Inorganica Chimica Acta 376 (2011) 152-157

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

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

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ARTICLE INFO

Article history: Received 18 March 2011 Received in revised form 20 May 2011 Accepted 2 June 2011 Available online 12 June 2011

Keywords: trans-Dioxoruthenium(VI) porphyrin Photolysis Homolytic cleavage Photo-oxidation

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 [Ru^{II}(Por)(CO)] in carbon tetra-chloride afforded dichlororuthenium(IV) complexes [Ru^{IV}(Por)Cl₂]. Facile exchange of the counterions in [Ru^{IV}(Por)Cl₂] with Ag(ClO₃) or Ag(BrO₃) gave the corresponding dichlorate [Ru^{IV}(Por)(ClO₃)₂] or dibro-mate [Ru^{IV}(Por)(BrO₃)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 [Ru^{VI}(Por)O₂] bearing different porphyrin ligands.

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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

* 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. 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 $Ru^{VI}(Por)(O)_2$, 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





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-CF₃-TPP, 5,10,15,20-tetra(4-trifuoromethylphenyl)porphyrin dianion; TPFPP, 5,10,15,20-tetrapentafluorophenylporphyrin dianion; *m*-CPBA, *meta*-chloroperoxybenzoic acid.

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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 varietv 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

 $\begin{array}{c} & hv \\ & & hv \\ & & hv \\ & & hv \\ & & homolysis \\ \hline M^n \\ & & & hv \\ & & & M = Mn, Fe \\ \hline M^n \\ & & & hv \\ & & & hv \\ & & & & hv \\ & & & & & M = Mn \end{array}$

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

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].

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 elec-Ru^{VI}(TPFPP)O₂ (TPFPP = tetrakistron-demanding 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-methoxy-phenyl 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 P₂O₅ prior to use. Free porphyrin ligand, H_2 TPFPP (**f**), was purchased from Aldrich and used as received. Others including H₂TMP (**a**) [40], H₂(D_4 -Por^{*}) (**b**) [41], H_2TPP (c) [42], $H_2(4$ -MeO-TPP) (d) [42], and $H_2(4$ -CF₃-TPP) (e) [42] were prepared according to the known methods. The corresponding ruthenium(II) carbonyl complexes Ru^{II}(Por)(CO) (Por = \mathbf{a} - \mathbf{f}) used for generation of Ru^{IV}(Por)Cl₂ (**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. 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.

2.2. Preparation of dichlororuthenium(IV) porphyrin [Ru^{IV}(Por)Cl₂] [43]

In a typical run, $\text{Ru}^{IV}(\text{Por})\text{Cl}_2$ (**1**) was prepared by refluxing Ru^{II} (Por)(CO) complexes (50 mg) in CCl₄ (30 mL) monitored by UV–Vis





Scheme 2. Photochemical generation of trans-dioxoruthenium(VI) porphyrins.

spectroscopy. The refluxing time, ranging from 2 h to overnight, depended on the porphyrin system employed. The Ru^{IV}(Por)Cl₂ with electron-deficient sterically unhindered porphyrin (4-CF₃-TPP and TPFPP) were readily purified by refluxing the crude mixture in a Soxhlet apparatus with diethyl ether to remove the μ -oxo dimer byproducts [44].

2.3. [Ru^{IV}(TMP)Cl₂] (1a)

Yield = 96%. ¹H NMR (500 MHz, CDCl₃) δ , ppm: -55.8 (s, 8H, β-pyrrole). IR (KBr, cm⁻¹): 1008 (oxidation state marker band). UV–Vis (CH₃CN) λ_{max} /nm: 407 (Soret), 529.

2.4. $[Ru^{IV}(D_4-Por^*)Cl_2]$ (**1b**)

Yield = 98%. ¹H NMR (500 MHz, CDCl₃) δ , ppm: -52.3 (s, 8H, β-pyrrole). IR (KBr, cm⁻¹): 1010 (oxidation state marker band). UV–Vis (CH₃CN) λ_{max} /nm: 409 (Soret), 532.

