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Highly Efficient and Selective Epoxidation of Alkenes by Photochemical Oxygenation Sensitized by a Ruthenium(II) Porphyrin with Water as Both Electron and Oxygen Donor

Shigeaki Funyu, Takehiko Isobe, Shinsuke Takagi, Donald A. Tryk, and
Haruo Inoue*

Contribution from the Department of Applied Chemistry, Graduate Course of Engineering, Tokyo Metropolitan University, 1-1 Minami-ohsawa, Hachiohji, Tokyo 192-0397 Japan, and CREST, Japan Science and Technology

Received November 29, 2002; E-mail: inoue-harou@c.metro-u.ac.jp

Abstract: Visible light irradiation of a reaction mixture of carbonyl-coordinated tetra(2,4,6-trimethyl)-phenylporphyrinatoruthenium(II) (Ru^{II}TMP(CO)) as a photosensitizer, hexachloroplatinate(IV) as an electron acceptor, and an alkene in alkaline aqueous acetonitrile induces selective epoxidation of the alkene with high quantum yield ($\Phi = 0.6$, selectivity = 94.4% for cyclohexene and $\Phi = 0.4$, selectivity = 99.7% for norbornene) under degassed conditions. The oxygen atom of the epoxide was confirmed to come from a water molecule by an experiment with $H_2^{18}O$. *cis*-Stilbene was converted into its epoxide, *cis*-stilbeneoxide, without forming *trans*-stilbeneoxide. *trans*-Stilbene, however, did not exhibit any reactivity. Under neutral conditions, an efficient buildup of the cation radical of Ru^{II}TMP(CO) was observed at the early stage of the photoreaction, while an addition of hydroxide ion caused a rapid reaction with the cation radical to promote the reaction with reversion to the starting Ru^{II}TMP(CO). A possible involvement of a higher oxidized state of Ru such as Ru^{IV}, Ru^{V}, Ru^{VI} through a dismutation of the Ru^{III} species was excluded by an experiment with Ru^{VI}TMP(O)$_2$. Decarbonylation of the Ru complex was also proven to be invalid. A reaction mechanism involving an electron transfer from the excited triplet state of Ru^{II}TMP(CO) to hexachloroplatinate(IV) and subsequent formation of OH$^-$-coordinated Ru^{III} species, leading to an oxo-ruthenium complex as the key intermediate of the photochemical epoxidation, was postulated.

1. Introduction

For the past several decades, extensive efforts have been made in the field of artificial photosynthesis, which involves photochemical reactions to convert light energy into chemical energy via endoergonic processes. Recent efforts on photoredox systems that can induce actual chemical reactions have focused much attention on the reduction terminal end of the photoredox systems rather than on the oxidation terminal end. Efficient hydrogen evolution[1] and even carbon dioxide reduction[2] have been reported. Only a very few reactions, however, can actually be coupled in the oxidative terminal end.[3-6] Incorporation of a water molecule into the oxidative terminal end, that is, oxidation of water as an ideal electron donor, should be one of the central subjects of study.[3-6] Among various approaches for the oxidation of water,[7-9] a semiconductor such as TiO$_2$ has been one

of the most promising candidates for the reaction. Ultraviolet light irradiation of a TiO$_2$ electrode connected with a Pt electrode in an aqueous electrolyte induces oxygen evolution from the TiO$_2$ surface and hydrogen evolution from the Pt surface.[10] This phenomena, that is, the photochemical splitting of water, is often referred to as the "Honda–Fujishima effect". The finding of the Honda–Fujishima effect on the photochemical splitting of

