nm (log ε) 308 (4.35), 405 (4.55), 423 (4.54), 583 (3.97), 631 (4.01). MS (ESI): *m/z* (%) 668.2 ([M]⁺, 100). **Manganese(III) 5,10,15-triphenylcorrole, F**₀**C-Mn(III).** UV-vis (CH₂Cl₂): λ_{max} , nm (log ε) 402 (4.48), 415 (4.45), 500 (4.13), 640 (3.87). MS (ESI): *m/z* (%) 578.2 ([M]⁺, 100).

Preparation of Mn(V)-oxo corroles. Mn(V)-oxo corroles (Chart 1) were prepared by treating Mn(III) corrole solution ($\sim 3 \times 10^{-5}$ M) with PhIO (molar ratio 1:10) at room temperature until solution color turns red. The superfluous PhIO was removed by flash column chromatography on basic alumina [16, 17]. Manganese(V)-oxo 5,10,15-tris(pentafluorophenyl) corrole, $F_{15}C-Mn(V)$ -oxo. UV-vis (CH₂Cl₂): λ_{max} , nm (log ε) 346 (4.56), 408 (4.44), 518 (3.80). MS (ESI): m/z (%) 864.0 ([M]⁺, 100), 848.2 ([M⁺ - O], 95). Manganese(V)-oxo 5,15-bis(pentafluorophenyl)-10-(phenyl) corrole, F₁₀C-Mn(V)-oxo. UV-vis (CH₂Cl₂): λ_{max} , nm (log ϵ) 347 (4.52), 409 (4.51), 521 (3.82). MS (ESI): m/z (%) 774.1 ([M]⁺, 100), 758.3 ([M⁺ – O], 45). Manganese(V)-oxo 5,15-bis(phenyl)-10-(pentafluorophenyl) corrole, F₅C-Mn(V)-oxo. UV-vis (CH₂Cl₂): λ_{max} , nm (log ε) 349 (4.54), 421 (4.38), 515 (3.86). MS (ESI): m/z (%) 684.2 ([M]⁺, 100), 668.2 ([M⁺ - O], 42). Manganese(V)-oxo 5,10,15-triphenyl corrole, F₀C-**Mn(V)-oxo.** UV-vis (CH₂Cl₂): λ_{max} , nm (log ε) 344 (4.44), 408 (4.30), 525 (3.73). MS (ESI): m/z (%) 595.3 $([M]^+, 100), 578.2 ([M^+ - O], 19).$

CONCLUSION

We report the first systematic study of the effect of solvent on the catalytic oxidation of styrene by four Mn(III) corroles having different electronic features in the presence of PhIO as oxidizing agent. We found that the properties of solvent itself has remarkable effect on the catalytic activity of Mn(III) corrole catalysts. The transformation of Mn(III) corroles into their corresponding Mn(V)-oxo corroles. and their subsequent reaction with styrene in a variety of solvents was also performed. It was observed that more electron-deficient Mn(V)-oxo corroles exhibit higher reactivity towards styrene in DCM and toluene, while less electron-deficient Mn(V)-oxo corroles exhibit higher reactivity towards styrene in basic solvents (DMF, DMAc). A plausible catalytic mechanism is suggested based on the combined catalytic and kinetic data. It is evident that the catalytic oxidation of styrene by manganese corroles may proceed via oxygen atom transfer (OAT) between Mn(V)and/or Mn(VI)-oxo corrole intermediate and the substrate, or via dioxygen involved free radical process, depending on the solvent used during the catalytic reaction. Further investigations of solvent effects on the properties of various Mn(V)-oxo corroles derived from various electrondonating and -withdrawing substituents and their catalytic oxidation reactions are currently underway.

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