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Photochemical generation and kinetic studies of a putative porphyrin-ruthenium(V)-oxo species

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Abstract

Photo-disproportionation of a *bis*-porphyrin-diruthenium(IV) μ -oxo dimer gave a porphyrin-ruthenium(III) species and a putative porphyrin-ruthenium(V)-oxo species that can be detected and studied in real time via laser flash photolysis methods. As determined by its spectral and kinetic behavior, the same oxo transient was also formed by photolysis of a porphyrin-ruthenium(III) *N*-oxide adduct. Second-order rate constants for reactions with several substrates at 22 °C were determined; representative values of rate constants were $k_{\text{ox}} = 6.6 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ for diphenylmethanol, $k_{\text{ox}} = 2.5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ for styrene, and $k_{\text{ox}} = 1.8 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ for cyclohexene. The putative porphyrin-ruthenium(V)-oxo transient reacted 5–6 orders of magnitude faster than the corresponding *trans*-dioxoruthenium(VI)-oxo porphyrins, and the rate constants obtained in this work were similar to those of corrole-iron(V)-oxo derivative. The high reactivity for the photochemically generated ruthenium-oxo species in comparison to other porphyrin-metal-oxo intermediates suggests it is a true ruthenium(V)-oxo species.

Keywords

Ruthenium; porphyrin; oxidation; kinetics; and laser flash photolysis

1. Introduction

Catalytic oxidations, associated with a variety of enzymes, play a key role in the oxidative transformation of endogenous and exogenous molecules in all forms of life.¹ Oxidations are also core processes in organic synthesis with millions of tons of oxygenated compounds annually produced and applied worldwide, ranging from pharmaceuticals to large-scale commodities.^{2, 3} In Nature, aerobic oxidation processes are carried out in a highly selective and ecologically sustainable manner by mono- or dioxygenases under mild conditions.^{1, 4–6} An ubiquitous type of monooxygenase is cytochrome P-450 enzymes (P450s), which feature an iron porphyrin core and catalyze a wide variety of oxidation reactions including important hydroxylation of unreactive hydrocarbons with exceptionally high reactivity and

selectivity.⁷ In humans, the P450s perform both highly specific reactions, such as oxidation of androgens to estrogens, and broad-spectrum oxidations of drugs, pro-drugs, and xenobiotics in the liver.⁵ Many transition metal catalysts, with a core structure closely resembling that of the iron porphyrin core of 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.^{8–10}

In biomimetic catalytic oxidations, most commonly, a transition metal catalyst is oxidized to a high-valent metal-oxo species by a sacrificial oxidant, and the activated transition metal-oxo intermediate then oxidizes a substrate like alkene, alkane, phosphine, amine and sulfide by oxygen atom transfer and/or insertion reactions.^{6, 11} 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;¹² however, in many cases, the active metal-oxo species does not accumulate to detectable quantities, and the actual oxidizing species remains speculative. Our particular interest in the context of metal-oxo chemistry is to explore the photochemical approach^{13, 14} that targets the direct detection and kinetic study of high-valent transition metal-oxo derivatives. In this regard, we have successfully introduced laser flash photolysis (LFP) techniques for generation and direct kinetic studies of a variety of high-valent transition metal-oxo species supported by porphyrin and corrole ligands.^{15–20} 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.²¹

Among the high-valent metal-oxo species, metal(V)-oxo complexes deserve special attention because they are highly reactive, although rare and elusive. The known porphyrin manganese(V) complexes showed higher reactivity than the well known iron(IV)-oxo radical cation in the same ligand system.^{15, 21, 22} Collins *et al.* reported an iron(V)-oxo complex supported by a tetraanionic ligand that showed truly unprecedented reactivity.^{23, 24} Goldberg and coworkers described the generation of new manganese(V)-oxo π -cation radical corrolazine that is more reactive oxidant than its one-electron-reduced analogue.²⁵ The same authors have also reported the spectroscopic evidence for a high-valent corrolazine-iron-oxo intermediate at the iron(V) oxidation level.^{26, 27} The putative porphyrin/corrole-iron(V)-oxo transients produced by LFP methods displayed the appropriate high level of reactivity.^{19, 28, 29} Similar to the well-established photo-disproportionation of cofacial *bis*-porphyrin-diiron(III) μ -oxo complexes,^{30, 31} we have discovered that a photo-disproportionation of a *bis*-corrole-iron(IV) μ -oxo dimer apparently gave the same type of corrole-iron(V)-oxo transient that was also observed by photolysis of the corresponding corrole-iron(IV) chlorate complex.^{32, 33}