2.5. [Ru^{IV}(TPP)Cl₂] (1c)

Yield = 95%. ¹H NMR (500 MHz, CDCl₃) *δ*, ppm: -58.2 (s, 8H, *β*-pyrrole). IR (KBr, cm⁻¹): 1005 (oxidation state marker band). UV–Vis (CH₃CN) λ_{max} /nm: 408 (Soret), 528.

2.6. [Ru^{IV}(4-MeO-TPP)Cl₂] (1d)

Yield = 86%. ¹H NMR (500 MHz, CDCl₃) δ, ppm: -53.8 (s, 8H, β-pyrrole). IR (KBr, cm⁻¹): 1006 (oxidation state marker band). UV–Vis (CH₃CN) λ_{max} /nm: 406 (Soret), 525.

2.7. [*Ru^{IV}*(4-*CF*₃-*TPP*)*Cl*₂] (**1e**)

Yield = 43%. ¹H NMR (500 MHz, CDCl₃) δ , ppm: -57.6 (s, 8H, β-pyrrole). IR (KBr, cm⁻¹): 1006 (oxidation state marker band). UV–Vis (CH₃CN) λ_{max}/nm : 406 (Soret), 530.

2.8. [Ru^{IV}(TPFPP)Cl₂] (**1f**)

Yield = 48%. ¹H NMR (500 MHz, CDCl₃) δ, ppm: -53.3 (s, 8H, β-pyrrole). IR (KBr, cm⁻¹): 1009 (oxidation state marker band). UV–Vis (CH₃CN) λ_{max}/nm : 405 (Soret), 525.

2.9. Generation procedure for photosynthesis of transdioxoruthenium(VI) porphyrins [Ru^{VI}(Por)(O)₂]

Treatment of compounds **1** (ca. 10 mg) with 2–5 folds excess of AgClO₃ in CH₃CN gave the dichlorate complexes **2** that were generated *in situ* in most runs, and directly used in subsequent photochemical reactions immediately after preparation. When the solution of **2** at desired concentration ($\sim 1 \times 10^{-5}$ M) was irradiated with a 100 W of visible light from a tungsten lamp at ambient temperature, the formation of **3** was complete in ca. 50 min monitored by UV–Vis spectroscopy. The dioxo complexes (**3**) were isolated as dark red–purple crystalline solids, and can be readily purified by passing through a short dry column (basic alumina) to give satisfactory spectroscopic characterization spectra.

2.10. [Ru^{VI}(TMP)O₂] (**3a**)

Yield = 92%. ¹H NMR (500 MHz, CDCl₃) δ, ppm: 8.79 (s, 8H), 7.23 (s, 8H), 2.62 (s, 12H), 1.89 (s, 24H). IR (KBr, cm⁻¹): 1018 (oxidation state marker band) and 820 (ν_{RuO_2}). UV–Vis (CH₂Cl₂) λ_{max} /nm: 422 (Soret), 521.

$$Ru^{IV}(Por)Cl_{2} \xrightarrow{CCl_{4}} Ru^{II}(Por)(CO) \xrightarrow{CCl_{4}} Ru^{IV}(Por)Cl_{2} + [Ru^{IV}Por)CI]_{2}O$$

$$Por = \mathbf{a} \cdot \mathbf{d}$$

$$Por = \mathbf{a} \cdot \mathbf{d}$$

$$Por = \mathbf{a} \cdot \mathbf{d}$$

Scheme 3. Synthesis of dichlororuthenium(IV) porphyrins complexes.

2.11. [Ru^{VI}(D₄-Por^{*})O₂] (**3b**)

Yield = 88%. ¹H NMR (500 MHz, C₆D₆): δ 9.24 (s, 8H), 7.40 (s, 4H), 3.46 (s, 8H), 2.78 (s, 8H), 2.03 (m, 8H), 1.66 (m, 8H), 1.41–1.11 (m, 24H) and 0.96 (m, 8H). IR (KBr, cm⁻¹): 1019 (oxidation state marker band) and 822 (v_{RuO_2}). UV–Vis (CH₂Cl₂): λ_{max}/nm (log ε) 424 (5.38), 521 (4.35).

