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Generation of *trans*-dioxoruthenium(VI) porphyrins: A photochemical approach

Rui Zhang *, Yan Huang, Chris Abebrese, Helen Thompson, Eric Vanover, Cathleen Webb *

Department of Chemistry, Western Kentucky University, Bowling Green, KY 42101-1079, USA

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ABSTRACT

trans-Dioxoruthenium(VI) porphyrin complexes have been developed as one of the best-characterized model systems for heme-containing enzymes. Traditionally, this type of compounds can be prepared by oxidation of ruthenium(II) precursors with peroxyacids and other terminal oxidants under different conditions, depending on the porphyrin ligands. In this work, a new photochemical generation of *trans*-dioxoruthenium(VI) porphyrins has been developed by extension of the known photo-induced ligand cleavage reactions. Refluxing ruthenium(II) carbonyl porphyrins [$\mathrm{Ru^{II}(Por)(CO)}$] in carbon tetrachloride afforded dichlororuthenium(IV) complexes [$\mathrm{Ru^{IV}(Por)Cl_2}$]. Facile exchange of the counterions in [$\mathrm{Ru^{IV}(Por)Cl_2}$] with $\mathrm{Ag(ClO_3)}$ or $\mathrm{Ag(BrO_3)}$ gave the corresponding dichlorate [$\mathrm{Ru^{IV}(Por)(ClO_3)_2}$] or dibromate [$\mathrm{Ru^{IV}(Por)(BrO_3)_2}$] salts. Visible-light photolysis of the photo-labile porphyrin–ruthenium(IV) dichlorates or dibromates resulted in homolytic cleavage of the two O–Cl or O–Br bonds in the axial ligands to produce *trans*-dioxoruthenium(IV) species [$\mathrm{Ru^{VI}(Por)O_2}$] bearing different porphyrin ligands.

1. Introduction

Catalytic oxidations are core transformations in organic synthesis. Millions of tons of oxygenated compounds are annually produced and applied worldwide, ranging from pharmaceutical to large-scale commodities [1–4]. In Nature, an ubiquitous type of monooxygenase is the cytochrome P-450 enzyme, which features an iron porphyrin core, and can catalyze a wide variety of oxidation reactions including unreactive hydrocarbons with exceptionally high reactivity and selectivity [5–7]. Many transition metal catalysts, with a core structure closely resembling that of the iron porphyrin core of the P450s, have been designed as models to probe the sophisticated mechanism of molecular oxygen activation together with a more goal oriented approach to invent enzyme-like oxidation catalysts [1,8].

In both synthetic and natural catalysts, high-valent transition metal-oxo species have been implicated as the active oxidizing species [9–11]. In a typical catalytic reaction, however, the concentrations of active oxidants will not build up to concentrations that permit detection and direct kinetic studies. Moreover, a high valent metal-oxo species detected in a reaction might not be the true oxidant but a precursor to the true oxidant that is formed in small, undetectable amounts [12]. The resulting lack of kinetic and mechanistic information complicates attempts to deduce the identities of the active oxidants. Indeed, most commonly, the nature of the active oxidants in homogeneous catalysis has been inferred indirectly from product studies [13–16]. The successful generation and characterization of the reactive metal-oxo species will allow a direct assessment of their reactivities and provide important insight into chemical modeling of the enzyme-like oxidants, and ultimately lead to catalyst development for the selective oxidation of organic substrates in large-scale industrial processes.

Ruthenium porphyrin complexes are among the most extensively studied biomimetic catalysts for hydrocarbon oxidation because of their rich coordination and redox chemistry [1,8,9,17]. In particular, *trans*-dioxoruthenium(VI) porphyrin complexes, abbreviated as $\mathrm{Ru^{VI}(Por)(O)_2}$, have received considerable attention as model systems for heme-containing enzymes [18–20]. This interesting family of high-valent ruthenium complexes exhibits significant reactivity toward organic substrates such as phosphines, sulfides, alcohols and hydrocarbons [21–23]. Notably, *trans*-dioxoruthenium(VI) porphyrins have been shown to catalyze the clean aerobic epoxidation of olefins in the absence of a reducing agent under mild conditions [24,25]. Although *trans*-dioxoruthenium(VI) derivatives are the best characterized oxidizing intermediates, their involvement as the active oxidant in the catalytic cycle of ruthenium porphyrins with aromatic *N*-oxides as the oxygen

