

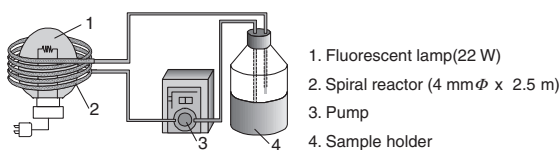
Efficient Photocatalytic Oxidation of Cycloalkenes by Dihydroxo(tetraphenylporphyrinato)-antimony Supported on Silica Gel under Visible Light Irradiation

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In order to develop a photocatalyst operating under visible light irradiation, silica gel-supported dihydroxo(tetraphenylporphyrinato)antimony (V) complex, $[\text{SbTPP}(\text{OH})_2]^+/\text{SiO}_2$, was prepared. The photocatalytic oxidation of cycloalkenes with oxygen molecule was performed on $[\text{SbTPP}(\text{OH})_2]^+/\text{SiO}_2$ particles under irradiation of fluorescent light. The photocatalytic oxidation of cycloalkenes gave the corresponding *cis*-1,2-epoxycycloalkane, 2-cycloalkene-1-ol, and *trans*-1,2-cycloalkanediol.

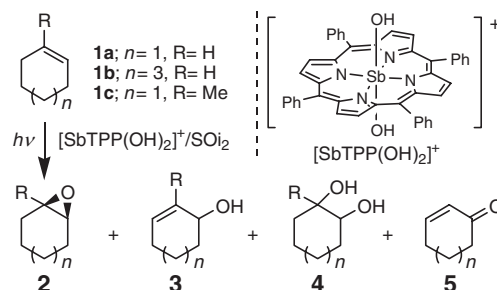
Catalytic oxidations with molecular oxygen have received much attention as an environmentally friendly material transformation.^{1,2} Our attention has paid to the development of the catalyst operating under visible-light irradiation. It has been known that dihydroxo(tetraphenylporphyrinato)antimony ($[\text{SbTPP}(\text{OH})_2]^+$) chromophore can sensitize electron and energy transfers^{3,4} as well as proton transfer.⁵ We have elucidated the catalytic activities of silica gel (SiO_2)-supported $[\text{SbTPP}(\text{OH})_2]^+$ ($[\text{SbTPP}(\text{OH})_2]^+/\text{SiO}_2$) for the dechlorination of 4-chlorophenol⁶ as well as the bactericidal effect for *E. coli*.⁷ under visible-light irradiation. However, the photocatalytic activity for oxidation of alkenes is still unknown. Here, we report on the preparative-scale photocatalytic oxidation of cycloalkenes (**1**) under visible-light irradiation of $[\text{SbTPP}(\text{OH})_2]^+/\text{SiO}_2$ catalyst.



Scheme 1.

A toluene–MeOH solution (4:1 v/v, 200 mL) of $[\text{SbTPP}(\text{OH})_2]\text{Br}$ (15 mg)⁸ was refluxed with silica gel (0.85–1.7 mm ϕ , 30 g), filtered, and then washed with acetone and water to give the $[\text{SbTPP}(\text{OH})_2]^+/\text{SiO}_2$ catalyst (catalyst A) where the content of $\text{SbTPP}(\text{OH})_2^+$ chromophore was 0.05 wt %. Irradiation of visible light was performed under aerated condition at room temperature by fluorescent lamp for a spiral glass tube (4 mm ϕ \times 2.5 m) containing the photocatalyst to which the reactants were fed continuously from the holder (Scheme 1). The photocatalytic oxidation of cyclohexene (**1a**) on catalyst A gave mainly *cis*-1,2-epoxycyclohexane (**2a**) and 2-cyclohexen-1-ol (**3a**) along with a small amount of 2-cyclohexen-1-one (**5a**) in benzene at low conversion (Scheme 2).⁹ As an increase of conversion, however, the formation of *trans*-1,2-cyclohexanediol (**4a**) gradually increased owing to the hydrolysis of **2a** on acidic site of SiO_2 . In order to reduce the effect of the residual silanol group, the catalyst A was modified by capping with

$(\text{Me}_3\text{Si})_2\text{NH}$, giving the catalyst B ($[\text{SbTPP}(\text{OH})_2]^+/\text{SiO}_2\text{-OSiMe}_3$).



