



A biomimetic oxidation catalyzed by manganese(III) porphyrins and iodobenzene diacetate: Synthetic and mechanistic investigations



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ARTICLE INFO

Article history:

Received 19 January 2015

Received in revised form 27 February 2015

Accepted 5 March 2015

Available online 19 March 2015

Keywords:

Manganese porphyrin

Catalytic oxidation

Iodobenzene diacetate

Manganese-oxo species

ABSTRACT

With iodobenzene diacetate [PhI(OAc)₂] as the oxygen source, manganese(III) porphyrin complexes exhibit remarkable catalytic activity toward the selective oxidation of alkenes and activated hydrocarbons. Conspicuous is the fact that the readily soluble PhI(OAc)₂ in the presence of a small amount of water is more efficient than the commonly used PhIO and other oxygen sources under same catalytic conditions. High selectivity for epoxides and excellent catalytic efficiency with up to 10,000 TON have been achieved in alkene epoxidations. It was found that the reactivity of manganese(III) porphyrin catalysts was greatly affected by axial ligand and the weakly binding perchlorate gave the highest catalytic activity in the epoxidation of alkenes. A manganese(IV)-oxo porphyrin was detected in the reaction of the manganese(III) porphyrin and PhI(OAc)₂. However, our catalytic competition and Hammett studies have suggested that the more reactive manganese(V)-oxo intermediate was favored as the premier active oxidant, even it is too short-lived to be produced in detectable concentrations.

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1. Introduction

Catalytic oxidation is a pivotal synthetic transformation in organic laboratories and chemical industries [1]. As the demand for greener processing increases [2,3], the transition metal catalyzed oxidations of hydrocarbons to oxygenated products with environmentally friendly oxygen sources such as molecular oxygen are becoming the most important and rewarding protocols in chemical industries [4,5]. In Nature, the ubiquitous cytochrome P-450 enzymes (P450s) [6] can catalyze a wide variety of oxidation reactions with exceptionally high reactivity and selectivity [7,8]. In this context, many transition metal catalysts with a core structure closely resembling that of the iron porphyrin core of P450s, have been synthesized as models to invent enzyme-like oxidation catalysts as well as to probe the sophisticated mechanism of molecular oxygen activation [9,10]. Among the most extensively studied systems are the epoxidation of alkenes and hydroxylation of alkanes catalyzed by transition metals in macrocyclic ligands, including those containing chiral auxiliaries for enantioselective oxidations [11]. Historically, synthetic manganese porphyrin complexes have shown catalytic promise as P450s enzyme model in oxidation reactions over decades [9,12]. The sacrificial oxidants compatible with manganese porphyrins were mostly restricted to PhIO, NaOCl,

H₂O₂, ^tBuOOH (*tert*-butylhydroperoxide), KHSO₅ and oxaziridines [9]. Molecular oxygen can also be used in the presence of an electron source [13]. The use of H₂O₂ often results in oxidative degradation of the catalyst due to the potency of this oxidant [9]. In contrast to epoxidations catalyzed by other metals, the manganese porphyrin-catalyzed oxidation gave low stereospecificity. For example, the epoxidation of *cis*-stilbene catalyzed by Mn^{III}(TPP)Cl (TPP = tetraphenylporphyrin) and PhIO generated *cis*- and *trans*-stilbene oxide in a ratio of 35:65 [14].