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Abbreviations: Por, porphyrin; TMP, 5,10,15,20-tetramesitylporphyrin dianion; D_4-Por*, 5,10,15,20-tetrakis[(1S,4R,5R,8S)-1,2,3,4,5,6,7,8-octahydro-1,4:5,8dimethanoanthracen-9-yl]porphyrin dianion; TPP, 5,10,15,20-tetraphenylporphyrin dianion; 4-MeO-TPP, 5,10,15,20-tetra(4-methoxyphenyl)porphyrin dianion; 4-$\mathrm{CF_3}$-TPP, 5,10,15,20-tetra(4-trifuoromethylphenyl)porphyrin dianion; TPFPP, 5,10,15,20-tetrapentafluorophenylporphyrin dianion; *m*-CPBA, *meta*-chloroperoxybenzoic acid.

* Corresponding authors. Address: Department of Chemistry, Western Kentucky University, 1906 College Heights Blvd. #11079, Bowling Green, KY 42101-1079, USA. Tel.: +1 270 745 8899; fax: +1 270 745 3803.

E-mail addresses: rui.zhang@wku.edu (R. Zhang), cathleen.webb@wku.edu (C. Webb).

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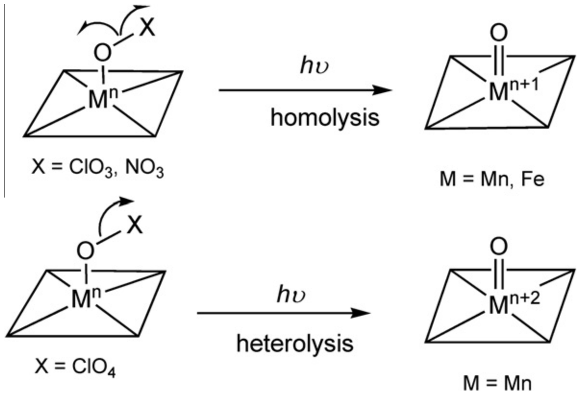
source has been ruled out in view of the low reactivity and enantioselectivity [26,27].

The first isolation and characterization of the sterically hindered *trans*-dioxoruthenium(VI) porphyrin complex Ru^{VI}(TMP)(O)$_2$ (TMP = 5,10,15,20-tetramesityporphyrinato dianion) by oxidation of Ru^{II}(TMP)(CO) with *meta*-chloroperoxybenzoic acid (*m*-CPBA) was reported by Groves and Quinn [28]. The steric hindrance imposed by the ortho substituents at the phenyl groups prevents the facile dimerization to give the inert diruthenium(IV) μ-oxo-bridged complex. Che and co-workers had reported the syntheses of non-sterically encumbered *trans*-dioxoruthenium(VI) porphyrins Ru^{VI}(TPP)(O)$_2$ (TPP = 5,10,15,20-tetraphenylporphyrinato dianion) and Ru^{VI}(OEP)(O)$_2$ (OEP = octaethylporphyrinato dianion) in the presence of coordinating solvents (such as methanol) [29]. The choice of solvent is very important to the success of the synthesis, presumably due to the coordination of alcohol on the ruthenium(IV) intermediate which can inhibit the formation of μ-oxo dimer. In addition to peroxyacids, other sacrificial oxidants such as iodosylbenzene (PhIO), periodate, and *tert*-butyl hydroperoxide (TBHP) were able to produce the *trans*-dioxoruthenium(VI) species [9,28]. Increasingly electronegative iodosylbenzene substituents like pentafluoroiodosylbenzene are seen to increase dramatically the rate of dioxo formation. Later, chiral *trans*-dioxoruthenium(VI) complexes were prepared in similar manners and characterized with satisfactory spectroscopic properties [30–32]. Some *trans*-dioxoruthenium(IV) porphyrin complexes are even determined by X-ray crystal structures [20,25].