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water by TiO_2[10] afforded a strong impact and has led to the recent progress in the field.[11,12] Even though the light energy utilized for the excitation of TiO_2 is discouragingly limited to that in the ultraviolet region, due to the large band gap (3.0 eV for rutile and 3.2 eV for anatase) of TiO_2,[13] interesting reports have recently appeared that visible light can drive similar reactions on semiconductors such as $TiO_{2-x}N_x$ and $In_{1-x}Ni_x$-TaO_4.[11,12] Dye-sensitized solar cells using nanocrystalline TiO_2 which can utilize the visible light energy have greatly improved the energy conversion efficiency and have attracted much attention.[14] On the other hand, metal complexes have been another potential candidate for the water splitting reaction. Binuclear ruthenium complex has been reported to exert an elegant four-electron oxidation of water,[3h,i,15] and binuclear manganese complexes have also been reported to exhibit a similar reaction.[7,8,16] The interesting reactions, however, that have thus far been reported are only driven by chemical or electrochemical oxidation upon the metal complexes and have not yet been connected with photoreactions. The difficulties in designing a photochemical reaction system with metal complexes for water oxidation would involve subjects to be solved such as (1) how the water molecule could be incorporated in the electron donor system of the photoreaction, (2) how the highly stereochemical arrangement among the metal complexes could be achieved for the four-electron oxidation processes, and (3) how the self-decomposition ascribed to the high oxidation state of the metal complexes could be avoided. The oxidation of water should involve one of the following: (1) a one-electron process,[17] (2) a two-electron one, or (3) a multielectron one.[3] The one-electron process, even the one-electron oxidation of the hydroxide ion, needs a rather high oxidation potential (>2.0 V), and the resultant hydroxide radical is too reactive to be handled. The multielectron one, such as the four-electron process, requires a highly specific stereochemical arrangement, as described above, although the thermodynamic requirement for the process is milder. To avoid the difficulties of these two processes, among the actual photoreactions, we have recently focused our attention on the two-electron oxidation of water, which also has a mild thermodynamic requirement, sensitized by several high-valent metalloporphyrins.[4−6] Here, we report that a ruthenium[II] porphyrin as a sensitizer induces a highly selective epoxidation of alkenes with water both as an oxygen donor and as a two-electron donor upon visible light irradiation.

The highest quantum yields of the photochemical epoxidation turned out to be 0.60 for the formation of cyclohexeneoxide from cyclohexene, with a selectivity of 94.4%, and 0.40 for norborneneoxide formation, with 99.7% selectivity. The reaction serves as one of the typical photoreactions that can incorporate a water molecule both as an oxygen atom donor and as a two-electron donor.

The synthesis of epoxide compounds usually requires rather strong oxidizing agents such as hydroperoxides.[18] From the viewpoints of synthetic methodology, this photochemical epoxidation with water as an oxygen atom donor by visible light would afford a novel synthetic method without using any strong oxidizing agent. When $H_2{}^{18}O$ is used in this photochemical epoxidation, it can serve as a synthetic tool of ^{18}O labeling in the corresponding epoxides.

2. Experimental Section

2.1. Materials. The free base porphyrin, tetra(2,4,6-trimethyl)-phenylporphyrin (H_2TMP), was synthesized according to the report of Lindsey.[19] The carbonyl-coordinated tetra(2,4,6-trimethyl)phenylpor-phyrinatoruthenium(II) ($Ru^{II}TMP(CO)$) was further synthesized from H_2TMP and $Ru_3(CO)_{12}$ by procedures similar to those reported for the tertraphenylporphyrin complex.[20a] $Ru^{VI}TMP(O)_2$ was prepared by oxidation of $Ru^{II}TMP(CO)$ by *m*-chloroperbenzoic acid in dichloromethane according to the literature.[21a] Acetonitrile (HPLC grade) was used as received from Nakalai Tesque. $K_2Pt^{IV}Cl_6$ and $[(CH_3CH_2CH_2-CH_2)_4N]_2Pt^{IV}Cl_6$ were used as received from Aldrich. Distilled water was passed through an ion-exchange column (G-10, ORGANO Co.). The specific resistance of the water was below 0.1 $\mu S/cm^2$. Cyclohexene (Tokyo kasei) was distilled under nitrogen before use and was stored under nitrogen. Styrene (Tokyo kasei) was purified by passing through an alumina column (eluent: hexane) before use and was stored under nitrogen. Cyclooctene, norbornene, and 1-hexene (all from Tokyo kasei) were distilled under nitrogen and were passed through an alumina column (eluent: hexane) before use. *trans*-Stilbene (Tokyo kasei) was purified by vacuum distillation, and *cis*-stilbene was passed through an alumina column before use (eluent: hexane). $H_2{}^{18}O$ (96.5% content) was used as received from EURISO-TOP.

2.2. Measurements. UV−vis spectra were measured on a Shimadzu UV-2400PC. Gas chromatographic analyses were performed on a Shimadzu GC-17A equipped with a TC-17 column (GL Sciences Inc. 30m, 60-250C) and a mass spectrograph (Shimadzu QP-5000) as a detector. The practical detection limit of the GC-MS was ca. 10^{-7} M. Quantitative analysis was carried out in the selected ion monitoring (SIM) detection mode. Fast atom bombardment (FAB) mass spectra were measured on a JEOL JMS-LX1000 with the use of *m*-nitrobenzyl alcohol matrix.