Identifying the kinetically competent oxidants could lead to better control of the catalytic oxidation reactions, especially in terms of selectivities. In general, high-valent transition metal-oxo transients are invoked as the active oxidizing species in many metal-catalyzed oxidations [15]. However, in most catalytic reactions, the concentrations of active metal-oxo oxidants do not build up to detectable amounts. For example, highly reactive porphyrin-manganese(V)-oxo derivatives were proposed as the key intermediates in catalytic processes for decades [14,16], but they eluded detection until 1997 when Groves and co-workers reported the synthesis of the first manganese(V)-oxo porphyrin complex [17]. Subsequently, additional examples of manganese(V)-oxo porphyrins were reported [18,19]. In contrast, the well characterized manganese(IV)-oxo derivatives are less reactive than manganese(V)-oxo species and unlikely to be the dominant oxidants in manganese porphyrin-catalyzed oxidations [20–22]. In previous laser flash photolysis (LFP) studies reported by Newcomb and coworkers, both porphyrin-manganese(IV)-oxo

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species and porphyrin-manganese(V)-oxo species were photochemically produced as a function of the identity of the counterions binding to the metal of the manganese(III) [23,24]. For homogeneous catalysts, where catalytic species have ready access to one another, high-valent metal-oxo species might be detected, but these species might not be reactive enough to be the true oxidants. Moreover, as reported studies of porphyrin-manganese(IV)-oxo species [24], and corrole-manganese(V)-oxo species [25], indicate, a high-valent metal-oxo species detected in a reaction might not be the true oxidant in the system. Specifically, the observable less reactive porphyrin-manganese(IV)-oxo species can react via a disproportionation pathway to give an manganese(V)-oxo intermediate that is the true oxidant but is not produced in detectable amounts [24].

Our group initiated a general program that aims to fully exploit the potential of metalloporphyrin complexes toward oxidation reactions, with an ultimate goal of developing practical metalloporphyrin oxidation catalysts for organic synthesis. In contrast to the sacrificial oxidants in common use for metal-catalyzed reactions, iodobenzene diacetate, i.e. $\text{PhI}(\text{OAc})_2$, has been less often employed for porphyrin-manganese-catalyzed oxidations due to its mild oxidizing ability. Of note, $\text{PhI}(\text{OAc})_2$ is readily soluble in organic media and safe to use. In particular, it does not show appreciable reactivity toward organic substrates nor damage the metal catalysts under the usual catalytic conditions. Collman and Nam reported, respectively, the use of $\text{PhI}(\text{OAc})_2$ as terminal oxidant for the iron(III) porphyrin catalyzed oxidation of hydrocarbons [26,27]. Xia and coworkers also described the manganese(III) porphyrin catalyzed epoxidation of several alkenes with $\text{PhI}(\text{OAc})_2$ in the ionic liquid/ CH_2Cl_2 mixed solvent [12,13]. Adam et al. described a highly selective oxidation of alcohols by chromium(III) salen with $\text{PhI}(\text{OAc})_2$ [28]. In addition, Nishiyama showed that $\text{PhI}(\text{OAc})_2$ is a better oxidant than PhIO in ruthenium-pyridine-2,6-dicarboxylate complex-catalyzed epoxidation of *trans*-stilbene [29]. We recently employed $\text{PhI}(\text{OAc})_2$ as an efficient oxygen source for the selective catalytic sulfoxidations by ruthenium porphyrins under visible light irradiation [30]. In our unpublished work, we have discovered that the electron-deficient corrole-iron(III) complex catalyzed efficient oxidation of alkenes with $\text{PhI}(\text{OAc})_2$ as a promising oxygen source. The inherent unstable corrole-catalyst against degradation was much improved owing to the mild oxidizing power of $\text{PhI}(\text{OAc})_2$. In this study, we present our detailed findings on the usefulness of $\text{PhI}(\text{OAc})_2$ for the highly efficient catalytic oxidation of alkenes and activated benzylic hydrocarbons by porphyrin-manganese(III) catalysts (**1a–c** in Scheme 1). In most cases, quantitative conversions of substrates, excellent selectivities and high turnovers of up to 10,000 TON were obtained. Meanwhile, we show that a low-reactivity

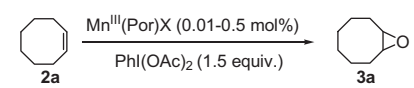
manganese(IV)-oxo porphyrin intermediate which was detected by the oxidation of the manganese(III) porphyrin with $\text{PhI}(\text{OAc})_2$, is not likely the sole oxidant. Instead, a more reactive porphyrin-manganese(V)-oxo species is favored as the premier active oxidant.