Our particular interest in the context of metal-oxo chemistry is to explore the photochemical approach that targets the direct detection and kinetic study of high-valent transition metal-oxo derivatives. With photochemical production of reactive metal-oxo transients, one has access to time scales that are much shorter than the fastest mixing experiments and kinetics of oxidation reactions of the transients of interest are not convoluted with the kinetics of reactions that form the transients. Recently, the photo-induced ligand cleavages reactions have been developed to generate a variety of metal-oxo species [33–35]. The concept of photo-induced ligand cleavage reactions is very straightforward as illustrated in Scheme 1. The precursors are metal complexes with the metal in the *n* oxidation state and an oxygen-containing ligand such as perchlorate, chlorate, or nitrate. Photolysis can result in homolytic cleavage of the O–X bond in the ligand to give an (*n* + 1) oxidation state metal-oxo species (one electron photo-oxidation) or heterolytic cleavage of the O–X bond in the ligand to give an (*n* + 2) oxidation state metal-oxo species (two electron photo-oxidation). Although straightforward in concept, the creation of photochemical methods for formation of metal-oxo species requires considerable development of the requisite photochemical methods and especially the photo-labile precursors. For examples, photochemical cleavages of porphyrin-manganese(III) nitrates [33] or chlorates [12], corrole-manganese(IV) chlorates [36] and corrole-iron(IV) chlorates [37], give neutral porphyrin-manganese(IV)-oxo, corrole-manganese(V)-oxo and corrole-iron(V)-oxo derivatives by *homolytic* cleavage of the O–Cl or O–N bond in the axial ligand. On the other hand, photolysis of porphyrin-manganese(III) perchlorate complexes gave much more reactive porphyrin-manganese(V)-oxo transients by *heterolytic* cleavage of the O–Cl bond in perchlorate [12,38].



Scheme 1. Generation of high-valent metal-oxo species by photo-induced ligand cleavage reactions.

Recently, we have extended the photo-induced ligand cleavage reactions to produce the well-known *trans*-dioxoruthenium(VI) complexes by irradiation of porphyrin–ruthenium(IV) dichlorate complexes with visible light (Scheme 2) [39]. This photochemical method can efficiently generate the *trans*-dioxoruthenium(VI) complexes in sterically bulky and non-bulky porphyrins without the limitation of porphyrin ligands as observed in chemical methods [39]. Herein, we report our full findings on the photochemical generation of *trans*-dioxoruthenium(VI) complexes by irradiation of porphyrin–ruthenium(IV) dichlorate or dibromate complexes that result in homolytic cleavage of the O–X bond in both axial ligands (Scheme 2). We show this photochemical method can be used to generate the *trans*-dioxoruthenium(VI) in various porphyrin systems under similar condition, in particular the very electron-demanding Ru^{VI}(TPFPP)O$_2$ (TPFPP = tetrakis-pentafluorophenylporphyrinato dianion).

The porphyrin systems that we have studied are shown in Scheme 2, using abbreviations that follow those conventionally established. Of these macrocyclic ligands, ligands **a** and **b** are generally considered as a sterically-encumbered porphyrin due to the presence of relatively large substituents on the *ortho* positions of the *meso*-phenyl groups, whereas ligands **c**–**f** are all typical sterically-unencumbered porphyrins. The different aromatic groups on the porphyrins also result in varying electron demands with the phenyl system least electron withdrawing, the 4-methoxyphenyl system, and the pentafluorophenyl system most electron withdrawing.

2. Experimental

2.1. General

All commercial reagents were of the best available purity and were used as supplied unless otherwise specified. HPLC grade acetonitrile (99.93%) was distilled over P_2O_5 prior to use. Free porphyrin ligand, H$_2$TPFPP (**f**), was purchased from Aldrich and used as received. Others including H$_2$TMP (**a**) [40], H$_2$(D_4-Por*) (**b**) [41], H$_2$TPP (**c**) [42], H$_2$(4-MeO-TPP) (**d**) [42], and H$_2$(4-CF$_3$-TPP) (**e**) [42] were prepared according to the known methods. The corresponding ruthenium(II) carbonyl complexes Ru^{II}(Por)(CO) (Por = **a**–**f**) used for generation of Ru^{IV}(Por)Cl$_2$ (**1**) were prepared by literature methods [20] and fully characterized, matching those reported [20,24,29]. UV–Vis spectra were recorded on an Agilent 8453 diode array spectrophotometer. IR spectra were obtained on a Bio-Rad FT-IR spectrometer. ^{1}H 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.

2.2. Preparation of dichlororuthenium(IV) porphyrin [Ru^{IV}(Por)Cl$_2$] [43]

In a typical run, Ru^{IV}(Por)Cl$_2$ (**1**) was prepared by refluxing Ru^{II} (Por)(CO) complexes (50 mg) in CCl$_4$ (30 mL) monitored by UV–Vis