2.3. Photochemical Oxygenation Reaction. All of the samples for the photoreactions were degassed by seven repeated freeze−pump−

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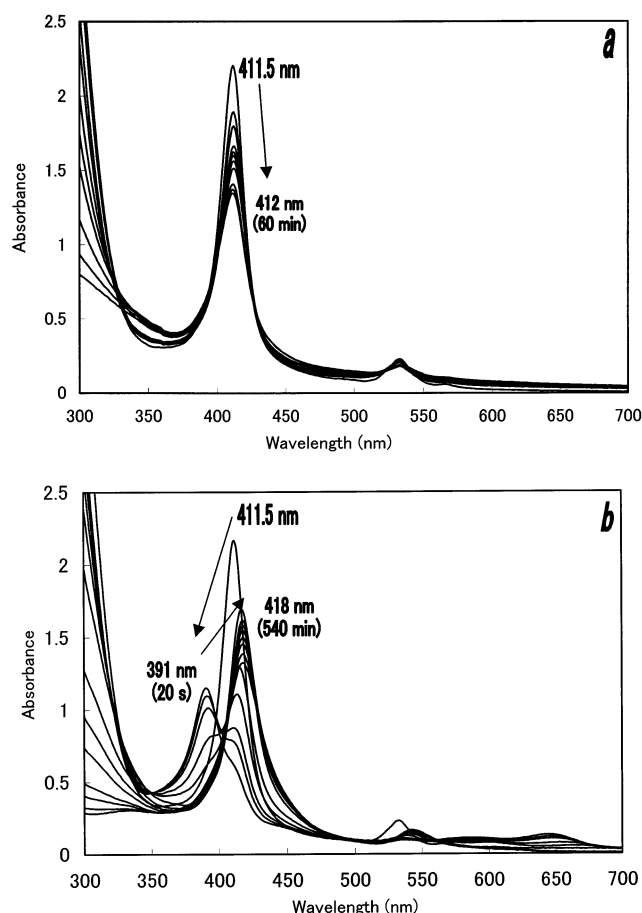
Figure 1. (a) The spectral changes under basic condition (aqueous acetonitrile solution (10% H_2O) containing $Ru^{II}TMP(CO)$ (1.0×10^{-5} M), $K_2Pt^{IV}Cl_6$ (5×10^{-4} M), cyclohexene (1.0×10^{-3} M), and KOH (1.5×10^{-3} M)). (b) The spectral changes under neutral condition (aqueous acetonitrile solution (10% H_2O) containing $Ru^{II}TMP(CO)$ (1.0×10^{-5} M), $K_2Pt^{IV}Cl_6$ (5×10^{-4} M), cyclohexene (1.0×10^{-3} M), and KOH (0 M)).

thaw cycles under 10^{-5} Torr. The degassed samples in a $1 \times 1 \times 4.5$ cm quartz cell (EIKO-SHA) were irradiated with monochromatic light (420 nm) through an interference filter KL-42 and a sharp cutoff filter L-39 from a 500W Xe arc lamp (USHIO 500-DKO). The photoreaction was monitored with UV−visible spectroscopy. The reaction mixture after the photoreaction was vacuum-distilled, and the products were analyzed by GC-MS spectroscopy. All of the procedures were performed at ambient temperature.

2.4. Labeling Experiment with the Use of ^{18}O. The ^{18}O content of the water, $H_2^{18}O/(H_2^{16}O + H_2^{18}O)$, was adjusted to 32.2% by mixing $H_2^{16}O$ and $H_2^{18}O$. The photoreactions were carried out under exactly the same conditions as were used for the experiment carried out with $H_2^{16}O$. The reaction mixtures after the photoreaction were vacuum-distilled, and the content of ^{18}O in the reaction product was determined by GC-MS (Shimadzu QP-5000).

3. Results and Discussion

3.1. Photochemical Epoxidation of Alkene Sensitized by $Ru^{II}TMP(CO)$ under Alkaline Conditions. A degassed aqueous acetonitrile solution (10% H_2O) containing $Ru^{II}TMP(CO)$, $K_2Pt^{IV}Cl_6$, cyclohexene, and KOH was irradiated with visible light (420 nm). Upon visible light irradiation for 60 min, K_2-$PtCl_6$ completely disappeared, while the absorption band of the porphyrin (411.5 nm) gradually shifted to 412.0 nm, with decreasing intensity, as shown in Figure 1a.