Scheme 2.

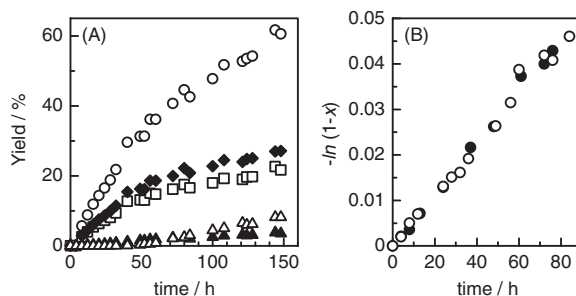


Figure 1. (A) Time-course profile for the photocatalytic oxidation of **1a** on catalyst B in benzene: total oxidation products (**2a** (\square), **3a** (\blacklozenge), **4a** (\triangle), and **5a** (\blacktriangle)). (B) Plots of $-\ln(1-x)$ vs time at the initial concentrations of 1.0 (\bullet) and 0.1 M (\circ) of **1a** in benzene.

Figure 1a shows a typical example of time-course plots for the photocatalytic oxidation of **1a** on catalyst B in benzene. After irradiation for 144 h, the conversion (x) reached to 63%, giving **2a**, **3a**, **4a**, and **5a** in ratio of 36:44:14:6. Turnover number (TON) of the catalyst was calculated to be >2650 by dividing the total yield by amount of the $[\text{SbTPP}(\text{OH})_2]^+$ chromophore on SiO_2 (0.59 $\mu\text{mol/g}$). Similarly, the photocatalytic oxidation of cyclooctene (**1b**) gave *cis*-1,2-epoxycyclooctane (**2b**), 2-cyclooctenol (**3b**), and *trans*-1,2-cyclooctanediol (**4b**). In the case of 1-methyl-cyclohexene (**1c**), *cis*-1,2-epoxy-1-methylcyclohexane (**2c**), 2-methyl-2-cyclohexenol (**3c**), and *trans*-2-methyl-1,2-cyclohexenediol (*trans*-**4c**) and its *cis*-isomer (*cis*-**4c**) were formed. Control experiments in the presence of catalyst under dark conditions and in the absence of catalyst gave no oxidized products. The primary products, **2** and **3**, were transformed into **4** and **5** during the further reaction, respectively. It is noteworthy that epoxidation ratio (γ), which is sum of product ratios of **2** and **4**, were relatively high in each case.

Regardless of the initial concentration of **1a**, the plots of $-\ln(1-x)$ vs irradiation time (t) laid on common straight line, showing that the reaction obeyed a pseudo-first-order reaction, as shown in Figure 1b. Therefore, the rate constants (k) were obtained from the slope of the plots at <5% of conversion. The results were summarized in Table 1. The photocatalytic oxidation was investigated in hexane, cyclohexane, toluene, benzene, CH_2Cl_2 , and CHCl_3 . As solvent is more polar, $\ln k$ increased whereas γ decreased. Indeed, the photocatalytic oxidation of **1a** in CH_2Cl_2 reached 99.8% of conversion, corresponding to 4490 of TON (Table 1).

Table 1. Photocatalytic oxidation of **1** in spiral apparatus^a

1	Solvent	t/h (h) ^b	Product ratio 2:3:4:5	Conv. ^c /%	$k \times 10^{-3}$ / $\text{h}^{-1}\text{g}^{-1}$	γ^d /%	TON ^e
1a	C_6H_6	144	36:44:14:6	63.2	1.24	50	2650
1a	C_6H_6^f	144	10:17:57:16	40.0	0.09	60	2970
1a	CH_2Cl_2	56	28:38:27:7	99.8	5.67	55	4490
1b	CH_2Cl_2	72	36:6:58:0	28.0	1.40	94	1185
1c	CH_2Cl_2	20	6:5:88:0	99.0	1.31	94	3300

^a Irradiation was performed by the fluorescent light for a spiral reactor (15 mL) packed with the catalyst B (6.0 g). A solution (150 mL) of **1** (0.10 mol dm^{-3}) was fed to the reactor from the sample holder at 30 mL/min by pump. ^b Irradiation time. ^c Conversion = amounts of **2-5**/initial amounts of **1**. ^d Epoxidation ratio (γ) = sum of products ratio of **2** and **4**. ^e Turnover number (TON) = amount of products (mol)/amount of SbTPP (mol) on the catalyst that equals to 0.590×10^{-6} mol per 1 g of catalyst. ^f By using catalyst A.

ICP analysis showed that amounts of antimony in the reaction solution were less than 0.05 ppm that is lower limit of the detection. It is, therefore, suggested that the $[\text{SbTPP}(\text{OH})_2]^+$ was strongly fixed on SiO_2 by strong force such as covalent Si–O–Sb bond and/or the hydrogen bond through axial OH ligands. The catalyst B was analyzed by a microspectrophotometer. The absorption spectra of catalyst B were slightly shifted from that of $[\text{SbTPP}(\text{OH})_2]\text{Br}$ in MeCN to shorter wavelength, but both spectra were very similar, regardless of supported by SiO_2 and capping by $(\text{Me}_3\text{Si})_2\text{NH}$ (Figure 2). Furthermore, catalyst B after photoreaction was not inactivated for the oxidation of **1a**.

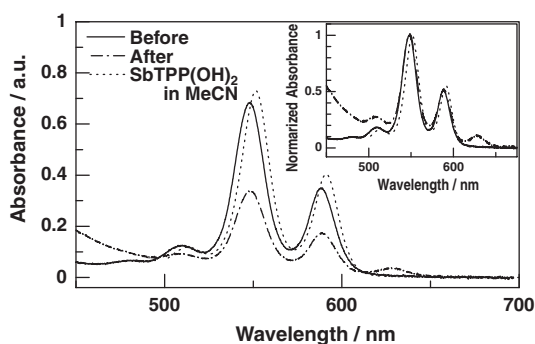


Figure 2. Absorption spectra of catalyst B before and after photocatalytic reaction along with $[\text{SbTPP}(\text{OH})_2]\text{Br}$ in MeCN. Inset was absorption spectra normalized at Q-band of SbTPP (ca. 550 nm).

Incident light from the fluorescent light was exclusively absorbed by the $[\text{SbTPP}(\text{OH})_2]^+$ chromophore on SiO_2 , since the absorption maxima of $[\text{SbTPP}(\text{OH})_2]^+$ chromophore were 419,

550, and 589 nm. Since **1** has much high oxidation potentials ($>1.50 \text{ V vs Ag/Ag}^+$) than that of $[\text{SbTPP}(\text{OH})_2]^+$ chromophore (1.17 V)¹⁰ and high excitation energy, direct electron transfer and/or energy transfer between **1** and the excited state of $[\text{SbTPP}(\text{OH})_2]^+/\text{SiO}_2$ scarcely occurred. We have previously elucidated that the excitation of $[\text{SbTPP}(\text{OH})_2]^+$ makes the axial hydroxo ligand more acidic.¹⁰ Therefore, $[\text{SbTPP}(\text{OH})_2]^+/\text{SiO}_2$ in the excited state will undergo the deprotonation from axial hydroxo ligand to form the excited state of the oxo-type complex, $[\text{O}=\text{SbTPP}(\text{OH})]^+/\text{SiO}_2$. It is, therefore, suggested that the oxo-type complex played as a key intermediate, as reported for the thermal epoxidation of olefins by iron(III) porphyrin complex where oxo-iron porphyrin complex was generated by the oxidants.¹¹ The quenching process of the excited oxo-type complex, $[\text{O}=\text{SbTPP}(\text{OH})]$, with cyclohexene was observed by a nanosecond laser flash photolysis.¹² The oxygen atom incorporated into substrates should be originated from molecular oxygen, since the photocatalytic reaction in the presence of H_2^{18}O gave no oxidation products involving ^{18}O atom. Mechanistic details are under investigation.

