

C–H bond activation with Ge-oxyl complex generated by photoinduced-electron-transfer of di(hydroxo)porphyrin Ge[™] complex

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> **ABSTRACT:** Visible-light irradiation of MeOH solution containing di(hydroxo)tetraphenylporphyrin atogermanium(IV) complex (tppGe(OH)₂; 1a), cumene, and Fe³⁺ ion (Fe(NO₃)₃) as an electron acceptor gave cumyl alcohol as an oxidative product along with Fe²⁺ ion as a reductive product. The quantum yield (Φ_{ox}) and turn over frequency (TOF) for the formation of cumyl alcohol was 0.033 and 111.1 h⁻¹, respectively. The addition of KOH aqueous solution (1 mM) into reaction solution led to an increase of $\Phi_{\alpha\alpha}$ to 0.047. The free energy change (ΔG) with electron transfer from excited triplet state (³1a^{*}) to Fe³⁺ was estimated as a large negative value (-1.37 eV). Furthermore, in **1a**-photosensitized oxidation of MeOH in the presence of K₂PtCl₆ as an electron acceptor, formaldehyde (HCHO) was formed in $\Phi_{ox} = 0.034$ and TOF = 120.0 h^{-1} . The isotope effect for the formation of HCHO ($\Phi_{\text{ox(H)}}/\Phi_{\text{ox(D)}} = 5.04$) was observed when MeOH- d_4 was employed as an substrate. Both formation of cumyl alcohol and formaldehyde was not observed at all in the case of photosensitized reactions by $tppGe(OMe)_2$ (1b) having two axial methoxo ligands. These findings indicate the photosensitized reaction was initiated by photoinduced electron transfer from ${}^{3}1a^{*}$ to Fe³⁺ or K₂PtCl₆ to generate porphyrin radical cation (1a^{+•}), which underwent a proton dissociation of hydroxo axial ligand to give tpp(OH)Ge-O[•] (Ge-oxyl complex) as key intermediate. The Ge-oxyl complex oxidized substrates through a hydrogen-atom abstraction. It is strongly suggested that **1a** can act as a good sensitizer for being able to activate C–H bond of organic compounds.

> **KEYWORDS:** carbon-hydrogen bond activation, germanium porphyrin, oxidation, photoinduced electron transfer.

INTRODUCTION

Metal-oxo porphyrin complexes are known as a key intermediate for various metabolic oxidation processes in P450 enzymatic model system [1, 2]. Therefore, many oxidation processes using metal-oxo porphyrin complexes are also developed. For example, in thermal process, some oxygen donors such as molecular oxygen [3], hydrogen peroxide [4, 5] or others [6, 7] are often employed for the formation of metal-oxo porphyrin complex. On the other hand, we previously found that di(hydroxo)tetraphenylporphyrinatoantimony(V) complex (tppSb(OH)₂⁺) efficiently occurred in the presence of K₂PtCl₆ as an electron acceptor in an aqueous acetonitrile solution under visible light irradiation [8, 9]. In this previous report, it was elucidated that Sb-oxo complex (tpp(OH)Sb=O) generated by a proton dissociation of axial hydroxo ligand of porphyrin radical cation (tppSb(OH)₂^{+•}), formed by photoinduced electron transfer from the excited triplet state of tppSb(OH)₂⁺ to K₂PtCl₆, could be a key intermediate for the oxidation of cyclohexene, resulting that the water molecule worked as an oxygen donor for the formation of Sb-oxo complex. Furthermore, we also reported that di(hydroxo)tetraphenylporphyrinatogermanium(IV) complex (tppGe(OH)₂; **1a**) supported on

the photoepoxidation of cyclohexene sensitized by

[◊]SPP full member in good standing

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Scheme 1. 1a-sensitized oxidation of cumene and MeOH

SiO₂ particle led to the photocatalytic oxidation of hydrocarbons and MeOH to the corresponding alcohols and HCHO under visible light irradiation, respectively [10]. In this system, it was indicated that tpp(OH)Ge-O[•] (Ge-oxyl complex) having *O*-radical character could be formed by similar photochemical process with tppSb(OH)₂ and could participate in the oxidation process of organic substrates. However, the mechanism is not clarified in detail due to the heterogeneous reaction system.