Much research has focused on ligand-iron-oxo chemistry, but porphyrin-ruthenium(V)-oxo complexes^{34–36} are also attractive candidates for catalytic oxidations. These species are proposed intermediates in very efficient catalytic processes,^{35, 37–39} although not yet observed directly; computational studies suggest that they are stable with respect to ruthenium(IV)-oxo porphyrin radical cations.⁴⁰ Recently, we have communicated a putative porphyrin-ruthenium(V)-oxo species via a photo-disproportionation reaction that has shown

great potential for aerobic photocatalytic oxidation.⁴¹ In the present study, we describe our full findings on the photochemical formation of a highly reactive porphyrin-ruthenium-oxo species (**1**) using LFP methods and direct measurements of the rate constants for oxidation reactions. As discussed below, the target oxidant **1** in this work can be formed either by photo-disproportionation of a *bis*-porphyrin-ruthenium(IV) μ -oxo dimer (**2**), or by photolysis of the porphyrin-ruthenium(III) *N*-oxide adduct (**3**) (Figure 1). In view of its spectral and kinetic behavior, the transients produced from both routes are spectroscopically and kinetically the same. It is very important to point out that its high reactivity generated from two methods in comparison to other metal-oxo complexes supports the original assignment of the structure of the oxidant **1** as a ruthenium(V)-oxo species.⁴¹

2. Results and discussions

Photo-disproportionation reaction

As mentioned previously, photolysis of a *bis*-corrole diiron(IV) μ -oxo dimer proceeded through a disproportionation pathway that gave a corrole-iron(III) species and a corrole-iron(V)-oxo species.³² Given the periodic relationship between ruthenium and iron and the nature of the similar macrocyclic system, we further inferred that the photo-disproportionation of *bis*-porphyrin-diruthenium(IV) μ -oxo dimer may produce the terminal ruthenium(V)-oxo intermediate with the concomitant formation of ruthenium(III) porphyrin (Figure 1). In this context, the *bis*-[5,10,15,20-tetraphenylporphyrin]-diruthenium(IV) μ -oxo precursor (**2a**) was synthesized according to a reported method.⁴² The hydroxyl axial ligands were readily replaced with chloride anions to give a μ -oxo complex, formulated as $[\text{Ru}^{\text{IV}}(\text{TPP})\text{Cl}]_2\text{O}$ (**2b**). The complexes were characterized by UV-visible (Figure 2), ¹H NMR, and IR spectra that matched those reported.⁴²

To ascertain the photolysis mechanism, we conducted laser flash photolysis (LFP) studies similar to those previously described for the *bis*-corrole-diiron(IV) μ -oxo complex.^{20, 32} As shown in Figure 3A, the photolysis of the *bis*-porphyrin-diruthenium(IV) μ -oxo complex (**2a**) exhibited a fast decay followed by a slow growth that were observed in different time scales (Figure 3A). Figure 3B shows a time-resolved *difference* spectra, which defined as spectrum (t) – spectrum (final) is a conventional way in LFP studies; in this type of spectral presentation, positive peaks are from species decaying with time, and negative peaks are from species forming with time. Irradiation of the complex $[\text{Ru}^{\text{IV}}(\text{TPP})\text{OH}]_2\text{O}$ (**2a**) with 355 nm laser light at ambient temperature in CH_3CN solution instantly produced a highly reactive transient **1** displaying a strong Soret band at 390 nm, which rapidly decayed to form a compound **4** with Soret band at 410 nm and Q band at 530 nm (Figure 3B). The spectrum of **4** was essentially identical to that of $\text{Ru}^{\text{III}}(\text{TPP})\text{OH}$, which was independently prepared from a reported method.³⁵ Accordingly, we assigned the structure of **1** as $[\text{Ru}^{\text{V}}(\text{O})(\text{TPP})\text{OH}]$ and that of **4** as $\text{Ru}^{\text{III}}(\text{TPP})\text{OH}$, supporting the proposed photo-disproportionation mechanism. In the Figure 3B, the only observable transients are **1** and its product **4** from reaction of **1** with solvent or organic impurities because those increase or decrease in concentration in a 50 ms time scale. Note that all of the Soret bands of complexes (**1**, **2** and **4**) overlap, however, difference spectra can show the Soret band of **1** most removed from the others which are relatively stable within this time scale. It is noteworthy that the photolysis