The major product was cyclohexene oxide (97.4% selectivity), with small amounts of 2-cyclohexenol (1.5%) and *trans*-2-chlorocyclohexanol (1.1%). The selectivity is defined as the percentage of each product among all of the reaction products. The quantum yield for the formation of cyclohexene oxide was 0.16. The turnover number of the reaction after 60 min irradiation, based on the initial concentration of sensitizer, was 34. Clearly, the reaction proceeded catalytically. Both K_2PtCl_6 and $Ru^{II}TMP(CO)$ were necessary for the photochemical epoxidation of cyclohexene. The net chemistry of the reaction can be expressed as follows:

$$C_6H_{10} + H_2O + Pt(IV)Cl_6^{2-} \xrightarrow[Ru^{II}TMP(CO)]{h\nu}$$
$$C_6H_{10}O + Pt(II)Cl_4^{2-} + 2HCl \quad (1)$$
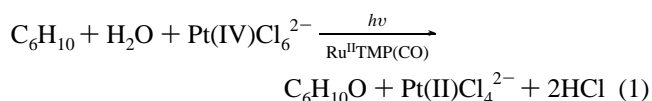
An experiment with $H_2^{18}O$ revealed that an ^{18}O atom was quantitatively incorporated into the oxygenated products under degassed conditions. When $H_2^{18}O$ (32.2% content) was used in the photoreaction, incorporation of ^{18}O into the oxygenated products was 32.2% in cyclohexane oxide and 31.8% in 2-cyclohexenol, respectively. This clearly indicates that a water molecule serves as an oxygen donor in the photochemical oxygenation reaction. Photoreactions with other alkenes under alkaline conditions also afforded epoxide as almost an exclusive product, as indicated in Table 1.

cis-Stilbene was converted into its epoxide, *cis*-stilbeneoxide, without forming *trans*-stilbeneoxide. Interestingly, *trans*-stilbene, however, did not exhibit any reactivity. Contrary to the results obtained here, a dioxo-complex of ruthenium octaethylporphyrin, $Ru^{VI}OEP(O)_2$, which has only a slight steric hindrance around the metal center, has been reported to afford both the *cis*-form and the *trans*-form of the epoxide from *cis*-stilbene and even exhibit a reactivity for *trans*-stilbene, in a study of P-450 model systems where alkene was converted to the corresponding epoxide by a catalytic action of the ground-state ruthenium porphyrins.[22] In the present photochemical system with $Ru^{II}TMP$, which has substantial steric hindrance in the vicinity of the metal center due to the methyl groups in the *ortho*-positions on the *meso*-substituted phenyl ring, *trans*-stilbene, with its extended molecular structure, might not be able to sufficiently access the metal center of the ruthenium complex, as observed in P-450 model systems.[23,24] The lack of formation of the isomerized form, *trans*-stilbeneoxide, from *cis*-stilbene strongly suggests that a concerted, stereoregulative mechanism is operating in the photochemical epoxidation.

The overall view of the reactivities of alkenes examined here does not necessarily show a direct correlation between the reactivities and the oxidation potentials of the alkenes (Table 1), but other factors such as steric ones could also be controlling the reactivity, which supports the idea that the reaction proceeds in a concerted manner on the metal center of the complex.
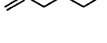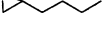
3.2. Photochemical Epoxidation under Neutral Conditions. Under neutral conditions (without added KOH), however, the photoreaction exhibited a somewhat different aspect. In the initial period of the light irradiation (20 s), the original

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Table 1. Photochemical Epoxidation of Alkenes Sensitized by Ru[II]TMP(CO)

In CH$_3$CN -H$_2$O (9 :1)[a]

Alkene	[KOH]/10^{-3}M	Products (selectivity/%)	Quantum yield/10^{-2}	Eox/ V vs. SHE[b]
(cyclohexadiene)	1.5	epoxide (97), OH (1), Cl/OH (1)	16	2.08
(cyclohexene)[c]	0.0	epoxide (87), OH (4), Cl/OH (5), ketone (2), Cl/Cl (2)	7.0	2.08
(cyclohexene)[d]	0.0	epoxide (1), OH (4), Cl/OH (59), OH/OH (32), Cl/Cl (4)	-	2.08
(norbornene)	1.5	epoxide (99.7), ketone (0.3)	11	2.17
(cyclooctene)	1.5	epoxide (99.9), ketone (0.1)	5.9	2.30
(stilbene/dibenzyl)	1.5	epoxide (100)	0.27	1.81
(styrene)	1.5	epoxide (100)	0.16	1.92
(1-pentene)	1.5	epoxide (100)	0.14	2.71
(trans-stilbene)	1.5	-	-	2.00

In CH$_3$CN - (benzene) - H$_2$O (8:1:1)[e]