Here, we will report on **1a**-sensitized oxidation of cumene and MeOH in homogeneous solution system from viewpoint of mechanistic approach (Scheme 1). This is the first example of an oxidation using Ge-oxyl porphyrin complex generated by a photochemical process. Therefore, this system can be regarded as a novel method to generate Ge-oxyl porphyrin complexes.

RESULTS AND DISCUSSION

Product analysis

The **1a**-photosensitized reaction was performed by the irradiation (550 nm) of MeOH solution containing **1a** (33 μ M), cumene (1 mM), and Fe(NO₃)₃·9H₂O (1 mM) acting as an electron acceptor. Cumyl alcohol was formed lineally toward the irradiation time without an induction period (Fig. 1). The formation of Fe²⁺, which is oneelectron reduction product of Fe³⁺, was also detected in the reaction solution after irradiation. No cumyl alcohol was obtained under an irradiation in the absence of Fe³⁺. The quantum yield (Φ_{ox}) and turn over frequency (TOF) for the formation of cumyl alcohol were estimated to be 0.033 and 111.1 h⁻¹, respectively (Table 1). Therefore, **1a** works as a photocatalyst in this system.

In the case of **1a**-photosensitized oxidation of MeOH which was performed for a MeOH– $H_2O(9:1 \text{ v/v})$ solution



Fig. 1. Time-course plots for the formation of cumyl alcohol in **1a**-sensitized oxidation of cumene



Fig. 2. Time-course plots for the formation of formaldehyde in **1a**-sensitized oxidation of MeOH

containing **1a** (33 μ M) and [PtCl₆]²⁻ (K₂PtCl₆, 0.5 mM) as an electron acceptor, HCHO was formed lineally towards an irradiation time (Fig. 2). Under irradiation in the absence of [PtCl₆]²⁻, HCHO was not obtained at all. The Φ_{ox} and TOF for the formation of HCHO were estimated to be 0.034 and 120.0 h⁻¹, respectively. These results indicate that the photooxidations of cumene and MeOH were sensitized by **1a** even in homogeneous solution system.

Kinetic analysis

A reaction mechanism was elucidated by the fluorescence quenching experiment of **1a** and the kinetic analysis for Φ_{ox} . In the presence of Fe³⁺, the fluoresc ence of **1a** was not quenched at all. Similar result was obtained even in the presence of [PtCl₆]²⁻. These results show that an initial step of photoreaction can proceed from the excited triplet state of **1a** (³**1a***), not excited singlet state of **1a** (¹**1a***). It is suggested that the initial step should be a photoinduced electron transfer (PET) process from ³**1a*** to Fe³⁺ or [PtCl₆]²⁻, because both free energy changes (ΔG) calculated by



Scheme 2. Reaction scheme for 1a-sensitized oxidation

Rehm–Weller equation [11] using E_{0-0} (1a) = 1.63 eV, $E_{1/2}^{\text{ox}}(1a) = 1.24$ V, $E_{1/2}^{\text{red}}(\text{Fe}^{3+}) = 0.98$ V [6], and $E_{1/2}^{\text{red}}([\text{PtCl}_6]^{2-}) = 0.73$ V vs. SCE [9] are much excergic ($\Delta G = -1.37$ eV for Fe³⁺, $\Delta G = -1.12$ eV for $[\text{PtCl}_6]^{2-}$). Assuming the reaction route shown in Scheme 2, Φ_{ox} is expressed with an equation (Equation 1), where Φ_{isc} is the quantum yield of intersystem crossing of 1a, α is the efficiency of charge separation, β is the efficiency of product formation from an intermediate, k_d is the rate constant for the deactivate process from ³1a* to ground state, k_r is the rate constant for electron transfer from ³1a* to the electron acceptor (A), k_{ox} is the rate constant for oxidation process of substrate (S), and k_x is the rate constant for other reaction process.

