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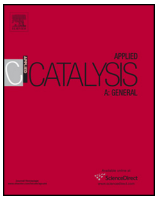

Enhanced iron(III) corrole-catalyzed oxidations with iodobenzene diacetate: Synthetic and mechanistic investigations

Tse-Hong Chen, Ka Wai Kwong, Aaron Carver, Weilong Luo, Rui Zhang*

Department of Chemistry, Western Kentucky University, Bowling Green, KY 42101, USA

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ABSTRACT

The electron-deficient iron(III) corrole complex catalyzes the efficient oxidation of hydrocarbons using $PhI(OAc)_2$ as an mild oxygen source. The catalyst stability against degradation was much enhanced owing to the mild oxidizing ability of $PhI(OAc)_2$. Excellent selectivity and high catalytic efficiency (with up to 1400 TON) have been achieved in alkene epoxidations. This promising oxygen transfer process is mechanistically rationalized in terms of a putative high-valent iron(V)-oxo species as the active oxidant.

1. Introduction

Catalytic oxidation is a pivotal transformation for chemical synthesis in organic laboratories and petrochemical industries, and the search for versatile and selective reagents for catalytic applications under mild conditions have been centers of research interest for decades [1]. In this regard, many transition metal catalysts [2–4] have been synthesized to mimic the metalloenzymes in Nature, notably the cytochrome P450s [5]. In most biomimetic catalytic oxidations, a transition metal catalyst is oxidized to a high-valent metal-oxo species by a sacrificial oxidant, and then the reactive transition metal-oxo intermediate oxidizes the substrate [6].

Owing to the advance in the synthesis of 19-membered macrocyclic triarylcorroles including *meso*-N-substituted triazocorroles(corrolazines) [7,8], metallocorroles, as a general class, have attracted considerable interest in their catalytic properties in view of their similarity to metalloporphyrins [9–12]. Being tri-anionic ligands, corrole has the capacity to access higher metal-oxo species which are inherently more stable than the corresponding porphyrin-metal-oxo species [13–15]. Thus, a number of metallocorroles have been prepared and explored in a wide variety of catalytic oxidations [9–11]. In 1999, Gross and coworkers reported the first example of catalytic oxidation with the iron(IV) complex of tris(pentafluorophenyl)corrole (H_3TPFC) using iodosobenzene (PhIO) as the sacrificial oxidant [16]. Later, biomimetic oxidations with Mn^{III}(TPFC) [13], albumin-conjugated manganese [17] and chromium corroles [18] 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 [19,20]. Recently, we reported aerobic oxidations catalyzed by a fluorinated iron(IV) μ-oxo biscorrole in a photo-disproportionation mechanism [21]. Meanwhile, Goldberg and coworkers have extensively investigated manganese and iron corrolazines as oxidation catalysts with different oxygen sources [22–25]. However, metallocorroles are less robust than metalloporphyrins and prone to oxidative degradation. Apparently, the choice of oxygen sources is crucial regarding their stability and reactivity in metallocorrole or metallocorrolazine mediated oxidations [24].

In contrast to the sacrificial oxidants in common use for metal-catalyzed reactions, iodobenzene diacetate, i.e. $PhI(OAc)_2$, which is readily soluble in organic media and safe to use, has been less often employed due to its mild oxidizing ability. Collman and Nam reported, respectively, the use of $PhI(OAc)_2$ as terminal oxidant for the iron(III) porphyrin catalyzed oxidation of hydrocarbons [26,27]. Adam et al. also described a highly selective oxidation of alcohols by chromium(III) salen with $PhI(OAc)_2$ [28]. Very recently, we employed $PhI(OAc)_2$ as an efficient oxygen source for the selective catalytic sulfoxidations by ruthenium porphyrins under visible light irradiation [12]. In particular, $PhI(OAc)_2$ does not show appreciable reactivity towards organic substrates nor damage the metal catalysts under the usual catalytic conditions. In this work, we communicate our findings on the usefulness of $PhI(OAc)_2$ for the efficient catalytic oxidation of alkenes and activated benzylic hydrocarbons by iron corroles. Our mechanistic studies also indicate that a corrole-iron(V)-oxo species detected in the previous

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* Corresponding author. Tel.: +270 745 3803; fax: +270 745 5361.
E-mail address: rui.zhang@wku.edu (R. Zhang).