Alkene	[KOH]/10^{-3}M	Products (selectivity/%)	Quantum yield/10^{-2}	Eox/ V vs. SHE[b]
(cyclohexene)	1.5	epoxide (94.4), OH (3.1), Cl/OH (1.2), Cl/Cl (0.7), ketone (0.6)	60	2.08
(norbornene)	1.5	epoxide (99.7), ketone (0.3)	40	2.17

[a] [Ru[II]TMP(CO)] = 1.0 × 10^{-5} M, [K$_2$PtCl$_6$] = 5.0 × 10^{-4} M, [alkene] = 1.0 × 10^{-3} M. Visible light (420 nm) was irradiated. [b] Reference 31. [c] 20 s. [d] 540 min. [e] [Ru[II]TMP(CO)] = 2.0 × 10^{-5} M, [[C$_4$H$_9$]$_4$N$_2$PtCl$_6$] = 2.5 × 10^{-3} M, [alkene] = 1.0 × 10^{-3} M. Visible light (420 nm) was irradiated.

absorption band (411.5 nm) disappeared completely and shifted to 391 nm, as shown in Figure 1b. On prolonged irradiation (540 min), the absorption at 391 nm gradually shifted to 418 nm. Within the initial 20 s light irradiation, the products obtained were cyclohexene oxide (87%), 2-cyclohexenol (4%), *trans*-2-chlorocyclohexanol (5%), cyclohexanone (2%), and *trans*-1,2-dichlorocyclohexane(2%) (Table 1). The apparent quantum yield of the products was 0.07. The selectivity and the reactivity for the epoxide were both lower than those obtained under alkaline conditions. On prolonged light irradiation (540 min), the selectivity dropped substantially for cyclohexene oxide (1%), 2-cyclohexenol (4%), *trans*-2-chlorocyclohexanol (59%), *trans*-cyclohexane-1,2-diol (32%), and *trans*-1,2-dichlorocyclohexane (4%). *trans*-2-Chlorocyclohexanol became the major product. Because the consumption of K$_2$Pt[IV]Cl$_6$ during the photoreaction induces the formation of HCl, as indicated in eq 1, the chloride ion can give rise to the chlorinated compounds, and acidification of the reaction mixture affects the product distribution, as observed in the case of antimony(V)porphyrin.[6] Actually, the pH of the reaction mixture decreased down to 3.2 after 540 min light irradiation in the neutral sample. In the dark, cyclohexeneoxide was confirmed to be efficiently converted into *trans*-2-chlorocyclohexanol and cyclohexane-1,2-diol in a 65: 35 ratio under acidic conditions ([HCl] = 7.5 × 10^{-4} M) in aqueous acetonitrile (9/1 v/v%). No formation of cyclohexane-

1,2-diol was observed in the initial stages (shorter than 20 s), but its appearance on prolonged light irradiation, as described above, strongly suggests that the diol is not directly formed by the photoreaction, but the initial photoproduct, the epoxide, undergoes conversion into the diol upon acidification of the system during the photoreaction. In fact, under alkaline conditions, the diol was not detected at all (Table 1). Even though *trans*-2-chlorocyclohexanol formed as the major product under neutral conditions on prolonged irradiation, and did not form under alkaline conditions, there still may be a possibility that *trans*-2-chlorocyclohexanol is the initial reaction product and the epoxide is derived from *trans*-2-chlorocyclohexanol by ring closure under alkaline conditions. The initial product distribution under neutral conditions, however, clearly indicates that the primary photoproduct should be the epoxide and that other products are derived from the epoxide upon acidification and the appearance of the chloride ion, as shown in eq 1, in the reaction system during the photoreaction.

3.3. Improvement of the Reactivity. This photochemical epoxidation is quite an attractive reaction, because it obviously involves the water oxidation process, as described later. The reactivity, however, could further be improved. The reaction mechanism, as described later, indicates that the photochemical formation of the cation radical of Ru[II]TMP(CO) is one of the key steps that governs the total reactivity, as described later.