$$\Phi_{\rm ox} = \Phi_{\rm isc} \cdot \alpha \cdot \frac{k_{\rm r}[A]}{k_{\rm d} + k_{\rm r}[A]} \cdot \frac{k_{\rm ox}[S]}{k_{\rm x} + k_{\rm ox}[S]}$$
(1)

$$\frac{1}{\Phi_{\rm ox}} = \frac{1}{\Phi_{\rm isc} \cdot \alpha} \cdot \left(1 + \frac{k_{\rm d}}{k_{\rm r}[{\rm A}]}\right) \cdot \left(1 + \frac{k_{\rm x}}{k_{\rm ox}[{\rm S}]}\right)$$
(2)

$$\beta = \frac{k_{\rm ox}[S]}{k_{\rm x} + k_{\rm ox}[S]} \tag{3}$$

According to Equation 1, the reciprocal of Φ_{ox} is proportional to the reciprocal of concentration of A and S, respectively (Equation 2). Indeed, Fig. 3 shows a double reciprocal plot (Stern–Volmer type plot) of Φ_{ox} against concentration of Fe³⁺ in photosensitized oxidation of cumene where Φ_{ox} was measured at various concentration of Fe³⁺ (0.5 mM–5 mM) and the fixed concentration of cumene at 1 mM. The plots laid well on a straight line. This result strongly indicates that the single excited species of **1a** should be responsible for an electron transfer to Fe³⁺ (Scheme 2). Furthermore, the reciprocal of Φ_{ox} was plotted against the reciprocal of concentration of cumene (Fig. 4), when Φ_{ox} was measured at various concentration of cumene (0.5 mM⁻¹ mM) and the fixed concentration of Fe³⁺ at 5 mM. This



Fig. 3. Double reciprocal plot of the Φ_{ox} against the concentration of Fe³⁺ in the **1a**-photosensitized oxidation of cumene under neutral condition (•) and in the presence of aqueous KOH solution (•)



Fig. 4. Double reciprocal plot of Φ_{ox} against the concentration of cumene in the **1a**-photosensitized oxidation of cumene under neutral condition (•) and in the presence of aqueous KOH solution (•)

plot also shows a straight line. On the other hand, even in the double reciprocal plots of Φ_{ox} against concentration of [PtCl₆]²⁻ (0.1 mM–0.5 mM) in the MeOH oxidation system, a straight line was obtained, as shown in Fig. 5. Table 1 summarizes the kinetic parameters obtained from both slope and intercept values in each plot. The results of kinetic analysis well supported the proposal reaction route shown in Scheme 2.

The limiting quantum yield (Φ_{lim}) for the formation of products is shown in Table 1. Since the values of Φ_{isc} on metalloporphyrin complexes are generally estimated to be around 0.9 [8], total efficiency ($\alpha\beta$) of oxidative process including PET became about 15% for cumene oxidation system under basic condition and about 30% for MeOH oxidation system, respectively.

In Scheme 2, two intermediates, porphyrin radical cation $(1a^{+\bullet})$ and Ge-oxyl complex, are assumed as the



Fig. 5. Double reciprocal plot of Φ_{ox} against the concentration of $[PtCl_6]^2$ in the **1a**-photosensitized oxidation of MeOH

active spices for the oxidation of substrate. First of all, if the oxidation process proceeds via 1a^{+•}, the hole transfer mechanism from $1a^{+}$ to substrate can be suggested as a plausible reaction mechanism. However, the free energy change (ΔG) for hole transfer from $1a^{+\bullet}$ to cumene calculated from the oxidation potentials of cumene $(E_{1/2})^{ox}$ = 2.27 V vs. SCE) and **1a** became a large positive value ($\Delta G =$ 1.03 eV) [12]. Similarly, in the case of methanol $(E_{1/2})^{\text{ox}} = 1.65 \text{ V} vs. \text{ SCE}$, the value of ΔG is also positive $(\Delta G = 0.41 \text{ eV})$ [10]. These values show that a hole transfer process scarcely occur thermodynamically in this system. On the other hand, the formation of Ge-oxyl complex needs a proton dissociation process of hydroxo ligand on 1a^{+•}. Therefore, if Ge-oxyl complex works as the active spices in the photoreaction, the increase of Φ_{ax} can be expected when the photoreaction was carried out under the basic condition. In the oxidation of cumene, the increase of Φ_{ox} to 0.047 was observed by the addition of aqueous KOH solution (1 mM) into reaction solution as shown in Table 1. Both double reciprocal plots of $\Phi_{\alpha x}$ against the concentration of Fe³⁺ and cumene gave a straight line even under the basic condition (Figs 3 and 4). The value of k_{0x}/k_x under basic conditions was larger than that under neutral conditions. Furthermore, when the photoreaction of cumene and MeOH were performed by using 1b having two axial methoxo ligands and same redox potential with 1a, no oxidative product was observed in both cases. These results show that the proton dissociation process from an axial hydroxo ligand is contributed to the formation of oxidative products, strongly indicating that an active species should be Ge-oxyl complex [10]. In general, it is known that an oxygen atom on metal-oxo complex has either ionic character or radical character. The isotope experiment is often a convenient procedure to check the character of oxygen atom on metal-oxo complex in a reaction. Isotope effect for the formation of HCHO $(\Phi_{\alpha_{N}(H)}/\Phi_{\alpha_{N}(D)})$ 5.04) was observed when MeOH- d_4 was employed as an substrate in 1a-photosensitized reaction. This value indicates that hydrogen-atom abstraction from methyl group should be involved in the oxidation process of MeOH [13, 14]. This result also supports that Ge-oxyl complex act as a key intermediate for the oxidation of substrates.

Reaction mechanism

A plausible reaction mechanism was shown in Scheme 3. Upon visible light irradiation, $1a^{+}$ is formed by an electron transfer process from the excited triplet state of **1a** to the electron acceptor, followed by Ge-oxyl complex through a proton dissociation process from 1a^{+•}. A homolytic cleavage of C-H bond of substrates are induced by the hydrogen-atom abstraction with an oxygen radical on Ge-oxyl complex, resulting that a carbon radical species (R*) is formed and 1a returns to an original state. The existence of Ge-oxyl complex having O-radical character was also reported in the photolysis of tpp(OH)Ge(OOEt) to give acetaldehyde and ethanol [15]. The ¹⁸O-labelling experiment using $H_2^{18}O$ in cumene reaction system revealed that the oxygen source for cumyl alcohol production should not be water since ¹⁸O atom was not incorporated into cumyl alcohol at all. Accordingly, we speculated that the oxygen source can be a small amount of molecular oxygen involved in argon gas in cumene reaction system.

Table 1. Turn over frequency (TOF), quantum yield (Φ_{ox}) and kinetic parameter in **1a**-sensitized oxidation

Substrates	TOF, h ⁻¹	$\Phi_{\rm ox}/10^{-2}$	$k_{\rm r}/10^6$, M ⁻¹ .s ^{-1 a}	$k_{\rm ox}/k_{\rm x}/10^2$	$\Phi_{\rm lim}{}^{\rm b}$	β	$\alpha \Phi_{isc}$
Cumene	111.1	3.3	5.1	4.5	0.05	0.28	0.18
Cumene ^c	157.8	4.7	1.4	5.1	0.15	0.33	0.46
MeOH	120.0	3.4	0.8		0.27		

 ${}^{a}k_{d} = 3.3 \times 10^{3} \text{ s}^{-1}$. ${}^{b}\Phi_{lim} = \Phi_{isc} \times \alpha \times \beta$ where Φ_{lim} was a quantum yield of limiting quantum yield at the fixed concentration of cumene at 1 mM. ${}^{b}\Phi_{isc}$ was quantum yield of intersystem crossing corresponding to the yield of excited triplet state. c Aqueous KOH solution (1 mM) was added.



Scheme 3. A possible reaction mechanism for 1a-sensitized oxidation

EXPERIMENTAL

Instruments

¹H NMR (400 MHz) spectrum was acquired with a Bruker AV 400M spectrometer by using SiMe₄ as an internal standard. Matrix-assisted laser desorption/ ionization mass spectrum (MALDI-MS) was measured on a Bruker Daltonics Autoflex III TOF/TOF in the positive ion mode. Calibration of mass number was performed by the internal standard method using polyethyleneglycol. UV-vis absorption spectra and fluorescence spectra of the reaction solution were obtained with a JASCO V-550 spectrophotometer and a Shimadzu RF 5300PC spectrophotometer, respectively.

Materials and preparation

2-Phenylpropane (cumene), 2-phenyl-2-propanol (cumyl alcohol), HCHO, iron(III) nitrate hydrate (Fe(NO₃)₃·9H₂O), germanium tetrachloride (GeCl₄) and some organic solvents were purchased from Wako Pure Chemical Industries as a guaranteed reagent grade (GR) and used without further purification. Potassium hexachloroplatinate(IV) (K₂PtCl₆) and tetraphenylporphyrin (H₂tpp) were purchased from Aldrich as a GR reagent. Also H₂¹⁸O was taken from Aldrich.

The tppGe(OH)₂(**1a**) was synthesized according to the literature [10]. The synthesis of di(methoxo)tetraphenylporpyrinatogermanium (tppGe(OMe)₂, **1b**) was performed by the reaction of H₂TPP (1.0 g) with GeCl₄ (2.0 g) in water-free quinolone (30 mL) at 150 °C for 15 h under N₂ atmosphere. The reaction mixture was poured into hexane to give the precipitate of crude complex having two axial chloro ligands. The crude **1b** was obtained by refluxing MeOH solution of crude complex having two axial chloro ligands in order to substitute two chloro ligands to two methoxo ligands. After evaporation, **1b** was isolated by column chromatography on SiO₂.

Di(methoxo)tetraphenylporpyrinatogermanium (**1b).** Yield 85%. UV-vis (MeCN): λ_{max} , nm (log ε) 420 (5.88), 553 (4.97), 590 (4.34). ¹H NMR (400 MHz; CDCl₃; Me₄Si): $\delta_{\rm H}$, ppm -2.56 (6H, s, –OCH₃), 7.73–7.79 (12H, m, Ph), 8.25 (8H, d, J = 5.2 Hz, Ph), 9.02 (8H, s, pyrrole). MS (MALDI-MS): m/z 717.16, (calcd. for [M – OCH₃]⁺ 717.25).

Measurements

The quantitative analysis of cumyl alcohol as an oxidative product of cumene was performed by using GC-MS (Shimadzu QP-2000) with a capillary column (DB-1; 25 m × 0.25 mm × 0.25 μ m). HCHO was quantitatively analyzed by the absorption spectrophotometry using 4-amino-3-hydrazino-5-sulfonyl-1,2,4-triazole as color-producing reagent [10]. The detection of Fe²⁺ cation was carried out by the absorption spectrophotometry using 1,10-phenanthrorine as color-producing reagent.

Photoreactions

MeOH solution (12 mL) containing **1a** (0.39 μ mol), cumene (0.5–1.0 mM, usually 1 mM) and Fe(NO₃)₃·9H₂O (0.5–5.0 mM, usually 1 mM) was introduced into a glass tube (20 mm $\phi \times 36$ mm) and bubbled with argon gas. MeOH was used without further purification. Photooxidation were performed in a glass tube at room temperature under argon atmosphere by an irradiation of 550 nm light obtained through the glass-filter with Xe lamp (500 W). The photon number was measured to be 19.0×10⁻⁶ einstein/minute at 550 nm as a relative value for the standard photoreaction [8]. Similarly photooxidation of MeOH was performed for MeOH solution (9 mL, 22.2 M) containing **1a** (0.33 μ mol), K₂PtCl₆ (0.1– 0.5 mM, usually 0.5 mM) and H₂O (1 mL) in a glass tube under argon atmosphere.

CONCLUSION

It was elucidated that the photochemical oxidation of cumene and MeOH could be occurred by using Ge-oxyl complex generated by photoinduced electron transfer from 1a under visible light irradiation. The Ge-oxyl complex can induce the C-H bond activation of organic substrates due to acting as an O-radical intermediate. This is the first example of a photocatalytic reaction using a Ge^{IV}-porphyrin complex [16–18]. Among the studies on C-H bond activation, either transition metal-complexes (Mn, Fe and Cu) [19–21] or noble metal complexes (Pd, Ru and Rh) [22-24] have been almost employed as a catalyst. Therefore, this study, in which the C-H bond activation was achieved by using non-transition metal (typical element) complex, may be significant from a viewpoint of "elemental strategy "in the region of catalysis.

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