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Chemical and photochemical oxidation of organic substrates by ruthenium aqua complexes with water as an oxygen source†

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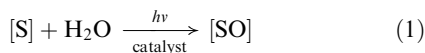
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Two ruthenium aqua complexes were shown to be effective catalysts in chemical and photochemical oxidation of hydrocarbons. A remarkable activity (up to 90% yield and 100% selectivity) was performed in conversion of sulfide to sulfoxide by homogeneous photooxidation.

In Photosystem II (PSII), water is oxidized by sunlight with the oxygen-evolving complex (OEC) providing electrons and protons for sustainable processes in nature. The key intermediate of this process is believed to be highly active manganese(v)-oxo species generated by stepwise proton-coupled electron transfer (PCET).¹ For the purpose of producing renewable clean energy, artificial photosynthesis systems based on transition metal complexes have been developed aiming at water splitting into molecular oxygen and hydrogen. So far, a few photocatalytic systems including electron acceptor, photosensitizer and molecular catalyst have been shown to be able to oxidize water driven by visible light.^{2–6} Success of these systems relies on the conversion of a catalyst to the corresponding metal-oxo complex by photo-generated oxidant and subsequent oxidation of water.

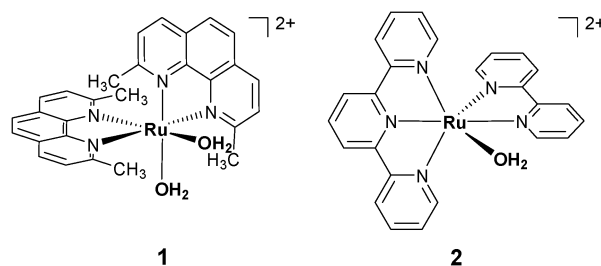
Since the oxidative high-valent metal-oxo complexes have also been identified to be involved in heme and nonheme metalloenzymes responsible for metabolic oxidation and the catalytic cycle of hydrocarbons oxidation by related model complexes,^{7,8} an artificial photosynthesis system can be applied in turn to organic substrate's oxidation as firstly proposed by Inoue *et al.* (eqn (1)).⁹



Despite many endeavors in light-driven water oxidation, attempts for light-driven organic substrate oxidation only occurred recently.^{9–14} As proof of concept, a mononuclear

ruthenium complex $[Ru(tpa)(H_2O)_2]^{2+}$ (tpa = tris(2-pyridylmethyl)amine) and a series of nonheme iron complexes were shown to catalyze the selective oxidation of hydrocarbons with $Ce(NH_4)_2(NO_3)_6$ (Ce^{IV}) as a sacrificial oxidant and water as an oxygen source.^{15,16} In an attempt to realize photocatalysis, a chemical oxidant should be replaced with a photogenerated oxidant such as $[Ru(bpy)_3]^{3+}$. By coupling photosensitizers to the $[Ru(tpy)(bpy)(H_2O)]^{2+}$ catalyst unit, Meyer *et al.* and Rocha *et al.* have constructed molecular dyad assemblies, their photocatalytic properties in dehydrogenation of alcohol were investigated.^{10,11} In addition, a three component homogeneous system consisting of photosensitizer, catalyst and sacrificial electron acceptor was also found to be effective in photocatalytic oxidation of hydrocarbons. For example, Fukuzumi and co-workers reported the remarkable photocatalytic activities of manganese porphyrins in epoxidation.¹² Recently, Nam *et al.* reported $Fe^{IV}=O$ species generated under light irradiation in the presence of $[Ru(bpy)_3]^{3+}$, indicative of the potential application of nonheme iron complexes in photocatalysis.¹⁴ However, the narrow substrate scope and poor efficiency are still great challenges to the practical application of photooxidation in solar energy conversion. To develop new artificial photosynthetic systems, we report here the chemical and photochemical catalytic behaviors of mononuclear $[Ru(dmp)_2(H_2O)_2](PF_6)_2$ (**1**, dmp = 2,9-dimethyl-1,10-phenanthroline) and $[Ru(tpy)(bpy)(H_2O)](ClO_4)_2$ (**2**) complexes (Scheme 1) in oxidation of hydrocarbons in a homogeneous system with water as an oxygen source.

The sterically hindered complex **1** (the *cis* isomer was used in this work) was previously investigated as a candidate for water oxidation catalyst,¹⁷ its catalytic ability in alkene oxidation with hydrogen peroxide or molecular dioxygen as oxidants has

Scheme 1 The cationic structures of complexes **1** and **2**.

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been well studied.^{18,19} The results show that Ru^{II} to Ru^{VI} can be stepwise generated under oxidative conditions accompanied with proton loss, providing a basis for multiple oxidant equivalents accumulation in photocatalysis. For comparison, complex **2** was also studied in this work due to its activity in supramolecular assemblies.^{10,11} It should be noted that the photocatalytic capability of **2** in a simple three component system has never been reported.