2.12. [Ru^{VI}(TPP)O₂] (**3c**)

Yield = 86%. ¹H NMR (500 MHz, CDCl₃): δ 9.1 (s, 8H), 8.6 (d, 8H). 8.4 (d, 4H), 7.8 (m, 8H). IR (KBr, cm⁻¹): 1016 (oxidation state marker band) and 819 (v_{RuO_2}). UV–Vis (CH₂Cl₂) λ_{max} /nm: 420 (Soret band), 520 (Q band).

2.13. [Ru^{VI}(4-MeOTPP)(O)₂] (3d)

Yield = 94%.¹H NMR (500 MHz, CDCl₃): δ 9.1 (s, 8H), 8.2 (d, 8H), 7.3 (d, 8H), 4.2 (s, 12H). IR (KBr, cm⁻¹): 1017 (oxidation state marker band) and 819 (ν_{RuO_2}). UV–Vis (CHCl₃) λ_{max} /nm: 425 (Soret band), 525 (Q band), 550 (sh).

2.14. [Ru^{VI} (4-CF₃TPP)O₂] (**3e**)

Yield = 89%. ¹H NMR (500 MHz, CDCl₃): δ 9.0 (s, 8H), 8.5 (d, 8H), 8.1 (d, 8H). IR (KBr, cm⁻¹): 1018 (oxidation state marker band) and 819 (ν_{RuO_2}). UV–Vis (CHCl₃) λ_{max} /nm: 418 (Soret band), 520 (Q band).

2.15. [Ru^{VI}(TPFPP)O₂] (**3f**)

Yield = 82%. ¹H NMR (300 MHz, CDCl₃): *δ*, ppm: 9.18 (s, 8H). IR (KBr, cm⁻¹): 1022 (oxidation state marker band) and 827 (v_{RuO_2}). UV–Vis (CH₂Cl₂) λ_{max} /nm: 412 (Soret), 506.

3. Results and discussion

3.1. Preparation of dichlororuthenium(IV) porphyrin [Ru^{IV}(Por)Cl₂]

Our study started with the preparation of dichlororuthenium(IV) porphyrins, $Ru^{IV}(Por)Cl_2$ (1), that can be readily prepared by heating the carbonyl precursor Ru^{II}(Por)(CO) in CCl₄ in air as described by Gross and Barzilay (Scheme 3) [43]. As expected, Ru^{II}(Por)CO with sterically hindered porphyrin (Por = TMP, D_4 -Por*) could be readily converted to the desired dichlororuthenium(IV) products (1a and 1b) in over 95% yields. The oxidative transformation is characterized by a distinct color change from orange red to dark brown, accompanied by the blue shift of the Soret bands (CHCl₃). Interestingly, Ru^{II}(Por)(CO) with sterically unhindered ligands (Por = TPP and 4-MeO-TPP) also gave the desired products 1c and 1d predominately. However, the same procedure for the sterically unhindered porphyrins with electron-withdrawing substituents (Por = 4-CF₃-TPP and TPFPP) led to the formation of substantial amounts of µ-oxo dimer byproducts, [Ru^{IV}(Por)Cl]₂O, along with Ru^{IV}(Por)Cl₂ (1c and 1d). The former byproducts were identified by its diamagnetic ¹H NMR signals similar to those of [Ru^{IV}(TPP)Cl]₂O [45]. Using an alternative method by reacting the corresponding Ru^{VI}(-Por)(O)₂ with Me₃SiCl or HCl gave a similar result [46]. The reason for the marked dependence of formation of µ-oxo dimer on the porphyrin substituents is not yet clear. It seems that electron-withdrawing substituents such as CF₃ and F on porphyrin ligand favor µ-oxo dimer formation. Presumably, the electronwithdrawing substituents would stabilize the ruthenium(IV) complex in a dimer form by reducing the electron density of metal atoms. We also found the amount of μ -oxo dimer was highly dependent on the reaction concentration, i.e. refluxing the carbonyl ruthenium(II) precursors in higher concentration in CCl₄ gave a less amount of µ-oxo dimers. The origin of the considerable effect of substituent and concentration on the formation of µ-oxo dimer is not apparent, and this subject deserves further study. Following a known procedure [44], complexes 2e and 2f with electron-deficient sterically unhindered porphyrin were