To improve the photochemical reactivity, a promising approach should be to improve the efficiency of the cation radical formation by increasing the concentration of electron acceptor. We have found that potassium hexachloroplatinate (K_2PtCl_6) is an efficient electron acceptor for the present photochemical epoxidation, but its solubility in aqueous acetonitrile is small. The present condition (5×10^{-4} M) is nearly the practical solubility limit in the present solvent system. Other more soluble electron acceptors are required to improve the reactivity. After an extensive search for other electron acceptors, only $Co^{III}(acac)_3$ and $Fe^{III}(NO_3)_3$ were found to exhibit reactivity, although small, while organic acceptors such as methyl viologen and quinones exhibited very little reactivity. Only hexachloroplatinate[IV] turned out to be an efficient electron acceptor. Among the hexachloroplatinate salts, tetrabutylammonium hexachloroplatinate[IV] was found to be more soluble than the potassium salt. The solvent system was also modified by adding benzene to aqueous acetonitrile to improve the solubility of the hexachloroplatinate. By choosing these experimental conditions, we were finally able to successfully find an efficient system for the photochemical epoxidation. Under the following conditions, [$Ru^{II}TMP$] = 2×10^{-5} M, [KOH] = 1.5×10^{-3} M, [alkene] = 1×10^{-3} M, $[[(C_4H_9)_4N]_2PtCl_6]$ = 2.5×10^{-3} M in acetonitrile/benzene/water ($8/1/1$ v/v%), visible light irradiation ($\lambda = 420$ nm) induced an efficient epoxidation of cyclohexene, with a quantum yield of 0.6 and a selectivity of 94.4%. Norbornene also showed a high quantum yield (0.4) for the photochemical epoxidation, with a selectivity of 99.7% (Table 1).

3.4. Is a Higher Oxidation State of Ru Involved in the Photochemical Epoxidation? Before discussing the reaction mechanism of the photochemical epoxidation, we first examined the possibility of whether the reaction involves a higher oxidation state of Ru such as Ru^{IV}, Ru^{V}, and Ru^{VI}, which are known to be strong oxidizing agents.[15,21] Some ruthenium complexes are known to exhibit P-450 oxygenation in the ground state, where dissolved molecular oxygen or another appropriate oxidizing agent is required.[21] Oxidation–reduction cycles among high oxidation states such as $Ru^{V}-Ru^{III}$ and $Ru^{VI}-Ru^{IV}$ have been proposed.[21b,i] The possibility involving high oxidation states of Ru, however, is rather questionable for this photoreaction, as described below. The appearance of the cation radical (391 nm species) and its trapping by hydroxide ion are convincing evidence for the formation of a hydroxide-coordinated Ru species in the photoreaction, which is presumed to be the Ru^{III} species. Supposing this process, however, we found that a further oxidation of the Ru^{III} species (I) to higher oxidation states by K_2PtCl_6 (E_{red} = 0.73V vs NHE) in the reaction system is quite unfavorable. Absence of an induction period for the photochemical formation of the epoxides strongly suggests that a further light irradiation step involving the Ru^{III} species would not contribute substantially to the oxygenation.

In the case of Ru^{II}octaethylporphyrin, one-electron oxidation of the Ru^{II} complex has been reported to afford the Ru^{IV} species via a dismutation process (two Ru^{III} species producing a Ru^{II} species and a Ru^{IV} species).[25] Furthermore, the Ru^{IV} species is readily converted to its μ-oxo-dimer, which is well characterized by the appearance of new absorption bands at 375, 510, and 570 nm. However, the characteristic bands of the μ-oxo-dimer were not observed during the present photoreaction and even

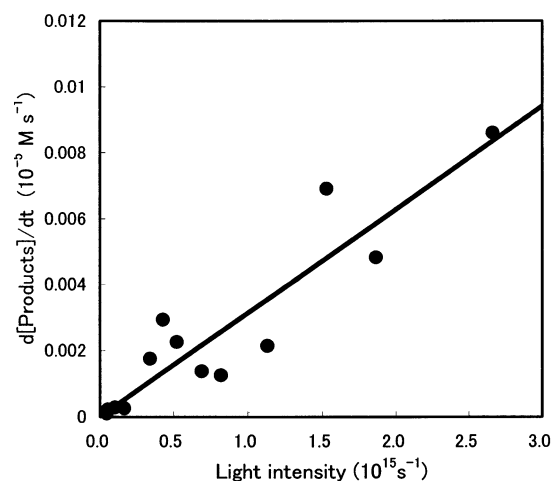(25) Mosseri, S.; Neta, P.; Hambright, P. *J. Phys. Chem.* **1989**, *93*, 2358.

Figure 2. Effect of the intensity of the incident light on the photochemical epoxidation under the condition of aqueous acetonitrile solution (10% H_2O) containing $Ru^{II}TMP(CO)$ (1.0×10^{-5} M), $K_2Pt^{IV}Cl_6$ (5×10^{-4} M), cyclohexene (1.0×10^{-3} M), and KOH (1.5×10^{-3} M).

upon one-electron electrochemical oxidation of $Ru^{II}TMP(CO)$. If the dismutation is involved in the photoreaction, the rate of the reaction should be proportional to the square of the light intensity, but that was not the case. As shown in Figure 2, the yield of the photochemical oxygenation was approximately proportional to the light intensity.

