A facile photosynthesis of *trans*-dioxoruthenium(VI) porphyrins†

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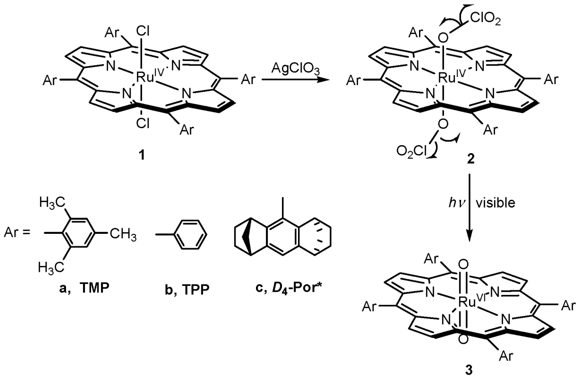
Photolysis of porphyrin-ruthenium(IV) dichlorate complexes with visible light results in homolytic cleavage of the O–Cl bond in the chlorates to form *trans*-dioxoruthenium(VI) species bearing either sterically encumbered or unencumbered porphyrin ligands.

Organic ligand-complexed transition metal-oxo intermediates have been proposed as the active oxidizing species in many metal-catalyzed oxidation reactions that employ sacrificial oxidants such as hydrogen peroxide, peroxy acids, and iodosobenzene.[1,2] Many transition metal catalysts have been designed to mimic the predominant oxidation catalysts in Nature, namely the cytochrome P450 enzymes.[3,4] In some cases, high-valent transition metal-oxo active intermediates can be observed spectroscopically by rapid mixing techniques or by the production of low-reactivity analogues;[5,6] but in many cases the active metal-oxo species does not accumulate to detectable quantities, and the actual oxidizing species remains speculative. In this regard, *trans*-dioxoruthenium(VI) porphyrin complexes have received much attention, and have been developed as a well-characterized model system for heme-containing enzymes.[7–15] This class of compounds is neutral and readily dissolves in nonpolar organic solvents, and yet is reactive toward useful organic oxidations including alkene epoxidations and alkane hydroxylations.[16] Furthermore, the reactive dioxoruthenium(VI) species can be regenerated by aerobic oxidation, and therefore, they can catalyze aerobic oxidation reactions in the absence of co-reductants.[10,17]

The first isolation and characterization of the sterically hindered *trans*-dioxoruthenium(VI) porphyrin complex $Ru^{VI}(TMP)O_2$ by oxidation of $Ru^{II}(TMP)(CO)$ with *m*-CPBA was reported by Groves and Quinn.[7] Che and co-workers had reported the syntheses of non-sterically encumbered *trans*-dioxoruthenium(VI) porphyrins $Ru^{VI}(TPP)O_2$ and $Ru^{VI}(OEP)O_2$ in the presence of coordinating solvents (such as methanol).[8] Later, chiral *trans*-dioxoruthenium(VI) complexes were prepared in a similar manner and characterized with satisfactory spectroscopic properties.[18–20] Some dioxoruthenium(VI) porphyrin complexes are even determined by the X-ray crystal structures.[10,16] Recently, we have developed photo-induced ligand cleavage reactions for production of a variety of high-valent transition metal-oxo derivatives.[21] Unlike the commonly used chemical oxidations, the photochemical approach produces metal-oxo species essentially instantly, and permits direct detection of metal-oxo species and kinetic studies of their oxidations within much shorter timescales than the fastest mixing experiments.[22–25] In this study, we describe our progress in the development of a new photochemical method that led to generation of dioxoruthenium(VI) complexes bearing sterically hindered, unhindered and chiral porphyrin ligands (Scheme 1).

We studied the three porphyrin systems shown in Scheme 1, using abbreviations that follow those previously established.‡ According to the method reported by Gross and co-workers,[26] the dichlororuthenium(IV) complexes (**1**) were prepared by heating corresponding $Ru^{II}(Por)(CO)$ in refluxing CCl_4. Each of these dichlororuthenium(IV) complexes was known and characterized by distinct ^1H NMR (paramagnetically shifted pyrrolic protons at δ −55.8 (**1a**), −58.2 (**1b**) and −52.3 (**1c**) ppm in $CDCl_3$) in agreement with those reported.[26,27] Exchange of the counterions in **1** with $Ag(ClO_3)$ gave the corresponding dichlorate salts **2** as desired photo-labile precursors that were subsequently used for photochemical reactions (See Fig. S1-3 in supporting information† for UV-visible and ^1H NMR spectra).