efficiency could be enhanced by adding benzophenone or anthracene, which presumably acts as a photosensitizer. In the presence of anthracene (10 mM), the photolysis of **2a** had a quantum yield of 1.1×10^{-3} (see Experimental section for details), which is 10 times greater than that reported for the photo-disproportionation of a *bis*-porphyrin-diiron(III) μ -oxo complex.³¹ In a slower subsequent phase of the reaction (Figure 3C), exposing photoproduct **4** to molecular oxygen led to regeneration of the *bis*-porphyrin-diruthenium(IV) μ -oxo complex **2a** through an autooxidation pathway.⁴³

The elements of a highly reactive, yet economical and green catalytic oxidation system exist in the photo-disproportionation reactions discussed above. In our recent report,⁴¹ we have shown that the ruthenium(IV)- μ -oxo bisporphyrins catalyzed efficient aerobic oxidation of alkenes and activated hydrocarbons using visible light and atmospheric oxygen. Quite surprisingly, the axial ligand on the metal has a significant effect and the $[\text{Ru}^{\text{IV}}(\text{Por})\text{Cl}]_2\text{O}$ (**2b**) gave a much lower activity compared to $[\text{Ru}^{\text{IV}}(\text{Por})\text{OH}]_2\text{O}$ (**2a**). Therefore, we have carried out the LFP experiments of $[\text{Ru}^{\text{IV}}(\text{TPP})\text{Cl}]_2\text{O}$ under identical conditions as described for **2a**. It is worth of note that no transient species at 390 nm or 410 nm was formed; instead, only a rapid reformation process of the starting precursor (**2b**) was observed (Figure 4). The LFP results suggest that the photolysis of **2b** *mainly* occurs at the Ru-Cl bond which gave ruthenium(IV) and chlorine radical followed by a rapid recombination reaction.

Photo-induced ligand cleavage reaction

The ability to produce the same ruthenium(V)-oxo species in an alternative way is very important. Notably, we have discovered a new photosynthetic entry to the well-known *trans*-dioxoruthenium(VI) porphyrins as a result of the simultaneous cleavages of two X-O bonds from ruthenium(IV) dichlorates or dibromates.^{44, 45} In this work, we have also extended the so called photo-induced ligand cleavage reactions²⁰ for the generation of the ruthenium(V)-oxo species. Instead of the *homolysis* of the Cl-O in ruthenium(IV) dichlorates that gave an one-electron oxidation, we expected a two-electron oxidation through *heterolysis* of the O-X bond in the oxygen-containing ligands to produce the ruthenium(V)-oxo species (Figure 5).

According to early studies by Groves and coworkers,^{35, 36} it is generally accepted that the pyridine *N*-oxide/ Ru^{III} complex is the precursor in the catalytic cycle that eliminates pyridine on *heterolytic* fragmentation to form the active ruthenium(V)-oxo species. The putative Ru^{V} -oxo oxidant (**1**) has not been detected in thermal reactions, however, suggesting that the oxidant reacts much faster than it is formed. Following the literature available procedure, the radical cation **5** was quantitatively generated by reaction of the corresponding carbonyl precursor (**6**) with ferric perchlorate in dichloromethane at ambient temperature.³⁵ As expected, species **5** shows a characteristic absorption band in the 600–700 nm region (Figure 6, dashed curve) and the EPR signal ($g = 2.000$) (Figure 6, inset) in agreement with the proposed structure for **5**. Reaction of **5** with an excess of pyridine-*N*-oxide or 2,6-dichloropyridine *N*-oxide at room temperature led to the formation of a metastable intermediate **3** that showed a distinct UV-vis absorption (Figure 6, solid curve), which is consistent with that of the ruthenium(III) *N*-oxide adduct from literature known work.³⁵

