Photochemical Oxygenation of Cyclohexene through Reductive Quenching of Excited Tetraphenylporphyrinatoantimony(V) by Triphenylphosphine

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When visible light (λ = 420 nm) was irradiated to a reaction mixture involving tetraphenylporphyrinatoantimony(V) **1** as a sensitizer, methylviologen as an electron acceptor and triphenylphosphine (PPh_3) as an electron donor in acetonitrile–water (95:5) under the degassed condition, oxygenation reaction of cyclohexene **2** proceeded and 2-cyclohexenone and 3-cyclohexenone which were four electron oxidized products of **2** were mainly produced with rather high quantum yields of 0.14 and 0.04, respectively. Formation of cation radical of PPh_3 ($PPh_3^{\bullet+}$) by an electron transfer from PPh_3 to the excited triplet state of **1** upon visible light (λ = 420 nm) irradiation was the key step of the photooxygenation. Addition of $PPh_3^{\bullet+}$ to **2** produced an adduct which suffered hydrolysis and further oxidation to afford the oxygenated products of **2**.

Many studies aiming at an artificial photosynthesis have been reported in viewpoint of solar energy storage. Visible light induced hydrogen evolution and fixation of carbon dioxide[1] are the typical examples. Such photoredox systems generally involve appropriate sacrificial electron donors, sensitizers and electron acceptors. Rather efficient hydrogen evolution in the reductive terminal end has already been obtained,[1] while few examples have been reported on useful chemical reaction coupled with the oxidative terminal end of photoredox cycle. Attention has thus been focused on how useful oxidation reactions could be coupled with the photoredox cycles.

In designing a photoredox system, selection of sensitizer is one of the most important factor. $Ru(bpy)_3^{2+}$, porphyrins, organic dyes, and semiconductors[1] have been frequently used as sensitizers. Light fastness, high absorptivity of visible light, and long lifetime of excited state might be prerequisite for the sensitizer. Metalloporphyrins mostly satisfy these requirements. One of the most attractive points in metalloporphyrins is a capability of regulating redox potentials. It is known that oxidation potential becomes more positive as the valence of central metal becomes higher.[2] In conventional studies of photo induced electron transfer and hydrogen evolution systems, low-valent metalloporphyrins such as Zn porphyrins[3] were frequently used as sensitizer. Since oxidation potentials of those low-valent metalloporphyrins lie around 0.8 V vs saturated calomel electrode (SCE)[4] and the excited energy of triplet states are ca. 1.6 eV,[4,5] the excited triplet states of Zn porphyrins have strong reducing power of E_{ox} (excited state) = −0.8 V.[4] When the reductive terminal end is fixed as hydrogen evolution and methylviologen (MV^{2+}: $E_{red} = -0.44$ V[6]) is used as a typical electron acceptor for hydrogen evolution, the electron transfer from the excited triplet Zn porphyrins to MV^{2+} would be highly exoergic ($\Delta G \sim -0.4$ eV). In other words, however, the electron transfer wastes the excitation energy. As far as the excited sensitizer could reduce MV^{2+}, it would be more preferable to use sensitizers having the more positive oxidation potentials. In the case, the more kinds of electron donors could be coupled in the oxidative terminal end. From these points of view, we have examined photoredox systems involving high-valent metalloporphyrins, such as Sb(V), P(V), Sn(IV), and Ge(IV) tetraphenylporphyrins as sensitizer and various kinds of electron donors such as alkenes.[7-9] The cyclic voltammogram of $[Sb(V)TPP(OH)_2]Br$(**1**) (Chart 1) in acetonitrile has peak potentials of one electron oxidation at 1.70 V vs SCE and one electron reduction at −0.50 vs SCE, respectively. The values are higher by almost 1 V than those of the usual low-valent porphyrins. We have reported that visible light irradiation (λ = 420 nm) of a reaction mixture involving **1**, MV^{2+}, hydroxide ion and cyclohexene **2** in acetonitrile–water (95:5) under the degassed conditions induced formation of cation radical of MV^{2+} ($MV^{\bullet+}$) and oxygenation reaction of **2**.[7-9] Cyclohexene oxide **3** was mainly produced. In this reaction system, $MV^{\bullet+}$ was produced at the reductive terminal end