Irradiation of dichlorate complexes **2** in anaerobic CH_3CN with visible light from a tungsten lamp resulted in changes in absorption spectra with isosbestic points at 596, 436, 412 and 336 nm (Fig. 1). In Fig. 1, **2a** decayed, and a new species **3a** was produced, displaying a stronger Soret band at 420 nm and a weaker Q band at 518 nm that is characteristic of $Ru^{VI}(TMP)O_2$. Accordingly, **3a** was assigned as $Ru^{VI}(TMP)O_2$. The spectral signature of $Ru^{VI}(TMP)O_2$ was further confirmed by ^1H NMR and IR (see Fig. S4 and S5



Scheme 1

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† Electronic supplementary information (ESI) available: UV-vis spectra of **1a** and **2a**, ^1H NMR spectra of **1a–3a**, IR spectrum of **3a**, and time-resolved spectra for generation of **3b** and **3c**. See DOI: 10.1039/c003094e

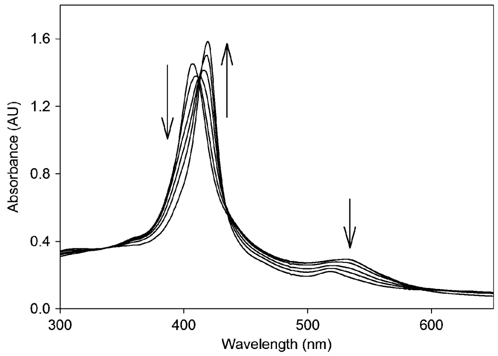

Fig. 1 Time-resolved UV-visible spectra of **2a** (8×10^{-6} M) upon irradiation with visible light in anaerobic CH_3CN solution at 22 °C. Spectra were recorded at t = 0, 6, 14, 20, 26 and 50 min.

in supporting information†). Control experiments showed that no dioxo species was formed in the absence of light. Thus, the photolysis reactions of the dichlorate complexes **2** result in homolytic cleavage of the O–Cl bond in the two chlorate counterions simultaneously to produce neutral dioxoruthenium(VI) species **3** *via* two one-electron photo-oxidation pathways. The photochemical reactions of chlorates **2** are analogous to the photochemical cleavages of porphyrin-manganese(III) chlorates,[24] corrole-manganese(IV) chlorates[28] and corrole-iron(IV) chlorates,[23] which give neutral porphyrin-manganese(IV)-oxo, corrole-manganese(V)-oxo and corrole-iron(V)-oxo derivatives by homolytic cleavage of the O–Cl bond in the chlorate.

In a fashion similar to that described for the generation of **3a**, the sterically unhindered $Ru^{VI}(TPP)O_2$ (**3b**) and chiral $Ru^{VI}(D_4\text{-Por*})O_2$ (**3c**) were also generated (See Fig. S6 and S7 in supporting information†), demonstrating the generality of this photochemical method. These complexes (**3**) were isolated and characterized by UV-visible, ^1H NMR and IR spectra that matched those reported.[7–8,10] The use of other solvents such as CH_2Cl_2 gave similar results. Product degradation was observed when higher-energy UV light (λ_{max} = 350 nm) was used instead of the visible light. Photolysis of $Mn^{III}(Por)(NO_3)$ complexes was reported to give $Mn^{IV}(Por)(O)$ species by homolytic cleavage of an O–N bond,[29] similar to those of chlorate complexes.[24] However, we found that photolyses of ruthenium(IV) dinitrate complexes did not afford the dioxo complexes **3** even with prolonged irradiation and higher-energy light (λ_{max} = 350 nm).

In conclusion, we report here a new preparation of *trans*-dioxoruthenium(VI) porphyrin complexes by an extremely easy photochemical approach. We have demonstrated the generality of the methodology in sterically encumbered and unencumbered systems under the same conditions, bypassing the ligand limitation observed in chemical methods. We believe these promising results will stimulate the further exploration of photo-synthetic methodology to produce other high-valent metal-oxo complexes. Given that porphyrin-ruthenium(V)-oxo transients are more attractive candidates for oxidations,[30] the extension of this method for generation of the putative ruthenium(V)-oxo species is underway in our laboratory.

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Notes and references

‡ Abbreviations used in this study: TMP = 5,10,15,20-tetramesitylporphyrin dianion (**a**); TPP = 5,10,15,20-tetraphenylporphyrin dianion (**b**); D_4-Por* = 5,10,15,20-tetrakis[(1*S*,4*R*,5*R*,8*S*)-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracen-9-yl]porphyrin dianion (**c**). 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. 5,10,15,20-Tetramesitylporphyrin ($TMPH_2$),[31] tetraphenylporphyrin ($TPPH_2$)[32] and D_4-Por*H_2[33] free ligands and their ruthenium(II) carbonyl complexes $Ru^{II}(Por)(CO)$ were prepared by literature methods.[16] $Ru^{IV}(Por)Cl_2$ (**1**) was prepared by refluxing $Ru^{II}(Por)(CO)$ complexes in CCl_4. Formation of **1b** required overnight refluxing and no μ-oxo dimer $[Ru(TPP)Cl]_2O$ was observed. Treatment of compounds **1** (typically 5–10 mg) with *ca.* 2-fold excess of $Ag(ClO_3)$ in anaerobic CH_3CN gave the dichlorate complexes **2**, characterized by UV-vis and ^1H NMR. When the solution of **2** with concentration in the range of $(5–12) \times 10^{-6}$ M was irradiated with visible light from a tungsten lamp at ambient temperature, the formation of **3** was complete in *ca.* 50 min, monitored by UV-visible spectroscopy. After purification by passing through a short Al_2O_3 dry column, the dioxo complexes (**3**) were isolated with >95% yields as dark red-purple crystalline solids, which gave satisfactory spectroscopic characterization spectra.

