

Communications to the Editor

Photochemical P-450 Oxygenation of Cyclohexene with Water Sensitized by Dihydroxy-Coordinated (Tetraphenylporphyrinato)antimony(V) Hexafluorophosphate

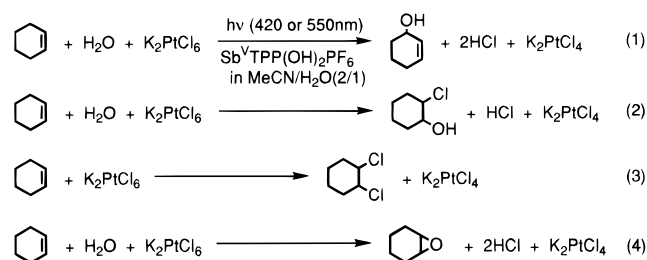
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Recently, many studies on water splitting, such as hydrogen or oxygen evolution by visible light in relation to artificial photosynthesis have been extensively reported.¹ In particular, highly efficient hydrogen evolution systems have been successfully achieved.² Much attention is now shifted to the oxidation of water and is focused on how a water molecule can be incorporated into the oxidation terminal end of photoredox systems.^{3,4} We have been examining photochemical redox reaction systems that could actually incorporate a water molecule upon visible light irradiation.⁴ An efficient photochemical oxygenation reaction of cyclohexene sensitized by dimethoxy-coordinated antimony(V) porphyrin [Sb^VTPP(OMe)₂]Br has already been reported.⁵ The key step of the reaction was a single electron transfer to cyclohexene from the cation radical of [Sb^VTPP(OMe)₂]Br generated by oxidative quenching of the triplet porphyrin by K₂PtCl₆. Since K₂PtCl₆ was revealed to be an efficient electron acceptor for excited Sb^VTPP, a substitution of the axial methoxyl ligands by hydroxyl groups is expected to generate another key intermediate metal–oxo complex for the oxygenation reaction through deprotonation of the axial hydroxyl group of the porphyrin cation radical.⁴ In this paper, we report the photochemical oxygenation of cyclohexene coupled with two-electron oxidative activation of water as an axial porphyrin ligand. A metal–oxo type complex is supposed to be a key intermediate in the oxygenation reaction which could be called a “photochemical P-450 reaction”.

Upon visible light irradiation⁶ of the reaction mixture containing cyclohexene (0.1 M), K₂PtCl₆ (5 × 10⁻⁴ M), and [Sb^VTPP(OH)₂]PF₆ (3.3 × 10⁻⁵ and 1.0 × 10⁻⁵ M for the irradiations at 550 and 420 nm, respectively) in acetonitrile–water (2/1% (v/v)) for 60 min, K₂PtCl₆ completely disappeared, while the porphyrin remained almost unchanged. The quantum yield of disappearance of K₂PtCl₆ was 0.2, which was identical with that of the oxygenated products. The major products were cyclohex-2-enol (34%), 1,2-dichlorocyclohexane (36%), 2-chlorocyclohexanol (cis, 12%; trans, 8%), cyclohexene oxide (2%), and small amounts of 3,3'-bicyclohexenyl, 3-acetaminocyclohexene, and cyclohexanone.⁷ Both K₂PtCl₆ and [Sb^VTPP(OH)₂]PF₆ were necessary for the photochemical oxygenation of cyclohexene. Zn^{II}TPP as a sensitizer instead of Sb^VTPP did not afford any products. The net chemistry of reaction could be expressed as in eqs 1–4.



Light irradiation of the reaction mixture containing AgNO₃ (5 × 10⁻³M) induced striking light scattering due to formation of AgCl particles. The addition of AgNO₃ suppressed the formation of dichlorocyclohexane (15%) and enhanced the formation of oxygenated products such as cyclohexene oxide (6%) and cyclohexanone (34%). An experiment using H₂¹⁸O revealed that an ¹⁸O atom was quantitatively incorporated into cyclohex-2-enol, 2-chlorocyclohexanol, cyclohexene oxide, and cyclohexanone under the degassed conditions. This clearly indicates that a water molecule serves as the oxygen donor in the photochemical oxygenation reaction. The turnover number of the reaction based on the initial concentration of sensitizer was 9.7, while the number based on the decomposed porphyrin reached 5 × 10². The product distribution drastically changed from that in the case of [Sb^VTPP(OMe)₂]Br as a sensitizer.⁵ The oxygenation reaction sensitized by [Sb^VTPP(OMe)₂]Br afforded only cyclohex-2-enol and small amounts of 3,3'-bicyclohexenyl and 3-acetaminocyclohexene, when the reaction simply proceeded through cyclohexene cation radical formed by hole transfer from the porphyrin cation radical upon oxidative quenching of the excited triplet porphyrin by K₂PtCl₆ (hole transfer mechanism, HTM).⁸ The results obtained above obviously indicate that the oxygenation reaction sensitized by dihydroxy-coordinated [Sb^VTPP(OH)₂]PF₆ proceeded by a mechanism other than HTM. Higher formation of the cis than the trans isomer of 2-chlorocyclohexanol suggests that some stereoregulative process, such as reaction on the porphyrin plane, was involved in the reaction. Since fluorescence of Sb^VTPP-

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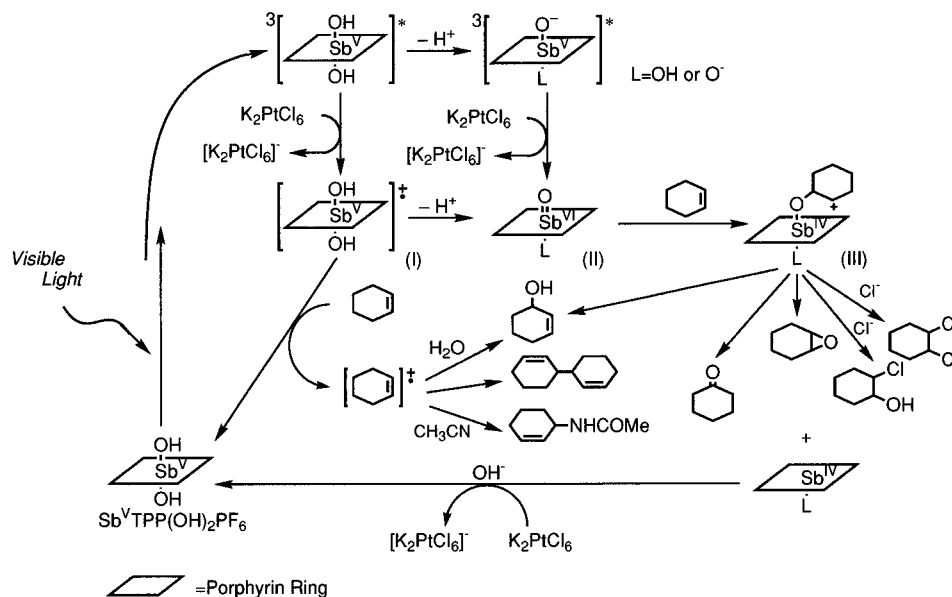
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(6) The sample was irradiated with visible light ($\lambda = 420$ or 550 nm which correspond to Soret band or Q-band of Sb^VTPP) from a 500 W Xe lamp (Ushio UXL 500DKO) through filters (420 nm, sharp cut filter Toshiba L-39 + interference filter Toshiba KL-42; 550 nm, sharp cut filter Toshiba Y-52 + interference filter Toshiba KL-55).

(7) The oxygenated products were analyzed by GC–MS (Shimadzu QP-5000). Quantitative analysis was carried out by SIM (selected ion monitoring method) detection mode. A GC column of TC-17 (GL Sciences Inc., 30 m) was used at temperatures 60–250 °C.

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Scheme 1



(OH)₂ was not affected by the addition of K₂PtCl₆, the excited state responsible for the reaction should be the excited triplet state of the porphyrin. An electron transfer from the triplet [Sb^V-TPP(OH)₂]₃PF₆ ($E_{\text{ox}} = 1.89$ V vs NHE, $E_{\text{T}} = 1.63$ eV) to K₂PtCl₆ ($E_{\text{red}} = 0.73$ V vs SCE)⁹ would be sufficiently exoergonic. A reaction scheme for the photochemical oxygenation is, thus, postulated in Scheme 1. Upon visible light irradiation of [Sb^V-TPP(OH)₂]₃PF₆, an electron transfer from the excited porphyrin to K₂PtCl₆ induces the formation of a porphyrin cation radical (**I**) which promotes HTM to form cyclohex-2-enol, 3,3'-bicyclohexenyl, and 3-acetaminocyclohexene,⁵ competing with its deprotonation to form another key intermediate metal-oxo complex (**II**). The metal-oxo complex **II** induces a two-electron oxidation through a reaction with cyclohexene. The strikingly different product distribution from the case of Sb^V-TPP(OMe)₂ strongly suggests that the reaction through the metal-oxo complex **II** predominates over HTM through the porphyrin cation radical **I**. Chloride ion is generated from the reduced K₂PtCl₆ (eqs 1–4) and causes the formation of chlorinated compounds through a reaction with the presumed intermediate **III**. Trapping of the chloride ion by Ag⁺ enhances the formation of oxygenated compounds. Since [Sb^VTPP(OH)₂]-PF₆ has also been revealed to suffer deprotonation in the excited triplet state, the metal-oxo complex may also be formed

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through electron transfer from the deprotonated excited species. Detailed laser flash photolysis studies are now in progress.

The oxygenation reaction through a metal-oxo complex is very important from the viewpoint of artificial photosynthesis, since the complex can directly transfer an oxygen atom derived from water molecule to organic compounds. Among various oxygenation reactions, P-450 and its model reaction are well-known as reactions catalyzed by a metal-oxo-type complex which requires molecular oxygen and two electrons or a powerful oxidizing agent such as a peroxide or iodosylbenzene.¹⁰ A similar metal-oxo complex as that in P-450 is presumably also involved in the present photochemical reaction without any powerful oxidizing agent. The reaction, thus, could be called a "photochemical P-450 reaction", wherein the key step is a two-electron oxidation of water, which is a four-electron reduced form of molecular oxygen.

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