2. Results and discussions

2.1. Screening studies

The potential of $\text{PhI}(\text{OAc})_2$ as an oxygen source was first evaluated in the catalytic epoxidation of *cis*-cyclooctene (**2a**) by different manganese(III) porphyrin catalysts (**1a–c** in Scheme 1). Under mild homogeneous conditions, the epoxidations were carried out with a catalyst: substrate: $\text{PhI}(\text{OAc})_2$ ratio of 1:200:300 (Table 1). After 30 min of reaction in CH_3CN , *cis*-cyclooctene oxide (**3a**) was obtained as the only identifiable oxidation product (>99% by GC)

Table 1
Manganese(III) porphyrin-catalyzed epoxidation of *cis*-cyclooctene with $\text{PhI}(\text{OAc})_2$.^a



Entry	Catalyst	Solvent	t (min)	Convsn (%) ^b	Yields(%) ^c
1 ^d	$\text{Mn}^{\text{III}}(\text{TPFPP})\text{Cl}$	CH_3CN	30	22	100
2			30	100	100
3			10	100	100 (93) ^e
4 ^f			(50 °C) 200	100	100
5		CH_3OH	30	37	99
6		CH_2Cl_2	30	67	100
7		$\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (v/v = 1)	30	90	100
8	$\text{Mn}^{\text{III}}(\text{TPP})\text{Cl}$	CH_3CN	30	7	100
9	$\text{Mn}^{\text{III}}(\text{TMP})\text{Cl}$	CH_3CN	30	8	100
10		CH_3CN	10 (50 °C)	23	100

^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), 1.5 equiv. of $\text{PhI}(\text{OAc})_2$ and 0.5 mol% of manganese(III) porphyrin catalysts.

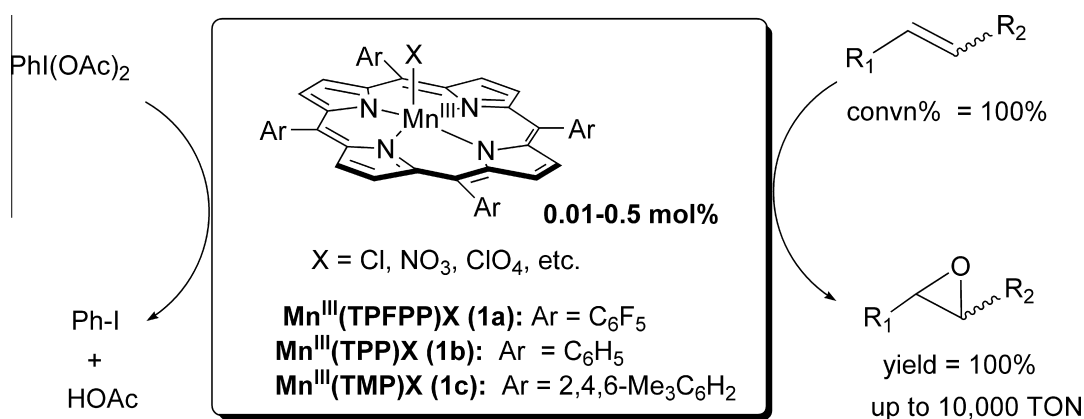
^b Determined by GC–MS analysis of the crude reaction mixture with a capillary column (J&W Scientific Cyclodex B).

^c Based on the amount of substrate consumed; material balances > 95%.

^d Without H_2O .

^e Isolated yield after column chromatography (silica gel).

^f 0.01 mol% catalyst loading.



Scheme 1. Biomimetic oxidations catalyzed by manganese(III) porphyrins (**1**) with $\text{PhI}(\text{OAc})_2$.

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