To explore the possibility of cooperation of water oxygen in an organic substrate, the catalytic reaction was carried out in water at ambient temperature using alkene as substrate and Ce^{IV} as oxidant. In accordance to previous results,¹⁵ cyclohexene was selectively converted to adipic acid catalyzed by both **1** and **2** in the biphasic reaction. With **1** as catalyst, the turnover number (TON) increased from 14 to 64 with the increase of oxidant from 2 to 8 equiv., while the consumption of Ce^{IV} was maintained at a level of about 60% (Table 1, entries 1–3). Using cyclooctene as substrate, the corresponding dicarboxylic acid product was formed with 24 and 19 TON catalyzed by **1** and **2** in the presence of 4 equiv. of oxidant (Table 1, entries 5 and 6), respectively. Satisfied conversions were received when sodium *p*-styrene sulfonate was used as substrate. In the presence of 4 equiv. of Ce^{IV}, complete conversion to benzaldehyde was observed using either **1** or **2** as catalysts (Table 1, entries 7 and 8). An attempt to expand the substrate scope to straight-chain alkene, for example, *n*-octene led to poorer yields of 14 TON and 9 TON for two catalysts (Table 1, entries 9 and 10). Control experiments confirm that the oxidation of alkenes produce negligible or unselective products in the absence of catalyst (see ESI† for details), demonstrating the unique catalytic properties of polypyridyl ruthenium aqua complexes with water as an oxygen source.

With these results in hand, the photocatalysis in the presence of complexes **1** and **2** was further examined in a three component homogeneous system consisting of catalyst, [Ru(bpy)₃]Cl₂ (photosensitizer) and [Co(NH₃)₅Cl]Cl₂ (electron acceptor). The reactions were run in phosphate buffer solutions (pH 6.8) and initiated by visible light illumination. In contrast to the results obtained with manganese porphyrin as catalyst,¹² we did not observe the formation of epoxide or other detectable product in alkene oxidation. Therefore we

Table 1 Catalytic oxidation of hydrocarbons with Ce^{IV} as oxidant

Entry ^a	Catalyst	Substrate	Product	TON ^b	Yield ^c
1 ^d	1	Cyclohexene	Hexanedioic acid	14	56
2	1	Cyclohexene	Hexanedioic acid	32	64
3 ^e	1	Cyclohexene	Hexanedioic acid	64	64
4	2	Cyclohexene	Hexanedioic acid	30	60
5	1	Cyclooctene	Octanedioic acid	24	48
6	2	Cyclooctene	Octanedioic acid	19	38
7	1	Sodium <i>p</i> -styrene sulfonate	Sodium 4-formyl benzenesulfonate	100	100
8	2	Sodium <i>p</i> -styrene sulfonate	Sodium 4-formyl benzenesulfonate	100	100
9	1	<i>n</i> -Octene	Octanoic acid	14	28
10	2	<i>n</i> -Octene	Octanoic acid	9	18

^a Reaction conditions: catalyst (1 × 10⁻³ mM), substrate (0.1 M), Ce⁴⁺ (0.4 M) in 1 mL D₂O. ^b TON was calculated as (mol of product)/(mol of catalyst). ^c Yield was calculated based on percentage conversion of oxidant. ^d 0.2 M Ce^{IV} was used. ^e 0.8 M Ce^{IV} was used.

Table 2 Photocatalytic oxidation of hydrocarbons in water

Entry ^a	Catalyst	Substrate	Product	TON ^b	Yield ^c
1 ^d	1	Benzyl alcohol	Benzaldehyde	40	16
2	1	Benzyl alcohol	Benzaldehyde	65	13
3 ^d	2	Benzyl alcohol	Benzaldehyde	85	34
4	2	Benzyl alcohol	Benzaldehyde	140	28
5 ^d	1	Thioanisole	Methyl phenyl sulfoxide	190	76
6	1	Thioanisole	Methyl phenyl sulfoxide	430	86
7	2	Thioanisole	Methyl phenyl sulfoxide	400	80
8	1	<i>p</i> -Methoxy thioanisole	Methyl <i>p</i> -methoxy phenyl sulfoxide	455	91
9	2	<i>p</i> -Methoxy thioanisole	Methyl <i>p</i> -methoxy phenyl sulfoxide	440	88

^a Reaction conditions: catalyst (2.0 × 10⁻⁵ M), [Ru(bpy)₃]²⁺ (2.0 × 10⁻⁴ M), substrate (2.0 × 10⁻² M), and [Co(NH₃)₅Cl]²⁺ (2.0 × 10⁻² M) in 5 mL phosphate buffer solution (pH 6.8) under light irradiation.

^b TON was calculated as (mol of product)/(mol of catalyst). ^c Yield was calculated based on percentage conversion of electron acceptor.

