

Efficient Photochemical Oxygenation of Cyclohexene with Water as an Oxygen Donor Sensitized by Dimethoxy-Coordinated Tetraphenylporphyrinatoantimony(V)

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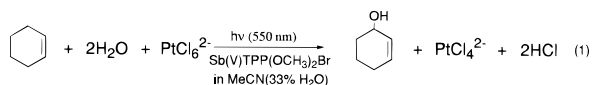
We have found that visible light irradiation of a reaction mixture of dimethoxy-coordinated tetraphenylporphyrinatoantimony(V) as a sensitizer, potassium hexachloroplatinate(IV) as an electron acceptor, and cyclohexene in aqueous acetonitrile induced formation of cyclohex-2-enol and 3,3'-bicyclohexenyl with a high quantum yield of around 0.4. The limiting quantum yield was estimated to be 0.8.

Photochemical redox reactions sensitized by metal complexes have been extensively studied.^{1–5} Sensitizers with higher oxidation potential are expected to incorporate more types of electron donors such as phosphine, sulfide, alkene, and even water molecules into the photoredox system.^{6,7} In general, high-valent metalloporphyrins have been known to have high oxidation potentials, though there have been few reports on their photochemical behaviors.^{8–10} From these viewpoints, we have recently focused our attention on some high-valent metalloporphyrins having antimony(V), phosphorus(V), germanium(IV), and tin(IV) as a central metal atom and how oxidation reactions could be coupled at the oxidation terminal end.⁷ We have already reported photochemical epoxidation and oxygenation of alkenes sensitized by antimony(V) porphyrins.^{7,11} The water molecule serves as an oxygen donor in each reaction. In this paper, we report that dimethoxy-coordinated tetraphenylpor-

phyrinatoantimony(V), ([Sb^VTPP(OCH₃)₂]Br), more efficiently sensitizes the photooxygenation of cyclohexene in the presence of both water as an oxygen donor and potassium hexachloroplatinate(IV) (K₂PtCl₆) as an electron acceptor by visible light irradiation.

The photoreaction was performed by irradiating visible light of $\lambda = 420$ or 550 nm to an aqueous acetonitrile solution (33% H₂O) containing the Sb^VTPP¹² (1.1×10^{-5} M), K₂Pt^{IV}Cl₆ (5×10^{-4} M) and cyclohexene (0.1 M) as typical conditions. The oxygenation products were analyzed by GC–MS spectroscopy (Shimadzu QP-5000). The practical detection limits of the possible products were around 10^{-7} M.

The photoreaction induced formation of cyclohex-2-enol and 3,3'-bicyclohexenyl. Other oxygenation products such as cyclohexene oxide, cyclohexane-1,2-diol, and cyclohex-2-enone were not detected at all in this system. The quantum yields for the formation of cyclohex-2-enol and 3,3'-bicyclohexenyl under the above conditions were 0.17 and 0.02, respectively. The quantum yield was easily improved up to 0.42 for cyclohex-2-enol formation by increasing the concentration of K₂PtCl₆ to 2×10^{-3} M as a practical solubility limit in the solvent system. From the analysis of Stern–Volmer plots, the limiting quantum yield was estimated to be 0.64 at 420 nm (Soret band of Sb^VTPP) irradiation for the formation of cyclohex-2-enol and 0.8 for the total oxidation of cyclohexene involving the dimer formation. An experiment using H₂¹⁸O revealed that ¹⁸O atom was quantitatively incorporated into cyclohex-2-enol under strictly degassed conditions.¹³ This clearly indicates that water molecule serves as an oxygen donor in the photochemical oxygenation reaction. The decomposition of Sb^VTPP was scarcely observed in the visible absorption spectrum during the irradiation, indicating that the photoreaction proceeds catalytically. Turnover of the catalytic cycles based on Sb^VTPP was more than 20 under the typical condition. The photooxygenation did not proceed at all without K₂Pt^{IV}Cl₆. Other porphyrins such as zinc(II) tetraphenylporphyrin (Zn^{II}TPP) or free base tetraphenylporphyrin also did not sensitize the reaction. Absorbance at 320 nm due to K₂PtCl₆ (Pt^{IV}) disappeared completely during the photoreaction, and no photooxygenation was observed when K₂PtCl₄ (Pt(II)), a two-electron-reduced product from K₂PtCl₆, was employed as an electron acceptor. The sum of quantum yields for the formation of oxidation products (0.19) is almost consistent with that for the disappearance of K₂PtCl₆ (0.17) under the above typical conditions. This result strongly indicates that the redox cycles at both the oxidative terminal end and the reductive one are well balanced in the present case. The net chemistry of the photoredox reaction in this system, thus, could be expressed as eq 1.



The equation indicates that hydrochloric acid is generated during the photooxygenation sensitized by Sb^VTPP. After light

(1) Kalyanasundaram, K.; Grätzel, M. *Photosensitization and Photocatalysis Using Inorganic and Organometallic Compounds*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1993.

(2) (a) Connolly, J. S. *Photochemical Conversion and Storage of Solar Energy*; Academic Press: London, 1981. (b) Kalyanasundaram, K. *Photoelectrochemistry, Photocatalysis and Photoreactors; Fundamentals and Developments*; Schiavarello, M., Ed.; Reidel: Dordrecht, The Netherlands, 1985; p 239 and references therein.

(3) (a) Lehn, J. M.; Sauvage, J. P. *Nouv. J. Chim.* **1977**, *1*, 449. (b) Moradpour, A.; Amoyal, E.; Keller, P.; Kagan, H. *Nouv. J. Chim.* **1978**, *2*, 547. (c) Kalyanasundaram, K.; Kiwi, J.; Grätzel, M. *Helv. Chim. Acta* **1978**, *61*, 2720. (d) Brown, G.; Brunschwig, B.; Creutz, C.; Endicott, J.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 1298. (d) DeLaive, P.; Sullivan, B.; Meyer, T.; Whitten, D. *J. Am. Chem. Soc.* **1979**, *101*, 4007.

(4) (a) Hawker, J.; Lehn, J. M.; Ziesel, R. *Helv. Chim. Acta* **1986**, *69*, 1990. (b) Willner, I.; Maidam, R.; Mander, D.; Durr, H.; Dorr, G.; Zrangerle, K. *J. Am. Chem. Soc.* **1986**, *108*, 1009. (c) Ishida, H.; Tanaka, K.; Tanaka, T. *Chem. Lett.* **1988**, 339.

(5) (a) McLendon, G.; Miller, D. S. *J. Chem. Soc., Chem. Commun.* **1980**, 553. (b) Kalyanasundaram, K.; Grätzel, M. *Helv. Chim. Acta* **1980**, *63*, 478. (c) Harriman, A.; Porter, G.; Richoux, M. C. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 833.

(6) Harriman, A.; Neta, P.; Richoux, M. C. *Homogeneous and Heterogeneous Photocatalysis*; Pelizzetti, E.; Serpone, N., Eds.; Reidel: Dordrecht, 1986; p 123 and references cited therein.

(7) (a) Inoue, H.; Sumitani, M.; Sekita, A.; Hida, M. *J. Chem. Soc., Chem. Commun.* **1987**, 1681. (b) Inoue, H.; Okamoto, T.; Komiya, M.; Hida, M. *J. Photochem. Photobiol. A* **1992**, *65*, 221. (c) Inoue, H.; Okamoto, T.; Kameo, Y.; Sumitani, M.; Fujiwara, A.; Ishibashi, D.; Hida, M. *J. Chem. Soc. Perkin Trans. 1* **1994**, 105.

(8) Furhop, J. H.; Kadish, K. M.; Davis, D. G. *J. Am. Chem. Soc.* **1975**, *95*, 514.

(9) Hopf, F. R.; Whitten, D. G. *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier: New York, 1975; p 667 and references cited therein.

(10) Inoue, H.; Chandrasekaran, K.; Whitten, D. G. *J. Photochem.* **1985**, *30*, 269.

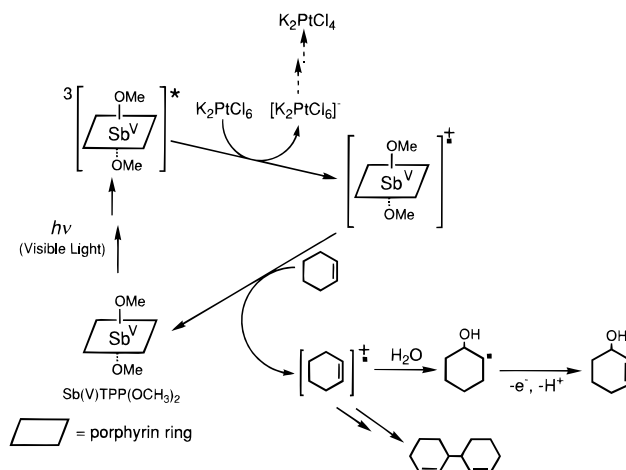
(11) (a) Takagi, S.; Okamoto, T.; Shiragami, T.; Inoue, H. *J. Org. Chem.* **1994**, *24*, 7373. (b) Okamoto, T.; Takagi, S.; Shiragami, T.; Inoue, H. *Chem. Lett.* **1993**, 687.

(12) The sensitizer was synthesized by a reaction of antimony(III) tribromide (SbBr₃) and free base tetraphenylporphyrin (H₂TPP) in pyridine, followed by oxidation to antimony(V) by bromine. The crude antimony porphyrin was further refluxed in methanol to replace two axial ligands with methoxy groups and then purified by alumina column chromatography (eluent CH₃CN:CH₂Cl₂ = 20:1). The obtained porphyrin complex was identified as the dimethoxy-coordinated species ([Sb^VTPP(OCH₃)₂]Br) by UV–vis, FAB–MS, and ¹H-NMR spectroscopies and elemental analysis. [Sb^VTPP(OCH₃)₂]Br·2H₂O (yield 11%); λ_{max} (CH₃CN)/nm 418 (log ϵ 5.72), 550 (4.26), and 590 (4.05); FAB–MS (M⁺) 795 and 797; ¹H-NMR δ_{H} (CDCl₃)/ppm –2.18 (6H, s, –OCH₃ (axial ligand)), 7.95–8.35 (20H, m, benzene ring), and 9.57 (8H, s, pyrrole β). Anal. (C₄₆H₃₈N₄O₄SbBr) calcd C, 60.92; H, 4.09; N, 6.14; found. C, 60.54; H, 4.20; N, 6.14.

(13) GC–MS SIM analysis indicated that ¹⁸O content in the obtained cyclohex-2-enol was 91% after the photoreaction when 96% H₂¹⁸O was used in the reaction mixture. This indicates that 95% of oxygen atom in the product came from water molecules.

irradiation for 1 h, in fact, the pH value of the solution decreased to 3.2, which corresponds to a stoichiometrical conversion of Pt(IV) to Pt(II) according to eq 1. Fluorescence of $\text{Sb}^{\text{V}}\text{TPP}$ was not affected at all by $\text{K}_2\text{Pt}^{\text{IV}}\text{Cl}_6$ and cyclohexene, indicating that the excited state responsible for the photooxygenation should be the triplet state of $\text{Sb}^{\text{V}}\text{TPP}$ ($^3\text{Sb}^{\text{V}}\text{TPP}^*$). The oxidation potential of $^3\text{Sb}^{\text{V}}\text{TPP}^*$ (+0.13 V vs SCE)¹⁴ and the reduction potential of $\text{K}_2\text{Pt}^{\text{IV}}\text{Cl}_6$ (+0.73 V)¹⁵ indicate an electron transfer from $^3\text{Sb}^{\text{V}}\text{TPP}^*$ to $\text{K}_2\text{Pt}^{\text{IV}}\text{Cl}_6$ being sufficiently exoergonic. The cation radical of $\text{Sb}^{\text{V}}\text{TPP}$ ($\text{Sb}^{\text{V}}\text{TPP}^+$) ($\lambda_{\text{max}} = 450 \text{ nm}$) was actually observed in a laser flash photolysis experiment for the aqueous acetonitrile solution (50% H_2O) of $\text{Sb}^{\text{V}}\text{TPP}$ and $\text{K}_2\text{Pt}^{\text{IV}}\text{Cl}_6$. These results strongly suggest the reaction mechanism for the photooxygenation as shown in Scheme 1. The oxidative quenching of $^3\text{Sb}^{\text{V}}\text{TPP}^*$ produces the cation radical $\text{Sb}^{\text{V}}\text{TPP}^+$ which has highly positive redox potential ($E_{\text{oxp}}(\text{Sb}^{\text{V}}\text{TPP}) = 1.76 \text{ V vs SCE}$). The one-electron oxidation potential of cyclohexene (+1.81 V vs SCE)¹⁶ suggests a hole transfer from $\text{Sb}^{\text{V}}\text{TPP}^+$ to cyclohexene. The formation of cyclohex-2-enol and 3,3'-bicyclohexenyl can be plausibly explained as proceeding through the nucleophilic attack of water on the cyclohexene cation radical and the following oxidation, and through the corresponding dimerization,¹⁷ respectively. We previously reported that the metal-oxo complex ($\text{Sb}=\text{O}$) formed by the oxidative quenching of triplet-excited dihydroxy-coordinated tetraphen-

Scheme 1



ylporphyrinatoantimony(V) ($[\text{Sb}^{\text{V}}\text{TPP}(\text{OH})_2]\text{Br}$) by methyl viologen as an electron acceptor can induce the photochemical epoxidation of alkene in the presence of water as both electron and oxygen donor with visible light irradiation. Since $\text{K}_2\text{Pt}^{\text{IV}}\text{Cl}_6$ was revealed to be an efficient electron acceptor for $\text{Sb}^{\text{V}}\text{TPP}$, it is expected to generate the metal-oxo complex more efficiently through oxidative quenching. Investigation along this line is now in progress.

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(14) The oxidation potential of the excited triplet state of $\text{Sb}^{\text{V}}\text{TPP}$ was estimated from its phosphorescence spectrum (E_{T} (triplet energy) = 1.63 eV) and the ground state oxidation potential ($E_{\text{oxp}} = +1.76 \text{ V vs SCE}$).

(15) *Lange's Handbook of Chemistry*; Dean, J. D., Ed.; McGraw-Hill Book Company: New York, 1985; pp 6–14.

(16) Garrison, J. M.; Ostovic, D.; Bruce, T. C. *J. Am. Chem. Soc.* **1989**, *111*, 4960.

(17) (a) Yoshida, K.; Kanbe, T.; Fueno, T. *J. Org. Chem.* **1977**, *42*, 2313. (b) Shono, T.; Ikeda, A. *J. Am. Chem. Soc.* **1972**, *94*, 7892.