Fig. 1. (A) UV–Vis spectra of Ru^{IV}(TMP)Cl₂ (1a, dashed) and Ru^{IV}(TMP)(ClO₃)₂ (2a, solid) in CH₃CN. (B) ¹H NMR spectrum of Ru^{IV}(TMP)Cl₂ (1a, top) and Ru^{IV}(TMP)(ClO₃)₂ (2a, bottom) in CDCl₃.

purified by refluxing the crude mixtures in a Soxhlet apparatus with diethyl ether to remove the μ -oxo dimer byproducts.

3.2. Preparation of porphyrin–ruthenium(IV) dichlorates [Ru^{IV}(Por)(ClO₃)₂]

Each of the dichlororuthenium(IV) complexes (1) were characterized by its distinct paramagnetically shifted pyrrolic protons (δ ranging from -52.3 to -58.2 ppm) [43]. Facile exchange of the counterions in 1 with Ag(ClO₃) gave the corresponding dichlorate salts 2 that were characterized by UV–Vis and ¹H NMR spectra. Complexes 2 are photo-labile and can be handled for a short time in solutions exposed to light. Interestingly, ruthenium(IV) dichlorate complexes 2 show featuring UV–Vis and paramagnetic ¹H NMR spectra, similar to those of dichloro compounds (1). The spectra of 1a and 2a are shown in Fig. 1A as an example. In the ¹H NMR



Fig. 2. Examples of generation of *trans*-dioxoruthenium(VI) species (**3**) by photolysis of the corresponding dichlorate precursors (**2**). In these time-resolved difference spectra, species **2** are decaying away with time, and species **3** with red-shifted Soret absorbance are growing in with time. (A) Spectrum of $\text{Ru}^{VI}(\text{TPP})(O)_2$ (**3c**) following photolysis of chlorate salt (**2c**) in CH₃CN over a total time of 45 min. (B) Spectrum of $\text{Ru}^{VI}(D_4\text{-Por}^*)(O)_2$ (**3b**) following photolysis of chlorate salt (**2b**) in CH₃CN over a total time of 60 min. (C) Spectrum of $\text{Ru}^{VI}(\text{TPFPP})(O)_2$ (**3f**) following photolysis of chlorate salt (**2f**) in CH₃CN over a total time of 160 min.

spectra of **1a** and **2a** (see, for example, Fig. 1B), the paramagnetic pyrollic signal of **2a** is located at ca. –20 ppm (Fig. 1B bottom), slightly more downfield than that of paramagnetic **1a** (Fig. 1B, top), consistent with weaker binding ability of chlorate than that of chloride.