Irradiation of complex **3** generated *in situ* in CH₂Cl₂ solution with 355 nm laser light gave a highly reactive transient that was monitored by UV-visible spectroscopy. A time-resolved difference spectrum is shown in Figure 7A, where the formed transient has a Soret band absorbance with λ_{max} at ca. 390 nm. The observed transient is remarkably reactive. When produced in CH₂Cl₂ in the absence of additional organic reductants, it decays with a 45 ms half-life, giving the ruthenium(III) species with λ_{max} at 410 nm. When organic substrates such as cyclohexene was present, the decay of the photochemically-generated species accelerated linearly with the substrate concentration (Figure 7B), indicating a second-order reaction. The plot slope gave a second-order rate constant of 740 M⁻¹ s⁻¹. Apparently, we have found that the same oxidizing species was produced from both photochemical routes, i.e. photolysis of **3** gave the species that is indistinguishable from that of photo-disproportionation of a *bis*-porphyrin diruthenium(IV) μ -oxo dimer (**2**), as judged by the transient UV-visible spectrum and kinetic behavior (see later discussion). Accordingly, the observed species in photo-induced ligand cleavage reaction (Figure 7) was assigned **1** as the ruthenium(V)-oxo structure. At this moment, we further assume the identity of axial ligand bound to the ruthenium of **1** (X in Figure 5) is the strong binding pyridine formed from the photolysis reaction. It is noteworthy that the photo-induced fragmentation reaction of *N*-oxide adduct **3** is directly analogous to the photochemical cleavages of porphyrin–manganese(III) perchlorates, which give porphyrin–manganese(v)-oxo intermediates by heterolytic cleavage of the O–Cl bonds in the perchlorates.^{15, 21}

Kinetic studies

Kinetic studies were accomplished by generating transient **1** using photo-disproportionation reactions in the presence of organic substrates at varying high concentrations under pseudo-first-order conditions. In all kinetic measurements, we monitored decay of the oxo species **1** at 390 nm (Soret band). Species **1** reacted rapidly when produced in CH₃CN solutions and the pseudo-first-order decay rate constant in the absence of substrate was defined as background rate constant (k_0). The background reaction is likely due to reaction of **1** with the solvent (CH₃CN) or organic impurities. In the presence of organic substrates, the pseudo-first-order decay rate constants increased linearly with substrate concentration. The kinetics are described by Eq. 1, where k_{obs} is the observed pseudo-first-order rate constant, k_0 is the background rate constant for decay in the absence of substrate, k_{ox} is the second-order rate constant, and [Substrate] is the concentration of substrate.

$$k_{\text{obs}} = k_0 + k_{\text{ox}}[\text{Substrate}] \quad (\text{eq. 1})$$

The kinetic plots from reactions of **1** formed by photolysis of **2a** with representative organic substrates are shown graphically in Figure 8, where plots of k_{obs} versus the concentrations of different substrates were linear, and the second-order rate constants for reactions of **1** with other substrates are collected in Table 1.

Reactions of species **1** with alkenes, and benzylic alcohols were studied. The rate constants listed in Table 1 demonstrate that oxidation of benzylic alcohols are faster than oxidation of alkenes, presumably due to a more energetically favorable mechanism. Of note, a significant solvent effect was observed for the reaction of **1**. Addition of small amount of methanol (5%

v/v) slowed down the reaction of cyclohexene with **1** (entry 4). In addition, **1** reacted about three times faster with cyclohexene in CH₃CN ($k_{\text{ox}} = 1.8 \times 10^3$, entry 3) than in CH₂Cl₂ ($k_{\text{ox}} = 7.4 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$, entry 5). It is literature known that axial ligand has a marked influence on the reactivity of the high-valent iron-oxo porphyrin intermediate.^{46, 47} One possible explanation for the observed solvent effect lies that ligation of solvent to the ruthenium(V) center could certainly impact its reactivity in the oxidation of cyclohexene. It is worth noting that the same rate constant for cyclohexene in CH₂Cl₂ was observed for the species **1** generated by two methods, i.e. photo-disproportionation and photo-induced ligand cleavage reactions.