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laser flash photolysis (LFP) studies [29,30] is favored as the active oxidant.

2. Experimental

2.1. Materials and instrument

Acetonitrile was obtained from Fisher Scientific and distilled over P_2O_5 prior to use. All reactive substrates for catalytic reactions were the best available purity from Sigma–Aldrich Chemical Co. and were purified by passing through a dry column of active alumina (Grade I) before use. Iodobenzene diacetate or (diacetoxyiodo)benzene, i.e. $PhI(OAc)_2$, was purchase from Aldrich Chemical Co. and used as such. Pyrrole (98%), benzaldehyde and pentafluorobenzaldehyde from Sigma-Aldrich Chemical Company were distilled prior to use.

Corrole free ligands employed in this study, including 5,10,15-tripentafluorophenylcorrole (H_3TPFC) [7,8] and 5,10,15-triphenylcorrole (H_3TPC) [31], were prepared according to the reported procedures, and their characterization data (^1H NMR and UV/Vis) were consistent with reported values. The corrole-iron(III) dietherate complexes were prepared as previously described [31]. In a typical procedure, a solution of H_3TPFC (50 mg, 63 μmol) and a large excess of iron(II) chloride (125 mg, 1.4 mmol) in dry DMF under argon was heated at reflux for 60 min. Evaporation of solvent followed by column chromatography on silica gel (diethyl ether) resulted in isolation of the desired $Fe^{III}(TPFC)(OEt_2)_2$ in > 90% yield. Following the known procedure [31], the corrole-iron(IV) chloride, formulated as $Fe^{IV}(TPFC)Cl$, and the fluorinated diiron(IV) μ-oxo biscorrole, formulated as $[Fe^{IV}(TPFC)]_2O$, were prepared by aerobic oxidation of $Fe^{III}(TPFC)(OEt_2)_2$ in the presence of hydrochloric acid (HCl) or in the solution of acetonitrile and n-heptane. All these known iron corrole complexes were characterized by UV–visible, IR and ^1H NMR spectra that matched those previously reported [31].

UV–vis spectra were recorded on an Agilent 8453 diode array spectrophotometer. ^1H NMR was performed on a JEOL ECA-500 MHz spectrometer at 298 K with tetramethylsilane (TMS) as internal standard. Chemical shrifts (ppm) are reported relative to TMS. Gas Chromatograph analyses were conducted on an Agilent GC7820A/MS5975 equipped with a flame ionization detector (FID) using a J&W Scientific Cyclodex-B (chiral) capillary column. The above GC/MS system is also coupled with an auto sample injector. Reactions of $Fe^{III}(TPFC)$ with excess of $PhI(OAc)_2$ or PhIO were conducted in a anaerobic methanol solution at 23 ± 2 °C.

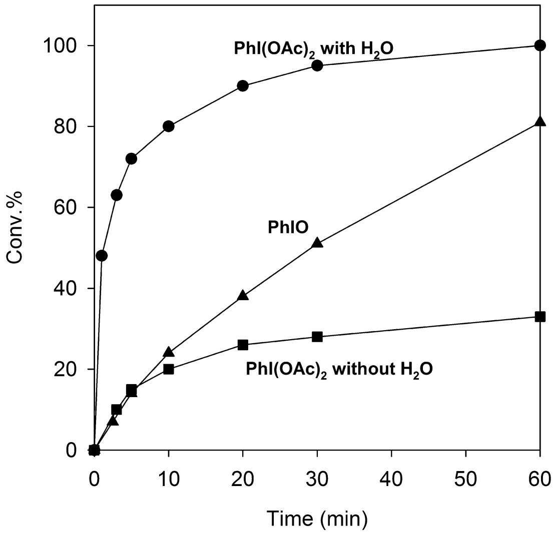


Fig. 1. Time courses for the corrole-iron(III)-catalyzed epoxidation of *cis*-cyclooctene in CH_3CN (0.5 mL) at 23 °C: substrate (0.2 mmol), $PhI(OAc)_2$ or PhIO (triangle) (0.24 mmol), $Fe^{III}(TPFC)$ catalyst (1.0 μmol) in the presence (dot) or absence (square) of H_2O (5 μL). Aliquots were taken at selected time intervals for product analyses by GC.