The absence of the dismutation may be due to the steric hindrance of the bulky substituents in RuTMP. In fact, a completely different product distribution, with less reactivity, was observed, as described below, when $Ru^{VI}TMP(O)_2$ was employed as a sensitizer, where the Ru^{IV} species could play a key role. Groves et al. have reported an oxygenation reaction of alkene catalyzed by $Ru^{VI}TMP(O)_2$ with the redox mechanism involving the cycles among $Ru^{VI}-Ru^{IV}-Ru^{II}$.[21b] We examined the high valent species, $Ru^{VI}TMP(O)_2$, for the reaction with cyclohexene in the dark under exactly the same experimental conditions ([KOH] = 1.5×10^{-3} M, in CH_3CN/H_2O ($9/1$ v/v %)) as were used for the present photoreaction. 2-Cyclohexene-1-ol was the exclusive reaction product with a selectivity of 99% in this case. We examined further a photoreaction sensitized by the high valent species, $Ru^{VI}TMP(O)_2$. A reaction mixture of $Ru^{VI}TMP(O)_2$ (1.0×10^{-5} M), cyclohexene (1.0×10^{-3} M), K_2PtCl_6 (5.0×10^{-4} M), and KOH (1.5×10^{-3} M) in a degassed aqueous acetonitrile solution (10% H_2O) was irradiated with 420 nm light. The starting $Ru^{VI}TMP(O)_2$ had already been transformed into the Ru^{IV} species before light irradiation, and the Ru^{IV} species was the light absorbing species. The photo-products were cyclohexeneoxide (27%), 2-cyclohexenol (56%), *trans*-2-chlorocyclohexanol (8%), and cyclohexen-2-one (5%), respectively. These results indicate that oxidation states higher than Ru^{III} are not involved in the present photochemical epoxidation.

A possible contribution of decarbonylation from the starting complex[26] to the photochemical oxygenation was also excluded by FAB-MS and IR studies on the sample for the initial 20 s irradiation. The starting $Ru^{II}TMP(CO)$ remained unchanged.

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Scheme 1
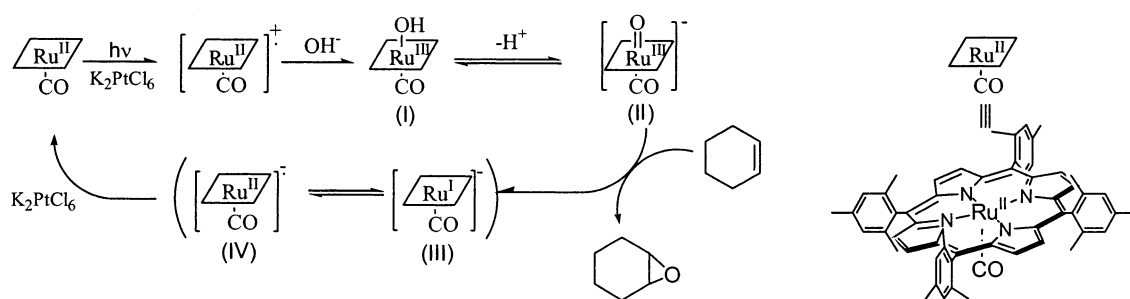
3.5. Reaction Mechanism of the Photochemical Epoxidation. Because $Ru^{II}TMP(CO)$ is almost nonfluorescent, with a lifetime shorter than 35 ps,[21b] the excited state responsible for the reaction should be the excited triplet state of the complex, which has a lifetime sufficiently long for the reaction to take place. The triplet lifetime was estimated to be 64 μs under basic conditions ([KOH] = 1.5×10^{-3} M) in aqueous acetonitrile (9/1 v/v%) by a laser flash photolysis experiment. Supposing the electron transfer from the excited Ru^{II}Complex to be diffusion-controlled as the maximum limit (10^{10} M^{-1} s^{-1}), we found that the maximum rate would become 5×10^6 s^{-1} with [K_2-$PtCl_6$] = 5×10^{-4} M. This cannot compete with the singlet decay rate (<35 ps), while the reaction can proceed within the triplet lifetime. The triplet state is considered to be the porphyrin triplet state rather than MLCT one.[20] An electron transfer from the triplet $Ru^{II}TMP(CO)$ (E_{ox} = -0.67 V vs NHE, E_T (excited triplet state energy) = 1.70 eV[27]) to K_2PtCl_6 (E_{red} = 0.73 V vs NHE)[28] would be sufficiently exoergic. The electrochemical oxidation of $Ru^{II}TMP(CO)$ (1.0×10^{-4} M) at +1.30 V versus NHE in acetonitrile in the presence of tetrabutylammonium perchlorate (0.1 M) as a supporting electrolyte afforded a species with absorption maxima λ_{max} of 391, 589, 646 nm, which are exactly the same for the species observed within the initial 20 s light irradiation under neutral conditions. A further addition of alkaline aqueous acetonitrile ([KOH] = 1.5×10^{-3} M in CH_3CN/H_2O = 9/1 V/V) in the presence of cyclohexene (1.0×10^{-3} M) to the electrochemically oxidized species induced a rapid reversion to one with λ_{max} = 411.5 nm. Treatment of $Ru^{II}TMP(CO)$ (1.0×10^{-5} M) with $Fe(ClO_4)_3$ (5×10^{-5} M) in acetonitrile also afforded a species (λ_{max} = 392, 589, 646 nm) very similar to those obtained in the electrolysis. The 391 nm species is well characterized as the cation radical of the complex ($Ru^{II}-P^{+\bullet}$).[29] The behavior described above is very suggestive in elucidating the mechanism of photoreaction. The appearance of the 391 nm species in the photoreaction under neutral conditions (but not under alkaline conditions) strongly suggests that the cation radical is formed upon light irradiation but that it is trapped by the hydroxide ion to result in a promotion of the oxygenation cycle. The coordination of hydroxide ion or water to the metal center of complex would be reasonable for forming a reactive species such as a metal-oxo complex for oxygen transfer. The hydroxide ion also prevents the acidification of the reaction mixture during