^d 4.0 × 10⁻⁵ M catalyst and 4.0 × 10⁻⁴ M [Ru(bpy)₃]²⁺ were used.

turned to the dehydrogenation of benzyl alcohol. Under the conditions of 0.04 mM **1**, 0.4 mM [Ru(bpy)₃]²⁺, 20 mM benzyl alcohol and 20 mM [Co(NH₃)₅Cl]²⁺, benzaldehyde was formed solely with a TON of 40 as determined by ¹H NMR (Table 2, entry 1). The turnover number increased to 65 by simultaneously reducing catalyst and photosensitizer amounts to 0.02 mM and 0.2 mM, respectively (Table 2, entry 2). Under the same conditions, a better result of 140 TON can be obtained with **2** as catalyst (Table 2, entry 4), which is comparable to the result obtained by photosensitizer–catalyst supramolecular assembly, indicating that a disperse system is as efficient as the assembly.¹¹

Concerning the importance of sulfoxide in synthetic chemistry and pharmaceutical industry, much effort has been made in selective sulfoxidation employing different oxidants,²⁰ but photocatalytic oxidation of sulfide is relatively rare.²¹ To our delight, the novel three component system based on cobalt electron acceptor, ruthenium diimine chromophore and ruthenium aqua catalyst exhibited superior efficiency and selectivity for sulfoxidation over previous photocatalytic systems. In the presence of 0.04 mM **1**, 0.4 mM [Ru(bpy)₃]²⁺, and 20 mM [Co(NH₃)₅Cl]²⁺, thioanisole (20 mM) was converted to sulfoxide in 76% yield (based on the amount of one electron acceptor [Co(NH₃)₅Cl]²⁺) by visible light irradiation (Table 2, entry 5). A more promising result of 86% yield corresponding to 430 TON was obtained by reducing the loading of both catalyst and photosensitizer to half (Table 2, entry 6). It was found that no overoxidation product of sulfone forms in the oxidation, confirming that the photocatalytic reaction is highly selective. The oxygen source of photocatalysis was determined using H₂¹⁸O as the reaction solvent. Mass spectra undoubtedly confirmed the incorporation of ¹⁸O into the product with water as the oxygen source (Fig. S1, ESI†). Control experiments show that there is essentially no product produced in the photoinduced oxidation reaction without catalyst or photosensitizer. Similar to **1**, complex **2** also exhibited high selectivity and reactivity in the conversion of thioanisole to sulfoxide affording the product in

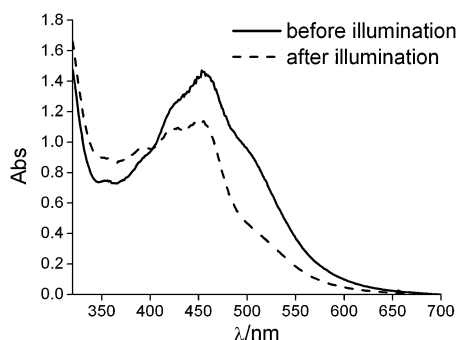


Fig. 1 The adsorption of phosphate buffer solution consisting of complex **1** (6×10^{-5} M), $[\text{Ru}(\text{bpy})_3]^{2+}$ (3×10^{-5} M) and $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ (3×10^{-4} M) before (solid line) and after (dashed line) visible light illumination.

80% yield (Table 2, entry 7). The remarkable catalytic abilities of **1** and **2** could be expanded to other sulfides. For instance, up to 91% yield (455 TON) and 100% selectivity in the oxidation of *p*-methoxyphenylmethyl sulfide to the corresponding sulfoxide was achieved (Table 2, entry 8).

The photooxidation process was investigated by means of UV-Vis spectroscopy. As shown in Fig. 1, the spectrum of $[\text{Ru}(\text{bpy})_3]^{2+}$ and complex **1** mixture exhibits intensive absorption bands at 420, 450 and 500 nm. Comparing with their own absorptions, the first two bands at 420 and 450 nm are ascribed to the MLCT transitions of $[\text{Ru}(\text{bpy})_3]^{2+}$ and the shoulder at 500 nm belongs to the MLCT transition of **1**. Upon light irradiation, the absorption at 500 nm gradually disappears and the MLCT transition bands of $[\text{Ru}(\text{bpy})_3]^{2+}$ are maintained. A similar phenomenon was also observed in the photooxidation of **2** (Fig. S2, ESI†). It is possible that high valent metal-oxo species such as $[\text{Ru}^{\text{IV}}(\text{dmp})_2(\text{H}_2\text{O})(\text{O})]^{2+}$ (Fig. S3, ESI†) and $[\text{Ru}^{\text{IV}}(\text{tpy})(\text{bpy})(\text{O})]^{2+}$ generated by photoinduced electron transfer (Fig. S4, ESI†) are involved in the current system.¹⁸ However, kinetic studies are required to elucidate the mechanistic details.

In conclusion, we have demonstrated the high chemical and photochemical catalytic properties of two polypyridyl ruthenium complexes in the oxidation of hydrocarbons using water as an oxidant. Specifically, this study represents a clean and efficient method to highly selective sulfoxidation, making it attractive in the practical relevance to green chemistry. Further investigations are currently underway to perform enantioselective photooxidation of sulfide with chiral catalysts.

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