2.2. General procedure for catalytic oxidations

Unless otherwise indicated, all catalytic reactions were typically carried out in the presence of a small amount of H_2O (5 μL) with 1 μmol of catalyst (*ca.* 0.5 mol%), 0.2 mmol of organic substrate and 1.2 equivalent of $PhI(OAc)_2$ (0.24 mmol) in 0.5 mL of acetonitrile at 23 °C or 50 °C in a water bath. Aliquots of the reaction solution at constant time interval were analyzed by GC/MS to determine the conversions, formed products and yields with an internal standard. The pure products were isolated by a flash column chromatography (silica gel with CH_2Cl_2 and hexane mixture) to give isolated yields (Table 1, entry 3 and Table 2, entries 1–9). All reactions were run 2 to 3 times, and the data reported represent the average of these reactions.

2.3. Catalytic competitive oxidations and kinetic isotope effect (KIE) studies

A CH_3CN solution containing equal amounts of two substrates, e.g. styrenes (0.2 mmol) and substituted styrenes (0.2 mmol), iron(III) corrole catalyst (1 μmol) and an internal standard of

Table 1
Catalytic oxidation of *cis*-cyclooctene with $PhI(OAc)_2$ and iron corrole complexes [a]

Entry	Catalyst	Solvent	*t* (min)	Convn (%)[b]	Yields(%)[c]
1[d]	$Fe^{III}(TPFC)$	CH_3CN	60	33	100
2			60	100	100
3			10 (50 °C)	100	100 (93)[e]
4[f]			360 (50 °C)	70	100
5[g]			60	83	99
6		CH_3OH	60	73	100
7		CH_2Cl_2	60	83	100
8	$Fe^{IV}(TPFC)Cl$	CH_3CN	60	87	100
9	$[Fe^{IV}(TPFC)]_2O$	CH_3CN	60	74	98
10	$Fe^{III}(TPC)$	CH_3CN	60	6	90

[a] Unless otherwise specified, all reactions were carried out in solvent (0.5 mL) with H_2O (5 μL) at 23 °C with *cis*-cyclooctene (0.20 mmol), 1.2 equiv. of $PhI(OAc)_2$ and 0.5 mol% of iron corrole catalyst.
[b] Determined by GC-MS analysis of the crude reaction mixture with a capillary column (J&W Scientific Cyclodex B).
[c] GC yields based on the amount of substrate consumed; material balances > 95%.
[d] Without H_2O.
[e] Isolated yield after column chromatography (silica gel).
[f] 0.05 mol% catalyst loading.
[g] PhIO (1.2 equiv.) was used.

1,2,4-trichlorobezene (0.1 mmol) was prepared (final volume = 0.5 mL). The internal standard was shown to be stable to the oxidation conditions in control reactions. $PhI(OAc)_2$ (0.2 mmol) as limiting reagent was added, and the mixture was stirred at ambient temperature (23 ± 2 °C) for 10 min. Relative rate ratios for catalytic oxidations were determined based on the amounts of substrates by GC (FID) as measured against an internal standard. In this work, all the catalytic epoxidation proceeded with good epoxide yields (> 80%) and mass balance (> 95%), and in all cases no traces of polymers or oligomers were detected. Thus, the rate of alkene disappearance should reasonably reflect the alkene reactivity toward the corrole-iron-catalyzed epoxidation. The values reported in Table 3 are the averages of 2–3 runs with standard deviations (1σ).