Chart 1

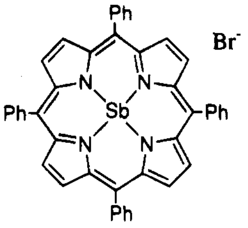

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Table 1. Additive Effect on Photosensitized Oxidation of 2[a]

		2ox. (10^{-7} M)					[**3** + **6** + diol]2 + [**4** + **5**]4
additive (10^{-2} M)	[$MV^{•+}$] (10^{-5} M)	**3**	**4**	**5**	**6**	cyclohexane-1,2-diol	[$MV^{•+}$]
none[b]	0.8	10.1	0	0	0	0	0.3
triethylamine	75.0	2.2	4	0	0	0	0.003
diisopropylamine	17.4	3.0	14	0	0	0	0.036
N-methylimidazole	0.5	0.8	0	0	8	0	0.4
imidazole	0.6	0.8	0	0	2	0	0.09
tribenzylamine	16.0	3.0	3	0	2	0	0.01
lithium bromide[c]	1.3	0.0		0	110	0	>1.7
triethyl phosphite	0.2	6.5	48	0	21	0	12
trimethyl phosphite	1.3	0.0	52	0	0	0	1.6
triphenylphosphine[c]	9.3	25.7	1666	494	402	50	10
triethyl phosphate	0.3	2.9	0	0	2	0	0.3
triphenylphosphine oxide[d]	4.7	6.8	11	0	0	0	0.12

[a] [**1**] = 1.7×10^{-6} M, [MV^{2+}] = 8.3×10^{-3} M, [**2**] = 0.1 M, in degassed CH_3CN/H_2O (95/5), 420 nm irradiation for 60 min. [b] [KOH] = 1×10^{-4} M. [c] [KOH] = 2×10^{-4} M. [d] [$OPPh_3$] = 2×10^{-3} M, [KOH] = 2×10^{-4} M.

and oxygenation of **2** proceeded at the oxidative terminal end. The oxygen atom of water molecule in the reaction system was confirmed as being incorporated into the oxidized products of **2** by an experiment using $H_2{}^{18}O$. Water molecule serves both as an electron donor and an oxygen donor. Though photochemical epoxidation is very interesting from the viewpoint of an artificial photosynthesis, the overall quantum yield was rather low ($\phi \sim 10^{-3}$). In this paper we will report extensive studies of additive effects on the epoxidation for improvement of the reactivity. Among the examined various kinds of additive, triphenylphosphine (PPh_3) induced change of oxygenation products from **3** to 2-cyclohexenone **4** and 3-cyclohexenone **5** which were four electron oxidized products of **2** with a large improvement of the reactivity (ϕ = 0.14 and 0.04, respectively).[10]

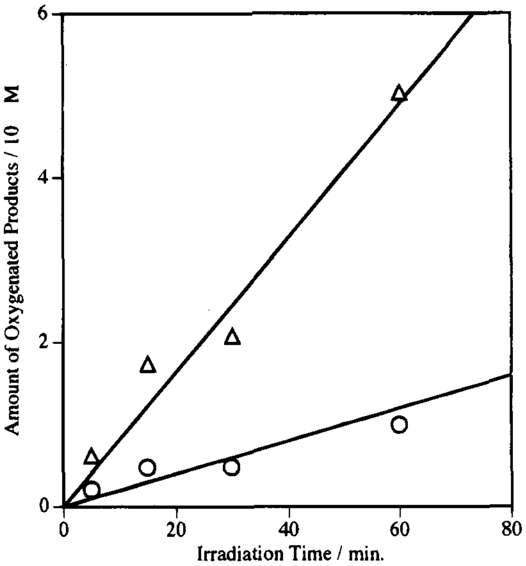

Figure 1. Time profiles of the formation of **4** and **6** by visible light irradiation to the reaction mixture involving **1** (2×10^{-6} M), MV^{2+} (8.3×10^{-3} M), PPh_3 (5×10^{-3} M), hydroxide ion (2×10^{-4} M), and **2** (0.1 M) under the degassed conditions (○, **4**; △, **6**).

Results and Discussion

Photochemical Oxygenation of Cyclohexene. As we have already reported,[7-9] visible light irradiation to **1** as a sensitizer in the presence of hydroxide ion, **2**, and MV^{2+} as an electron acceptor in a degassed aqueous acetonitrile afforded $MV^{•+}$ and **3**. The reactivity of the epoxidation, however, was rather low; the quantum yield was in the order of 10^{-3}. Charge separation of the resultant radical ion pair generated by the oxidative electron transfer quenching of the excited **1** by MV^{2+} might be one of the most crucial factors which determine the total efficiency of the net electron transfer. Since addition of ionic species, potential electron donors and acceptors as the third molecule have been known to affect the net efficiency of charge separation,[11] additive effects on the photochemical epoxidation were examined for improvement of the reactivity. Additive effects on oxidation reaction of **2** was shown in Table 1 when **1** was used as sensitizer. Some additive induced formation of other oxidation products such as **4**, **5**, 2-cyclohexenol **6**, and cyclohexane-1,2-diol than **3**. Formation of **3**, **6**, and the diol are two-electron oxidation processes and the oxidation products **4** and **5** require four-electron processes, while $MV^{•+}$ is one electron reduced product. The redox balance, [[**3** + **6** + diol]2 + [**4** + **5**]4]/[$MV^{•+}$], would indicate how many cycles of the reduction induce the oxidation ones. The redox balances are also compared in Table 1. When amines were added, formation of $MV^{•+}$ increased, while the epoxidation of **2** was retarded. The very low redox balances indicate that a reaction producing $MV^{•+}$ other than the oxidation of **2** operates in the photoreaction. Since the epoxidation proceeds through the oxidative quenching of the excited triplet **1** by MV^{2+},[7-9] this strongly suggests that the reductive quenching of the excited triplet **1** by the amines producing the radical anion of porphyrin predominates over the oxidative quenching by MV^{2+}. $MV^{•+}$ was considered to be produced by electron transfer between the resultant radical anion of porphyrin and MV^{2+}. A remarkable effect was observed in the case of PPh_3. PPh_3 caused an increase of $MV^{•+}$ formation and a change of the main oxidation product from **3** to **4** with large increase of the efficiency. The quantum yields of formation of **4** and **5** and the total oxidation were 0.14, 0.04, and 0.22, respectively. UV–vis spectral change indicates that any decomposition of **1** was not observed during the light irradiation and only formation of $MV^{•+}$ was observed. Cyclohexenones could be easily speculated to be produced by the further oxidation of **6** once generated in the reaction system upon light irradiation. Time profiles of the formation of **4** and **6** are shown in Figure 1. The compounds **4** and **6** were both monotonically produced with the light irradiation without showing any induction period. This clearly excluded the postulate and indicates

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(10) Preriminal results were published in Okamoto, T.; Takagi, S.; Shiragami, T.; Inoue, H. *Chem. Lett.* **1993**, 687.

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Table 2. Effects of the Concentration[a] of PPh_3 on the Photochemical Oxygenation Reaction of 2

	products (10^{-7} M)				
PPh_3 (10^{-3} M)	**3**	**4**	**5**	**6**	cyclohexane-1,2-diol
0.0[b]	10	0	0	0	0
2.0[c]	46	478	115	38	62
10.0[c]	26	1666	494	402	50

[a] [**1**] = 1.7×10^{-6} M, [MV^{2+}] = 8.3×10^{-3} M, [**2**] = 0.1 M, CH_3CN/H_2O (95/5), 420 nm irradiation, 1 h, degassed. [b] [KOH] = 1×10^{-4} M. [c] [KOH] = 2×10^{-4} M.

Table 3. The Effect of Hydrolysis Procedure on the Amount of Oxidized Products from 2[a]

	products (10^{-7} M)		
treatment	**4**	**5**	**6**
none	17	9	79
addition of water	510	119	160
addition of *p*-toluenesulfonic acid and potassium hydroxide	1666	494	402

[a] [**1**] = 1.7×10^{-6} M, [MV^{2+}] = 8.3×10^{-3} M, [**2**] = 0.1 M, [PPh_3] = 1.0×10^{-2} M, in degassed CH_3CN/H_2O (95/5), 420 nm irradiation for 60 min.

that **4** was directly produced from **2**. Quantitative analysis of the oxidation products at various concentration of PPh_3 was shown in Table 2. Quantity of oxidation products obviously depended on the concentration of PPh_3. This suggests that PPh_3 plays a key role for the enhancement of the total oxygenation reactivity and the predominant formation of **4**. The simple comparison of redox balance in Table 1, however, indicates that the oxidation cycles apparently exceeds the reduction ones. