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Di(hydroxo)porphyrin Ge^{IV} Complex/Silica Gel Composite as Visible Light-assisted Radical Generator

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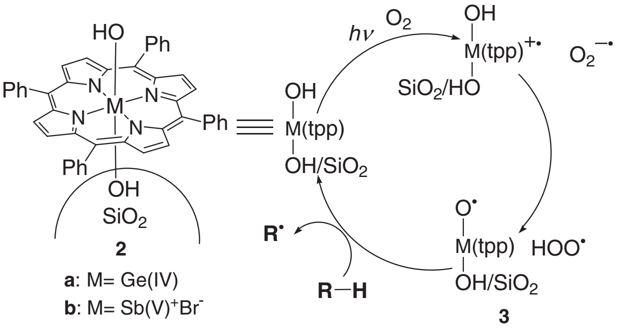
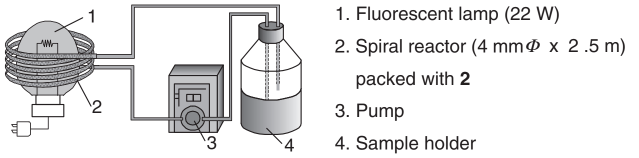
A composite of di(hydroxo)germaniumporphyrin with silica gel was used as radical generator which oxidized MeOH to HCHO and hydrocarbons to alcohols in aqueous solution.

Visible-light driven radical generators have received much attention from a viewpoint of environmentally conscious synthetic processes[1,2] and P450 models.[3] Hydroxometallotetraphenylporphyrins, (tpp)(R)M(OH), which have strong visible light absorption and an HO-axial ligand, are candidates as O-radical generators to catalyze the hydrogen abstraction from alkanes (R–H) (Scheme 1). The character of HO-ligands strongly depends on the central metal atom. Porphyrin complexes of high-valent typical elements which can covalently bond to axial HO-ligands have unique properties.[4] The photogenerated radical cation $(tpp)(R)Sb^{V}(OH)^{+\bullet}$ can easily release a proton of axial ligand, generating metal–oxo complex, (tpp)(R)Sb=O or $(tpp)(R)Sb{-}O^{\bullet}$, which catalyzes the oxidation of organic substrates.[5] However, Sb complexes have oxidation potentials too high to be oxidized by usual oxidants. Since $(tpp)Ge^{IV}(OH)_2$ (**1a**) has lower oxidation potential, we turned our attentions toward it. The generation of $(tpp)(R)Ge{-}O^{\bullet}$ was postulated in the photoreaction of (tpp)(HO)Ge(OOEt) to give acetaldehyde and ethanol.[6] Therefore, the ability of **1a** as an O-radical generator will be examined.

1a[7] was insoluble in polar solvents such as MeOH and MeCN and was poorly soluble even in relatively nonpolar solvents. Therefore, **1a** was used as $\mathbf{1a}/SiO_2$ composite **2a** dispersed in solution. The composite was prepared by dipping SiO_2 (20 g, Fuji Silysia CARiACT Q10, particle size: 1.7–4.0 mm, surface area: $636\,m^2\,g^{-1}$) into a CH_2Cl_2–toluene solution (1:4, $150\,cm^3$) of **1a** (147 mg). Most **1a** was adsorbed on SiO_2. The particles were filtrated, washed with acetone, and dried under reduced pressure overnight to yield **2a** (content of **1a**: 0.53 wt %).



Scheme 1.



Scheme 2.

Table 1. Photocatalytic oxidation of MeOH in spiral apparatus[a]

Run	Catalyst	Oxidant	t/h[b]	Product (yields/10^{-6} mol)	TON[c]	r[d]
1	**2a**	O_2	180	HCHO (30.6)	3.0	0.027
2[e]	**2a**	O_2	60	DCDO (7.8)	0.77	0.013
3	**2b**	O_2	36	HCHO (3.4)	0.03	0.0008
4[f]	**2b**	$Fe(NO_3)_3$	132	HCHO (24.6) Fe(II) (139.6)	0.20	0.0018

[a]Irradiation was applied by fluorescent light to a spiral reactor ($15\,cm^3$) packed with the catalyst **2** (10 g). An aqueous solution ($200\,cm^3$) of MeOH (50 mM) was fed to the reactor from the sample holder at $30\,cm^3\,min^{-1}$ by pump. [b]Irradiation time. [c]Turnover number (TON) was calculated by the division of the molar amount of HCHO by amount of **1** on **2** that equals to $7.36 \times 10^{-6}\,mol\,g^{-1}$ for **1a** and $10.3 \times 10^{-6}\,mol\,g^{-1}$ for **1b**. [d]r = (HCHO in mole)/{(irradiation time in h) × (the mole of **1** in **2**)}. [e]Using MeOH-d_3. [f]Using $Fe(NO_3)_3$ (5.0 mM) as oxidant.

Photooxidation of MeOH to HCHO was performed at room temperature by irradiation with fluorescent light in a spiral glass tube (4 mmϕ × 2.5 m) packed with **2** (12 g) to which an aerated aqueous solution ($200\,cm^3$) containing MeOH (50 mM, 1 mM = $10^{-3}\,mol\,dm^{-3}$) was fed continuously by pump from the holder (Scheme 2). The result was shown in Table 1. HCHO was formed for 180 h with a turnover number (TON) of 3.0, calculated by division of the molar quantities of HCHO by **1a** on **2a**.[8] No decomposition of **1a** was observed in solution, although **1a** was eliminated from SiO_2. Moreover, the reaction efficiency was estimated to be r: r = (HCHO in mole)/{(irradiation time in h) × (the mole of **1** in **2**)}. In the photooxidation of CD_3OH, the r values decreased to 48% of that in CH_3OH, showing the isotope effect for hydrogen abstraction by radical reactions ($r_H/r_D = 2.1$),[9] as shown in Figure 1.

Incident light was absorbed exclusively by **1** on **2**. However, the direct reaction of **1** with MeOH did not occur since the oxidation potential of MeOH is higher ($E_{1/2}{}^{ox} = 0.56$ V vs. SCE).[10] The oxidation of MeOH to HCHO is reasonably initiated by a hydrogen abstraction from the α-carbon of MeOH. As a reactive species, we suggest $(tpp)(HO)Ge{-}O^{\bullet}/SiO_2$ radical (**3a**) and hydroperoxyl radical ($HOO^{\bullet}$) which were generated by an electron transfer from the excited triplet state of **1a** ($^3\mathbf{1a}^*$) to O_2. The electron transfer from $^3\mathbf{1a}^*$ to O_2 was predicted to be exoergic by the calculation of the free energy change by the Rehm–Weller equation[11] using $E_{0\text{–}0}(\mathbf{1a}) = 1.63$ eV, $E_{1/2}{}^{ox}(\mathbf{1a}) = 1.18$ V, and $E_{1/2}{}^{red}(O_2) = -0.40$ V vs. SCE.[12] The

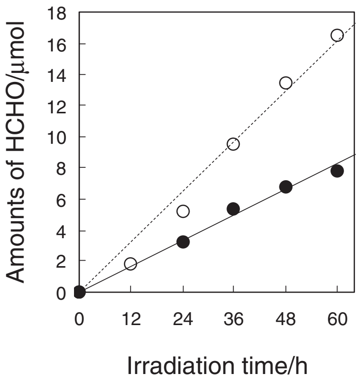
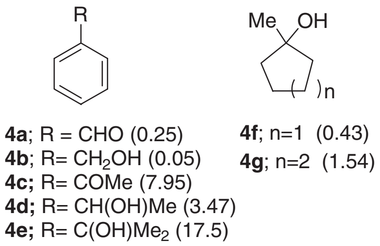


Figure 1. Time conversion plots of the **2a**-photosensitized oxidation of MeOH (○) and MeOH-d_3 (●).

resulting $(tpp)Ge(OH)_2{}^{+\bullet}/SiO_2$ and $O_2{}^{-\bullet}$ underwent proton transfer to give **3a** and $HOO^{\bullet}$. These O-radicals underwent hydrogen abstraction from MeOH. The resulting $^{\bullet}CH_2OH$ was transformed to HCHO through the further oxidation. Although it is possible that the reaction of ^{3}**1a*** with O_2 generates singlet oxygen ($^1O_2{}^*$), abstraction of hydrogen from MeOH by $^1O_2{}^*$ was ruled out due to insufficient hydrogen affinity.

The photoinduced electron-transfer mechanism was confirmed by the use of a composite **2b** (content of **1b**: 0.87 wt %) which was prepared from the reaction of $(tpp)Sb(OH)_2{}^+Br^-$ (**1b**) with SiO_2.[13] The photoreaction of **2b** in an aqueous MeOH solution under aerated conditions scarcely gave HCHO. Therefore, the photoctalytic reaction of **1b** was performed using $Fe(NO_3)_3$ as oxidant instead of O_2. Irradiation of **2b** (50 g) was performed using an apparatus of Scheme 2 by feeding a degassed aqueous solution containing MeOH (50 mM) and $Fe(NO_3)_3$ (5.0 mM) to give HCHO along with the formation of Fe^{II} ion. In this case, the electron transfer from ^{3}**1b*** to O_2 did not proceed since it was endothermic. However, it is suggested that electron transfer from the excited triplet state of **1a** to Fe^{III} ion was responsible for initiation since the free energy change from the triplet state of **1b** to Fe^{III} ion was calculated to be negative using $E_{0\text{–}0}(\mathbf{1b}) = 1.63\,\text{eV}$, $E_{1/2}{}^{\text{ox}}(\mathbf{1b}) = 1.40\,\text{V}$ and $E_{1/2}{}^{\text{red}}(\text{Fe}^{\text{III}}) = +0.98\,\text{V}$ vs. SCE.[13] It is suggested that the hydrogen abstraction from MeOH by $(tpp)(HO)Sb\text{–}O^{\bullet}$ radical (**3b**) generated by the deprotonation of $(tpp)Sb(OH)_2{}^{2+}$ should be responsible for the oxidation of MeOH.

The radical generator **2a** was applied to photooxidation of hydrocarbons **4**. A heterogeneous solution of **4** (4 cm^3) and H_2O (10 cm^3) in the presence of powdered **2a** (2.5 wt %, particle size: 40 µm) was irradiated under stirring. The photooxidation of toluene, ethylbenzene, cumene, methylcyclopentane, and methylcyclohexane gave a mixture of **4a** and **4b**, a mixture of **4c** and **4d**, **4e**, **4f**, and **4g**, respectively (Scheme 3). Especially, their reactivity was quenched under Ar atmosphere. It was elucidated that **1a** could act as an O-radical generator assisted by visible-light irradiation. This is the first example of a photocatalytic radical reaction using a Ge^{IV}–porphyrin complex.[14]



Scheme 3. Photooxidation products of hydrocarbons. The values in parenthesis are the *r* values.

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7 The preparation of **1a** was performed by the reaction of tetraphenylporphyrin (1.0 g) with $GeCl_4$ (2.0 g) in water-free quinoline (30 cm^3) at 150 °C for 15 h under N_2 atmosphere. The reaction mixture was poured into hexane to give the precipitate of crude **1a**. The CH_2Cl_2 solution of the resulting precipitate was washed with aqueous HCl solution and aqueous NaOH. During the follow-up process, axial chloro ligands turned to hydroxo ligand. After evaporation, **1a** was isolated by column chromatography on SiO_2. Yield 94%. ^{1}H NMR (400 MHz, $CDCl_3$): δ −2.60 (brs, 2H), 7.77–7.86 (m, 12H), 8.37 (d, $J = 5.2$ Hz, 8H), 9.04 (s, 8H). ^{13}C NMR (100 MHz): δ 119.3, 128.0, 128.9, 131.3, 134.6, 141.2, 145.7. UV–vis (in MeOH) λ_{max} ($\log\varepsilon$) 421 (5.89), 553 (4.34), 591 (4.99) nm.
8 HCHO was quantitatively analyzed by the absorption spectrophotometry using 4-amino-3-hydrazino-5-sulfanyl-1,2,4-triazole.
9 Deuterium isotope effect was reported to be 2.03 in $W_{10}O_{32}{}^{4-}$-catalyzed oxygenation of 1,1-diphenyl-3,3,3-trideuterio-2-methylpropene. I. N. Lykakis, G. C. Vougioukalakis, M. Orfanopoulos, *J. Org. Chem.* **2006**, *71*, 8740.
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