3. Results and discussion

3.1. Screening studies

The potential of $PhI(OAc)_2$ as an oxygen source was first evaluated in the catalytic epoxidation of *cis*-cyclooctene by the electron-deficient iron(III) 5,10,15- tris(pentafluorophenyl) corrole, i.e. Fe^{III}(TPFC).[32] Under mild homogeneous conditions, the epoxidations were carried out with a catalyst: substrate: $PhI(OAc)_2$ ratio of 1:200:220 (Table 1). After 1 h of reaction in CH_3CN, *cis*-cyclooctene oxide was obtained as the only identifiable oxidation product (> 99% by GC) with *ca.* 33% conversion (Table 1, entry 1). Gratifyingly, the same reaction proceeded much more rapidly with a small amount of H_2O (5 μl), and thus, 100% conversions were obtained within 60 min at 23 °C (entry 2) or 10 min at 50 °C (entry 3). Fig. 1 depicts the time courses for the epoxidation in the presence and absence of water. Similar water accelerating effect observed in the reported iron(III) porphyrin-catalyzed oxidations was rationalized in terms of the formation of more oxidizing PhIO [27]. Remarkably, the catalyst loading can be as low as of 0.05 mol% (entry 4) without significant loss of activity, illustrating an unequivocally the high efficiency (1400 TON). Although PhIO is a common oxygen source generally used in metal-catalyzed oxidations, it was found that the use of PhIO under the same conditions led to a lower catalytic activity (entry 5 and Fig. 1), presumably due to its poor solubility in CH_3CN and/or causing more catalyst bleaching. Moreover, no accelerating effect of water was observed in the catalytic oxidation by PhIO in the presence of acetic acid (data not shown). The use of CH_3OH or CH_2Cl_2 as solvent instead of CH_3CN resulted in reduced activity (entries 6 and 7). Quite interestingly, the oxidation state on the metal gave a minor effect, and the Fe^{IV}(TPFC)Cl (entry 8) and $[Fe^{IV}(TPFC)]_2O$ (entry 9) gave a slightly reduced catalytic activities compared to Fe^{III}(TPFC). Catalyst degradation was a problem when the non-halogenated Fe^{III}(TPC) (TPC = 5, 10,15-triphenylcorrole) was used as catalyst, showing a sluggish catalytic activity (entry 10). Control experiments showed that no epoxide was formed in the absence of either the catalyst or the $PhI(OAc)_2$ even at elevated temperature (50 °C) or in the presence of acetic acid.

3.2. Substrate scope and scale

Consequently, the catalytic oxidations of a variety of organic substrates were investigated under optimized conditions. Table 2 lists the oxidized products and corresponding substrate conversions and product yields including isolated yields using the Fe^{III}(TPFC) as catalyst. As evident in Table 2, in many cases, quantitative conversions, excellent selectivity and rapid turnovers (up to 20 TOF min^{-1}) were observed. For example, epoxidation of cyclohexene was completed within 10 min, giving primarily epoxide with negligible amounts of allylic oxidation products (entry 2). Remarkably, Fe^{III}(TPFC) performs as well as one of the best porphyrin catalysts known Fe^{III}(TPFPP)Cl (TPFPP = tetrakis(pentafluorophenyl)porphinato) with respect to the epoxidation of cyclohexene under similar reaction conditions [27]. This catalytic activity (TOF) and product selectivity is a major improvement over previously reported metallocorrole catalysts [13,16] including perhalogenated $Mn^{III}(F_8TPFC)$ [20] and $Mn^{III}(Br_8TPFC)$ [19]. Epoxidation of *cis*- and *trans*-stilbenes afforded corresponding expoxides exclusively with complete stereoretention (entries 3 and 4). In the epoxidation of styrene and substituted styrene, moderate conversions were observed albeit with small amounts of aldehyde products (entries 6 and 7). Similarly, the oxidation of secondary benzylic alcohols gave the corresponding ketones with moderate catalytic activities (entries 8 and 9). Activated alkanes including ethylbenzene and diphenylmethane were oxidized to the corresponding alcohols and/or ketones from over-oxidation with lowest activity (entries 10 and 11). It is noteworthy that monitoring catalytic reactions by UV–vis spectroscopy indicated no significant catalyst bleaching in the end of reactions (see Fig. S1 in Supporting Information). Thus, in comparison to other oxidants such as PhIO, the corrole catalyst stability against degradation was much enhanced owing to the mild oxidizing ability of $PhI(OAc)_2$.

To show the synthetic utility of the method, the epoxidation of *cis*-stilbene was scaled up to 2.0 mmol and to our delight, a similar result was obtained in 100% conversion and 95% isolated yield exclusively for *cis*-stilbene oxide.

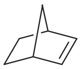
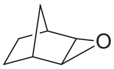
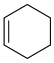
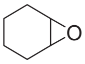
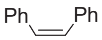
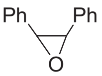
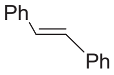
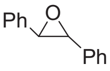
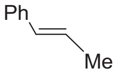
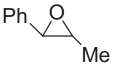
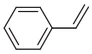
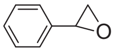
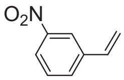
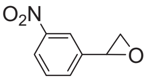
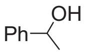
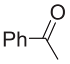
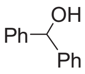
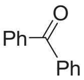
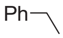
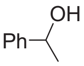
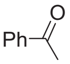
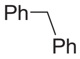
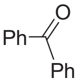
3.3. Catalytic competition studies

Prior to the present study, the use of metallcorroles for catalytic oxidations has met with limited success in view of the poor selectivity, low efficiency and, in most cases, inherent catalyst degradation. The synthetic value of the $Fe^{III}(TPFC)/PhI(OAc)_2$ system presented above are indisputable, and the observed high catalytic activity and complete stereoretension in the epoxidation of *cis*-alkenes strongly implicates a high-valent corrole-iron-oxo species as the active oxidant, although they are still rare and elusive. Goldberg and coworkers have recently reported the spectroscopic evidence for a high-valent corralizine-iron-oxo species as Compound I heme analogues [24,25]. In fact, we reported LFP generation and kinetic studies of highly reactive corrole-iron-oxo intermediates that are best described as iron(V)-oxo species [29,30]. To evaluate the identity of the active oxidant during the catalytic conditions, the competition studies with Fe^{III}(TPFC) and $PhI(OAc)_2$ were conducted as described in Table 3. Evidently, the results of the competition reactions between cyclohexene and *cis*-cyclooctene and between ethylbenzene and ethlybenzene-d_{10} are in good agreement with the ratios of the absolute rate constants found in direct kinetic studies of the corrole-iron(V)-oxo species from LFP studies [29,30]. Notably, the competitive catalytic oxidation of PhEt-d_0 and PhEt-d_{10} revealed a kinetic isotope effect (KIE) of $k_H/k_D = 4.40 \pm 0.21$ at 298 K, similar to the KIE reported for the same reaction with an electron-deficient iron(IV)-oxo porphyrin radical cation species (model Compound I).[33] The observed KIE is larger than those observed in autooxidation processes (typical KIE = 1–2),[34] supporting a non-radical mechanism.

3.4. Hammett correlation studies

A further reflection of the high reactivity of active intermediate involved is seen in the linear Hammett plot for competitive oxidations of the series of substituted styrenes (Y-styrene, *Y* = 4-MeO, 4-Me, 4-F, 4-Cl, and 3-NO_2). Fig. 2 depicts a linear correlation ($R = 0.996$) of log k_{rel} [$k_{rel} = k(\text{Y-styrene})/k(\text{styrene})$] versus

Table 2
Iron(III) corrole-catalyzed oxidations with $PhI(OAc)_2$ [a]

Entry	Substrate	*t* (min)	Convn (%)[b] (TOF[min^{-1}])[c]	Products	Yields(%)[d] (isolated yield)
1		10	71 (14)		100[e] (84)
2[f]		10	100 (20)		96 (92)
3		10	100 (20)		99 (95)
4		30	100 (6.8)		91 (90)
5		30	100 (6.8)		96 (89)
6[g]		10	60 (12)		83 (81)
7		10	51 (10)		95 (92)
8		30	54 (3.6)		100 (82)
9		30	70 (4.6)		100 (95)
10		180	10 (0.11)		40
					60
11		180	14 (0.15)		100

[a] All reactions were carried out at 50 °C with 0.5 mol% catalyst of Fe^{III}(TPFC) in 0.5 mL of CH_3CN containing 0.2 mmol of substrate, 0.25 mmol of $PhI(OAc)_2$ and 5 µl H_2O.

[b] Determined by GC-MS analysis of the crude reaction mixture with an internal standard (1,2,4-trichlorobenzene); material balances > 95%.

[c] TOF = turnovers frequency (min^{-1}).

[d] GC yields based on the amount of substrate consumed.

[e] Isomeric ratio (*exo:endo*) > 95:5.

[f] 3% of 2-cyclohexenol was detected.

[g] 10% of 1-phenylacetaldehyde and 3% benzaldehyde were also formed.

Table 3
Relative rate constants for competitive oxidations catalyzed by Fe^{III}(TPFC) with $PhI(OAc)_2$[a]

Entry	Substrate	k_{rel}[b]	k_{rel}[c]
1	cyclohexene/*cis*-cyclooctene	1.21 ± 0.08	1.25 ± 0.10
2	ethylbenzene-d_0/ethylbenzene-d_{10}	4.40 ± 0.26	3.70 ± 0.40
3	4-fluorostyrene/styrene	1.15 ± 0.02	
4	4-chlorostyrene/styrene	1.03 ± 0.05	
5	3-nitrotyrene/styrene	0.33 ± 0.02	
6	4-methylstyrene/styrene	1.95 ± 0.12	
7	4-methoxystyrene/styrene	4.71 ± 0.33	
8	*cis*-stilbene/phenylethanol	3.62 ± 0.21	

[a] All competition reactions were conducted in CH_3CN (0.5 mL) with H_2O (5 µl) containing equal amounts of two substrates, e.g., PhEt-d_0 (0.2 mmol) and PhEt-d_{10} (0.2 mmol), $PhI(OAc)_2$ (0.2 mmol) and Fe^{III}(TPFC) (1.0 µmol). The mixture was stirred for 10 min at room temperature.

[b] Ratios of relative rate constants from competition reactions were determined based on the conversions of substrates. All competition ratios are averages of 2–3 determinations with standard deviations (1σ).

[c] Ratios of absolute rate constants were obtained from LFP kinetic studies of photo-generated corrole-iron(V)-oxo species (refs [29,30]).

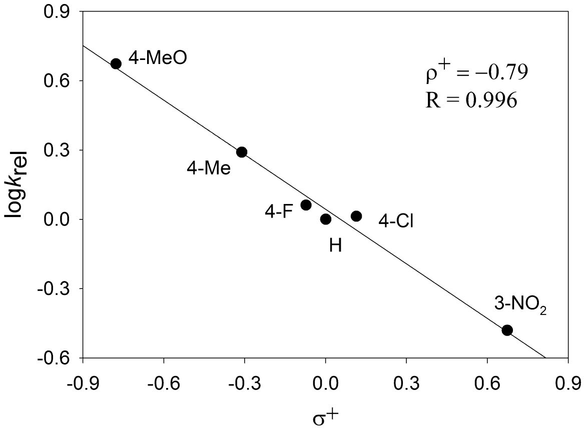


Fig. 2. Hammett correlation studies (log k_{rel} vs σ^+) for the Fe^{III}(TPFC)-catalyzed epoxidation of substituted styrenes by $PhI(OAc)_2$ in CH_3CN at 23 ± 2 °C.

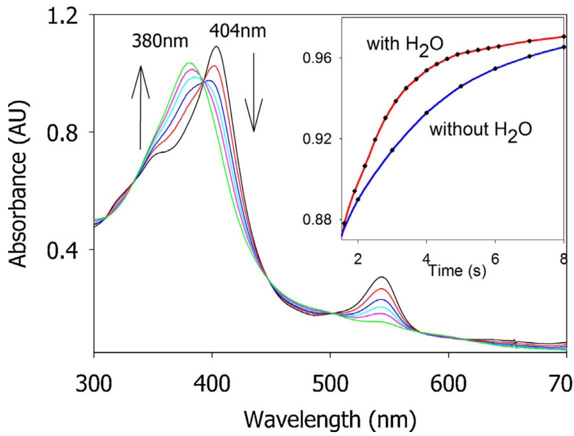


Fig. 3. Time-resolved spectra of the oxidation of Fe^{III}(TPFC) (2.5×10^{-5} M) by $PhI(OAc)_2$ (2.5 equiv.) in anaerobic CH_3CN at 23 ± 2 °C over 10 s. Inset: kinetic traces monitored at 380 nm without and with H_2O (*ca.* 30 mM).