The k_{ox} values determined in this work provide a quantitative comparison of the kinetics of reactions of the porphyrin-ruthenium(V)-oxo species **1** to those of related porphyrin/corrole-metal-oxo complexes (Table 2). In the alkene epoxidations by the well characterized *trans*-dioxoruthenium(VI) porphyrins, the second order rate constants obtained under similar conditions are in the ranges of 4.0×10^{-3} to $4.1 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$.⁴⁸ Remarkably, the observed rate constants for reactions of **1** with cyclohexene and other organic substrates (Table 1) are 5–6 orders of magnitude greater than those for similar reactions of the *trans*-dioxoruthenium(VI) complexes including much more electron-demanding porphyrin system.⁴⁸ The putative 5,10,15,20-tetraphenylporphyrin-iron(V)-oxo complex²⁹ is 2 orders of magnitude more reactive in cyclohexene oxidations than **1**. This is in agreement with the general observation that porphyrin-ruthenium-oxo complexes are expected to be more stable than the corresponding iron-oxo analogues. The rate constants of species **1** produced in this work are similar to those of iron(V)-oxo corrole.^{28, 32} Corrole macrocycles are tri-anionic, whereas porphyrins are di-anionic, and therefore, corrole-iron(V)-oxo complexes are less reactive than porphyrin-iron(V)-oxo complexes. Importantly, species **1** is much more reactive than the corresponding iron(IV)-oxo porphyrin radical cation (Compound I analogues).⁴⁹ Comparison of the kinetics of reactions of the porphyrin-ruthenium-oxo species **1** to those of various porphyrin/corrole-metal-oxo complexes (Table 2) suggests it is a true ruthenium(V)-oxo species.

3. Conclusion

In conclusion, photo-cleavage of a *bis*-porphyrin-ruthenium(IV) μ -oxo dimer proceeds in a disproportionation mechanism to generate a putative ruthenium(V)-oxo and ruthenium(III) porphyrin species. Laser flash photolysis production of porphyrin-ruthenium(V)-oxo species has permitted the detection of the highly reactive intermediates in organic solvents and direct kinetic studies of their reactions with typical organic substrates. More importantly, the photo-cleavage of a ruthenium(III) *N*-oxide adduct proceeds by heterolysis of Ru-O bond to give an oxo transient that is spectroscopically and kinetically indistinguishable from the species formed by photolysis of the corresponding *bis*-porphyrin-ruthenium(IV) μ -oxo dimer, confirming that the same oxidizing ruthenium(V)-oxo species was produced from both methods. The putative ruthenium(V)-oxo species has shown a remarkably high reactivity in comparison to the well characterized *trans*-dioxoruthenium(VI) porphyrins and porphyrin-iron(IV)-oxo radical cations. Further studies to characterize the observed transients more fully and to define synthetic applications are ongoing in our laboratory.

Experimental section

Materials and instruments

Acetonitrile and methylene chloride were obtained from Fisher Scientific and distilled over P_2O_5 prior to use. All organic substrates for LFP kinetic studies were the best available purity from Aldrich Chemical Co. and were passed through a dry column of active alumina (Grade I) before use. Pyridine *N*-oxide was obtained from Aldrich and used as such. 2,6-Dichloropyridine *N*-oxide was prepared by oxidation of the corresponding pyridine precursors by H_2O_2 (50%) in trifluoroacetic acid according to the known procedure.⁵⁰ 5,10,15,20-Tetraphenylporphyrin free ligand (H_2TPP)⁵¹ and its ruthenium(II) carbonyl complex $Ru^{II}(TPP)(CO)$ (**6**) were prepared by literature methods.⁴⁸ Complexes **2** were prepared according to the literature procedure⁴² and purified by chromatography on basic alumina. All the compounds were characterized by UV-vis, 1H NMR and IR spectra, matching those reported data.