3.3. Photolysis of porphyrin–ruthenium(IV) dichlorates [Ru^{IV}(Por)(ClO₃)₂]

Irradiation of chlorate complexes (2) in anaerobic CH₃CN with visible light from a tungsten lamp (100 W) resulted in homolytic cleavage of the O-Cl bond in the two chlorate counterions to produce neutral dioxoruthenium(VI) species (3). Fig. 2 shows three representative time-resolved formation spectra of Ru^{VI}(Por)(O)₂ in three different porphyrin systems, i.e. sterically encumbered **3b**. non-sterically hindered 3c and electron-efficient 3f. These time-resolved UV–Vis spectra show decay of photo-labile precursors (2) and growth of the products (3) in absorption spectra with clean isosbestic points. In each case, the formed species 3 display a stronger red-shifted Soret and a blue-shifted weaker Q bands that are characteristic for the corresponding trans-dioxoruthenium(VI) porphyrins [28,29]. This general approach is applicable to the evidently most reactive **3f** bearing the most electron demanding porphyrin (TPFPP) [26]. The formation of **3f** by photochemical oxidation was also observed with a slowest rate among all systems studied (Fig. 2C); this is in line with the expected highest oxidation potential of the Ru^{IV} species (2f) with the most electron-withdrawing porphyrin ring of TPFPP [20]. The identities of complexes 3 as Ru^{VI}(Por)(O)₂ generated in photochemical reactions were further confirmed by UV-Vis, ¹H NMR and IR spectra (see Section 2). Control experiments showed that no dioxo species was formed in the absence of light. As expected, using more intensive light $(\lambda_{max} = 420 \text{ nm}, \text{ ca. } 300 \text{ W})$ resulted in faster formation of **3** in the same solvent. The use of other non-coordinating solvent such as CH₂Cl₂ or THF as the solvent also gave similar results. However, no reaction was observed when methanol or ethanol was used. Presumably, the weakly binding chlorate counterions were displaced by these coordinating solvents.

It is noteworthy that the photochemical reactions of chlorates **2** appears to present a reaction manifold similar to that of porphyrinmanganese(III) chlorates [12], corrole-manganese(IV) chlorates [36] and corrole-iron(IV) chlorates [37], which result in homolytic cleavage of the O–Cl bond in the chlorate. Photolysis of Mn^{III}(Por) (NO₃) complexes was reported to give Mn^{IV}(Por)(O) species by homolytic cleavage of an O–N bond [33], similar to those of chlorate complexes albeit with considerably less efficiency [12]. However, we found that photolyses of dinitrate ruthenium(IV) complexes did not afford the dioxo complexes **3** even with prolonged irradiation and higher-energy light (λ_{max} = 350 nm). The reaction generated an unknown product with slightly blue shifted Soret band (data not shown). We did not observe any photochemical reactions when we irradiated the ruthenium(IV) diperchlorates, i.e. Ru^{VI}(Por)(ClO₄)₂ under similar conditions.

3.4. Photolysis of porphyrin–ruthenium(IV) dibromates [Ru^{IV}(Por)(BrO₃)₂]

Photolysis of Ru^{IV}(Por)(BrO₃)₂ complexes producing dioxoruthenium(VI) species also were possible. We produced the photolabile ruthenium(IV) dibromates *in situ* from the chlorides (**1**) by counterion exchange with AgBrO₃. Irradiation of resulting dibromate species with visible light gave *trans*-dioxoruthenium(VI) porphyrin with well-anchored isosbestic points (Fig. 3). The photochemical reaction that gave homolytic cleavage of the O–Br bonds is directly the same as that of the ruthenium(IV) chlorates.



Fig. 3. UV-Vis spectral change of 1a (8 × 10⁻⁶ M) with 5-fold excess of AgBrO₃ in anaerobic CH₃CN solution upon irradiation with a 100 W tungsten lamp at 22 °C over 80 min.

4. Conclusions

In conclusion, we have reported a photochemical approach to prepare *trans*-dioxoruthenium(VI) porphyrin complexes by photolysis of the corresponding ruthenium(IV) dichlorates or dibromates with visible light. With this method, we have produced a variety of *trans*-dioxoruthenium(VI) porphyrins without the limitation of porphyrin ligands. This work also demonstrates, for the first time, that a two electron photo-oxidation can be achieved by two simultaneous homolytic bond cleavages, i.e. two one-electron photooxidation. We are currently investigating the photo-synthetic methodology to produce other high-valent metal-oxo complexes. Given that porphyrin–ruthenium(V)-oxo transients are more attractive candidates for oxidations [26,44,47], the extension of this method for generation of the elusive ruthenium(V)-oxo species is underway in our laboratory.

Acknowledgments

This work was supported by the Petroleum Research Fund (PRF 48764-GB4) and an internal Grant from WKU Office of Research (RCAP).

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