1 B. Meunier, *Chem. Rev.*, 1992, **92**, 1411.
2 R. A. Sheldon, *Metalloporphyrins in Catalytic Oxidations*, Marcel Dekker, New York, 1994.
3 I. G. Denisov, T. M. Makris, S. G. Sligar and I. Schlichting, *Chem. Rev.*, 2005, **105**, 2253.
4 P. R. Ortiz de Montellano, in *Cytochrome P450 Structure, Mechanism, and Biochemistry*, Kluwer Academic/ Plenum, New York, 2005.
5 B. Meunier, in *Metal-Oxo and Metal-Peroxo Species in Catalytic Oxidations*, Springer–Verlag, Berlin, 2000.
6 M. Costas, M. P. Mehn, M. P. Jensen and L. Que, *Chem. Rev.*, 2004, **104**, 939.
7 J. T. Groves and R. Quinn, *Inorg. Chem.*, 1984, **23**, 3844.
8 W. H. Leung and C.-M. Che, *J. Am. Chem. Soc.*, 1989, **111**, 8812.
9 C. L. Ho, W.-H. Leung and C. M. Che, *J. Chem. Soc., Dalton Trans.*, 1991, 2933.
10 T.-S. Lai, R. Zhang, K.-K. Cheung, C.-M. Che and H.-L. Kwong, *Chem. Commun.*, 1998, 1583.
11 T.-S. Lai, H.-L. Kwong, R. Zhang and C.-M. Che, *J. Chem. Soc., Dalton Trans.*, 1998, 3559.
12 C.-M. Che and W.-Y. Yu, *Pure Appl. Chem.*, 1999, **71**, 281.
13 C.-J. Liu, W.-Y. Yu, C.-M. Che and C.-H. Yeung, *J. Org. Chem.*, 1999, **64**, 7365.
14 R. Zhang, W.-Y. Yu, T.-S. Lai and C.-M. Che, *Chem. Commun.*, 1999, 409.
15 R. Zhang, W.-Y. Yu, H.-Z. Sun, W.-S. Liu and C.-M. Che, *Chem.–Eur. J.*, 2002, **8**, 2495.
16 C.-M. Che, J.-L. Zhang, R. Zhang, J.-S. Huang, T.-S. Lai, W.-M. Tsui, X.-G. Zhou, Z.-Y. Zhou, N. Zhu and C. K. Chang, *Chem.–Eur. J.*, 2005, **11**, 7040.
17 J. T. Groves and R. Quinn, *J. Am. Chem. Soc.*, 1985, **107**, 5790.
18 P. Le Maux, H. Bahri and G. Simonneaux, *J. Chem. Soc., Chem. Commun.*, 1994, 1287.
19 P. Le Maux, H. Bahri and G. Simonneaux, *Inorg. Chem.*, 1995, **34**, 4691.
20 Z. Gross, S. Ini, M. Kapon and S. Cohen, *Tetrahedron Lett.*, 1996, **37**, 7325.
21 R. Zhang and M. Newcomb, *Acc. Chem. Res.*, 2008, **41**, 468.
22 R. Zhang and M. Newcomb, *J. Am. Chem. Soc.*, 2003, **125**, 12418.
23 D. N. Harischandra, R. Zhang and M. Newcomb, *J. Am. Chem. Soc.*, 2005, **127**, 13776.
24 R. Zhang, J. H. Horner and M. Newcomb, *J. Am. Chem. Soc.*, 2005, **127**, 6573.
25 Z. Pan, R. Zhang, L. W. M. Fung and M. Newcomb, *Inorg. Chem.*, 2007, **46**, 1517.

26 Z. Gross and C. M. Barzilay, *J. Chem. Soc., Chem. Commun.*, 1995, 1287.

27 R. Zhang, W.-Y. Yu, K.-Y. Wong and C.-M. Che, *J. Org. Chem.*, 2001, **66**, 8145.

28 R. Zhang, D. N. Harischandra and M. Newcomb, *Chem.–Eur. J.*, 2005, **11**, 5713.

29 K. S. Suslick and R. A. Watson, *New J. Chem.*, 1992, **16**, 633.

30 J. T. Groves, M. Bonchio, T. Carofiglio and K. Shalyaev, *J. Am. Chem. Soc.*, 1996, **118**, 8961.

31 J. Lindsey and R. D. Wagner, *J. Org. Chem.*, 1989, **54**, 828.

32 A. D. L. Adler, F. R. Finarelli, J. D. Goldmacher, D. Assour and J. Korsakoff, *J. Org. Chem.*, 1967, **32**, 476.

33 R. L. Halterman and S. T. Jan, *J. Org. Chem.*, 1991, **56**, 5253.