UV-vis spectra were recorded on an Agilent 8453 diode array spectrophotometer. IR spectra were obtained on a Bio-Rad FT-IR spectrometer. NMR was performed on a JEOL ECA-500 MHz spectrometer at 298K with tetramethylsilane (TMS) as internal standard. Chemical shifts (ppm) are reported relative to TMS. X-band ESR spectra were recorded on a Varian E109E spectrometer equipped with a low-temperature dewar.

LFP and Kinetic studies

Laser flash photolysis (LFP) experiments were conducted at ambient temperature (22 ± 2 °C) on an Applied Photophysics LKS-60 kinetic spectrometer equipped with an SX-18MV stopped-flow mixing unit. Oversampling (64:1) was employed in all cases to improve the signal-to-noise. In experiments with the *bis*-porphyrin-diruthenium(IV) μ -oxo dimer **2**, 100 μ L of a CH_3CN solution of freshly prepared dimer **2** (ca. 2×10^{-5} M) was mixed in a 2 mm $\times$ 10 mm optical cell with an equal volume of acetonitrile (for self-decay studies) or acetonitrile containing a reactive substrate, and the solution was irradiated with a ca. 5 mJ of 355 nm light from a Nd-YAG laser (ca. 7 ns pulse). The signal was monitored at fixed wavelengths with 3–20 nm steps to produce a time resolved spectrum.

In the photo-induced ligand cleavage reaction, the metastable precursor **3** was prepared by rapid mixing of radical cation **5** with pyridine *N*-oxide salt in CH_2Cl_2 followed by irradiation. In a typical reaction, a 100 μ L CH_2Cl_2 solution of **5** (2.0×10^{-5} M) was mixed with 100 μ L of a CH_2Cl_2 solution of pyridine *N*-oxide (5.0×10^{-4} M) in a 2 mm $\times$ 1 cm quartz cell. After a delay for the formation of **3** (5–10 s), the sample was subsequently irradiated with ca. 30 mJ of 355 nm light from an Nd-YAG laser (ca. 7 ns pulse). The reaction mixtures were monitored at single wavelengths with 5–10 nm intervals. Data was acquired and analyzed with the Applied Photophysics software. For kinetic studies of reactions with cyclohexene, the substrate at the desired concentration was present in the solution containing species **5** before the photolysis.

For kinetic studies, the signal decay at $\lambda_{max} = 390$ nm was monitored. The traces were well fit by single exponential decay functions using either the Applied Photophysics software or SigmaPlot software and are reported with errors of 1σ . Plots of the observed pseudo-first-

order rate constants were linear. The rate constants for reactions with substrates were determined from the observed decay rate constants via Eq 1. The results in text are averages of 2–3 runs, and the errors in the rate constants are 2σ in Table 1.

Quantum yield measurement

The method of Hoshino *et al.* was employed.⁵² A solution of the ruthenium(IV)- μ -oxo dimer **2** with absorbance of 0.5 AU at 355 nm was irradiated with the third harmonic of the Nd-YAG laser (355 nm) at 30 mJ of power per pulse, and the absorbance decrease at λ_{max} of the Soret band for the precursor was measured. The molar yield loss of the precursor was determined using the known extinction coefficient, and the yield was compared to the yield of benzophenone triplet formed by 355 nm irradiation, where the standard solution of benzophenone had an absorbance of 0.5 AU at 355 nm. In this method, the quantum yield for excitation of benzophenone is taken to be 1.0 as described previously. The quantum yield for cleavage of the precursor was calculated from the ratio of molar yields and ratio of molar extinction coefficients for the precursor of interest and the standard.

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Figure 1.
Two-route photochemical approaches to the putative porphyrin-ruthenium(V)-oxo species

Figure 2. UV-visible spectra of [Ru^{IV}(TPP)OH]₂O (**2a**, solid lines) and [Ru^{IV}(TPP)Cl]₂O (**2b**, dashed lines) in CH₃CN

Figure 3.