Metalloporphyrin-photosensitized epoxidation previously reported have usually required such additives as reductants (e.g. Zn^{13}) and oxidants (e.g. $\text{H}_2\text{O}_2^{14}$ and $t\text{-BuOOH}^{15}$). Although another photoepoxidation on $\text{TiO}_2\text{-SiO}_2$ catalyst and thermal oxidation on isopolyoxometalates without any additives has been reported, the conversion was still low.¹⁶ The present photocatalytic epoxidation required no additives and proceeded up to high conversion.

References and Notes

- 1 A. L. Pruden and D. F. Ollis, *J. Catal.*, **81**, 1481 (1983).
- 2 T. Hisanaga, K. Harada, and T. Tanaka, *J. Photochem. Photobiol., A*, **54**, 113 (1990).
- 3 S. Takagi, T. Okamoto, T. Shiragami, and H. Inoue, *Chem. Lett.*, **1993**, 793.
- 4 Y. Andou, T. Shiragami, K. Shima, and M. Yasuda, *J. Photochem. Photobiol., A*, **147**, 191 (2002).
- 5 S. Takagi, M. Suzuki, T. Shiragami, and H. Inoue, *J. Am. Chem. Soc.*, **119**, 8712 (1997).
- 6 T. Shiragami, Y. Shimizu, K. Hinoue, Y. Fueta, K. Nobuhara, I. Akazaki, and M. Yasuda, *J. Photochem. Photobiol., A*, **156**, 115 (2003).
- 7 H. Yokoi, T. Shiragami, J. Hirose, T. Kawauchi, K. Hinoue, Y. Fueda, K. Nobuhara, I. Akazaki, and M. Yasuda, *World J. Microbiol. Biotechnol.*, **19**, 559 (2003).
- 8 Y. Andou, K. Ishikawa, K. Shima, T. Shiragami, M. Yasuda, and H. Inoue, *Bull. Chem. Soc. Jpn.*, **75**, 1757 (2002).
- 9 A homogeneous photoreaction of **1a** (10 mmol) in CH_2Cl_2 using $[\text{SbTPP}(\text{OH})_2]^+\text{Br}^-$ (0.59 μmol) as catalyst under aerated conditions occurred in low TON and the product distribution was different from the above cases: **2a:3a:4a:5a** = 1:18:53:28, TON = 133, $k = 0.44 \times 10^{-3} \text{ h}^{-1}\text{g}^{-1}$. In homogeneous system, the catalytic activity extremely decreased owing to the decomposition of SbTPP.
- 10 T. Shiragami, Y. Andou, Y. Hamasuna, F. Yamaguchi, K. Shima, and M. Yasuda, *Bull. Chem. Soc. Jpn.*, **75**, 1577 (2002).
- 11 C. Gilmartin and J. R. Lindsay Smith, *J. Chem. Soc., Perkin Trans. 2*, **1995**, 243.
- 12 An unpublished data. See ref. 5.
- 13 Y. Tsuda, K. Takahashi, T. Yamaguchi, S. Matsui, and T. Komura, *J. Mol. Catal. A: Chem.*, **130**, 285 (1998).
- 14 E. Jorda, A. Tuel, R. Teissier, and J. Kervennal, *J. Chem. Soc., Chem. Commun.*, **1995**, 1775.
- 15 J. M. Fraile, J. Garcia, A. Mayoral, M. G. Proietti, and M. C. Sanchez, *J. Phys. Chem.*, **100**, 19484 (1996).
- 16 a) H. Yoshida, C. Murata, and T. Hattori, *Chem. Commun.*, **1999**, 1551. b) Y. Liu, K. Murata, M. Inada, H. Nakajima, M. Koya, and K. Tomokuni, *Chem. Lett.*, **33**, 200 (2004).