the photoreaction and presumably exerts a key role in the product-determining step in the reaction mechanism. A simple electron transfer from the alkene to the cation radical of Ru^{II}-$TMP(CO)$ (E_{ox} = 1.03 V vs NHE) is most unfavorable, because the oxidation potentials of the alkenes (Table 1) indicate that the electron undergoes a considerable endoergonic process, in contrast to the case for Sb^VTPP.[6] In fact, the cation radical is stable enough to be observed under neutral conditions, even in the presence of alkene, as described above (Figure 1b).

Even though the reaction mechanism is not yet fully understood, one of the most probable reaction schemes for the photochemical oxygenation is, thus, postulated in Scheme 1. Upon visible light irradiation of $Ru^{II}TMP(CO)$, an electron transfer from the triplet excited porphyrin to $PtCl_6^{2-}$ would form a porphyrin cation radical ($Ru^{II}-P^{+\bullet}$), because the first oxidation peak (1.03 V vs NHE) in the cyclic voltammogram is considered to correspond to an oxidation of the porphyrin ligand, with the second peak (1.44 V vs NHE) corresponding to Ru^{II}/Ru^{III}.[20a,29] Coordination of hydroxide ion or water to the one-electron oxidized species of the starting complex would form a Ru^{III} species (I). Although the formation of the Ru^{III} species from $Ru^{II}-P^{+\bullet}$ is an endoergonic process, stabilization by coordination of OH^- or H_2O to the Ru^{III} center may render the conversion possible. Successive deprotonation would result in the formation of the metal-oxo complex (II). The metal-oxo complex (II) induces a two-electron oxidation through a reaction with the alkene to form the corresponding epoxide and the Ru^I species (III), leading to the formation of the porphyrin radical anion ($Ru^{II}-P^{-\bullet}$)(IV), which is reoxidized to $Ru^{II}-P$ by $PtCl_6^{2-}$. Because the first reduction peak (-0.63 V vs NHE) of Ru^{II}-$TMP(CO)$ in the cyclic voltammetry is considered to be the reduction of porphyrin ring,[20a,29] the presumed reduced species Ru^I would readily result in the formation of $Ru^{II}-P^-$. The reoxidization to $Ru^{II}-P$ by K_2PtCl_6 (+0.73 V vs NHE) is sufficiently exoergic.

A metal-oxo complex is presumably involved in the present photochemical oxygenation, without the presence of a powerful oxidizing agent, wherein the key step is a two-electron oxidative activation of water, which can be thought of as a four-electron reduced form of molecular oxygen. This should be in sharp contrast to the well-known P-450 oxygenation system and its model reactions, which require either molecular oxygen and a

(27) The triplet excited energy (E_T) of $Ru^{II}TMP(CO)$ was estimated from the phosphorescence (729 nm) in EPA.

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two-electron reduction or powerful oxidizing agents.[21,30] The oxygenation reaction through a metal-oxo complex is especially crucial from the viewpoint of artificial photosynthesis, because the complex can directly transfer an oxygen atom derived from a water molecule to organic compounds, and water acts as a two-electron donor in the reaction cycle.