(A) Kinetic trace at λ_{max} (390 nm) showing a rapid decay over 50 ms followed by a slow growing process over 1 s after laser pulse; (B) Time-resolved *difference* spectra at 0.2, 1, 2, 5, 8 and 10 ms, following 355 nm irradiation of $[\text{Ru}^{\text{IV}}(\text{TPP})\text{OH}]_2\text{O}$ (**2a**) in the presence of benzophenone (10 mM) in CH_3CN at 22 °C; difference spectra = spectrum(*t*) - spectrum (final= 50 ms). In this representation, decaying peaks have positive absorbances, whereas growing peaks have negative absorbances. (C) Time-resolved *difference* spectra over 1 s following 355 nm irradiation of $[\text{Ru}^{\text{IV}}(\text{TPP})\text{OH}]_2\text{O}$ in the presence of benzophenone (10 mM) in oxygen-saturated CH_3CN . In this period, the ruthenium(III) species (**4**) is converting to μ -oxo ruthenium(IV) dimer (**2a**).

Figure 4. Time-resolved *difference* spectrum following 355 nm irradiation of $[\text{Ru}^{\text{IV}}(\text{TPP})\text{Cl}]_2\text{O}$ (**2b**) in the presence of benzophenone (10 mM) in CH_3CN at 22 °C; difference spectrum = spectrum(t) - spectrum (final= 20 ms).

Figure 5.
Generation of the porphyrin-Ruthenium(V)-oxo species via photo-induced ligand cleavage reaction

Figure 6. Superimposed UV-visible spectra of **3** (solid lines), **5** (dashed line) and **6** (dotted lines) at room temperature in CH_2Cl_2 . Inset: X-band EPR of **5** at 298 K.

Figure 7.

(A) Time-resolved difference spectrum following 355 nm irradiation of species **3** over 100 ms in CH_2Cl_2 at $22 \pm 2^\circ\text{C}$. (B) Observed rate constants for reactions with cyclohexene in CH_2Cl_2 at 22°C , monitored at 390 nm.

Figure 8.

Representative plots of observed pseudo-first-order rate constants for reactions of **1** versus concentrations of diphenylmethanol (square), cyclohexene (circles), *cis*-cyclooctene (triangles) in CH_3CN .

Table 1Second-Order Rate Constants for Reactions of **1**^a.

Entry	Substrate	k_{ox} (M ⁻¹ s ⁻¹)
1	none ^b	340 s ⁻¹
2	none ^c	15 s ⁻¹
3	cyclohexene	$(1.8 \pm 0.2) \times 10^3$
4 ^d		$(1.2 \pm 0.2) \times 10^3$
5 ^c		$(7.4 \pm 0.6) \times 10^2$
6	cis-cyclooctene	$(1.3 \pm 0.3) \times 10^3$
7	styrene	$(2.5 \pm 0.3) \times 10^3$
8	α -methylstyrene	$(1.8 \pm 0.1) \times 10^3$
9	diphenylmethanol	$(6.6 \pm 0.6) \times 10^3$
10	1-phenylethanol	$(8.6 \pm 0.7) \times 10^3$

^aReactions at 22 ± 2 °C under single-turnover conditions in CH₃CN except otherwise specified. Standard deviations are 2 σ .^bPseudo-first-order decay rate constant in the absence of substrate, defined as background rate constant (k_0).^cin CH₂Cl₂^dCH₃CN:CH₃OH (v/v = 20:1).

Table 2Rate constants for reactions with cyclohexene.^a

Metal-oxo	k_{ox} ($\text{M}^{-1} \text{s}^{-1}$)	reference
1	1.8×10^3	this work
(TPP)Ru ^{VI} O ₂	4.0×10^{-3}	ref. 48
(TPP)Ru ^{IV} O	n.d. ^b	
^c (TPFPP)Ru ^{VI} O ₂	4.1×10^{-2}	ref. 48
(TPP)Fe ^V O(ClO ₄)	2.2×10^6	ref. 19
^d (TPFC)Fe ^V O	7.4×10^3	refs. 28 and 32
^e (TMP) ⁺ ·Fe ^{IV} O(ClO ₄)	68	ref. 49

^a Second-order rate constants at ambient temperature.^b Too slow to measure.^c TPFPP = 5,10,15,20-*tetrakis*-(pentafluorophenyl)porphyrin.^d TPFC = 5,10,15,-tripentafluorophenylcorrole.^e TMP = 5,10,15,20-tetramesitylporphyrin.