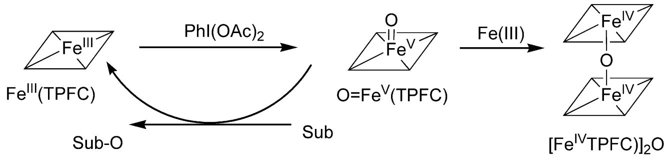
Hammett σ^+ substituent constant. The slope (ρ^+) of the plot is–0.79, again, which is similar to the values found with model Compound I species with a strong binding chloride counterion ($\rho^+ = -0.89$) [33]. However, this observed ρ^+ value is about 2-fold larger in magnitude than the previously reported value (−0.28) found for a related chloroperoxidase (CPO) Compound I [35]. Apparently, the competitive product analysis and Hammett correlation studies strongly suggest that the highly reactive corrole-iron(V)-oxo species [29,30] as the premier reactive intermediate is plausible, even though it could not be detected during the catalytic reactions.

3.5. Spectral studies

To further probe the nature of the active oxidizing species, we conducted the chemical oxidation reaction of Fe^{III}(TPFC) by $PhI(OAc)_2$ in CH_3CN or CH_3OH in the absence of substrate. As shown in Fig. 3, with 2.5 equivalents of $PhI(OAc)_2$, the Fe^{III}(TPFC) (λ_{max} = 404 nm) was quantitatively converted to a stable compound with clearly resolved isosbestic points. The formed product with an absorption at λ_{max} = 380 nm was essentially identified as the known *bis*-corrole-diiron(IV) μ-oxo dimer, which was independently prepared from a reported method [32]. In our recent study, the formation of $[Fe^{IV}(TPFC)]_2O$ exhibited a marked dependence on the electron-demanding F groups on phenyl ring [21]. Presumably, the F groups would stabilize the iron(IV) complex in a dimeric form by reducing the electron density of the metal atom. Noticeably, the formation rate was accelerated by adding a trace amount of water (inset in Fig. 3). Clearly, addition of H_2O in the oxidation reaction allows for the release of stable HOAc (detected by GC) instead of anhydride Ac_2O under anhydrous condition, resulting a faster reaction. Furthermore, the formation rate of the μ-oxo dimer accelerated linearly as the function of $PhI(OAc)_2$ concentration, and the slope of the plot gave an apparent second-order rate constant of $k_2 = (3.5 \pm 0.3) \times 10^3\ M^{-1}\ s^{-1}$ (Fig. S2 in Supporting Information). By comparison, the formation rate of the same μ-oxo dimer is approximately six times slower using the less soluble PhIO under the same conditions (Fig. S3 in the Supporting Information)

3.6. Proposed catalytic cycle

On the basis of the present experimental facts, a catalytic cycle is proposed with a high-valent corrole-iron(V)-oxo species as the active oxidant, which accounts adequately for the high reactivity and selectivity (Scheme 1). In the absence of organic substrate, the highly reactive iron(V)-oxo oxidant may form the stable μ-oxo dimer possibly through a reaction with unreacted iron(III) precursor. The proposed corrole-iron(V)-oxo oxidant has not been detected in reaction of Fe^{III}(TPFC) and $PhI(OAc)_2$, however, suggesting that the oxidant reacts much faster than it is formed.



Scheme 1. A proposed catalytic cycle.

In this work, we found that the addition of some water gives clear accelerating effect, similar to previously reported iron(III)-porphyrin catalyzed oxidations which has been ascribed to the formation of PhIO from $PhI(OAc)_2$ and water [27]. So most likely this is also operative with the iron(III) corrole catalyst. The slow and continuing, i.e. a steady state, formation of PhIO in the presence of water may explain the enhanced catalytic activity, stability of the catalyst and/or improved solubility.

4. Conclusion

In conclusion, we have demonstrated that the electron-deficient corrole-iron(III) complex catalyzed efficiently oxidation of alkenes and activated hydrocarbons with $PhI(OAc)_2$ as a promising oxygen source. The iron(III) corrole catalyst exhibits high reactivity, good selectivity, and improved stability in the epoxidation of alkenes with $PhI(OAc)_2$. The competition and Hammett correlation studies have implicated a high-valent iron(V)-oxo intermediate as the active oxidant.

5. Supplementary data

Figs. S1–S3, and copies of ^1H and ^{13}C NMR spectra and GC traces. This material is available free of charge via the Internet at http//pubs.acs.org.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2015.02.047.

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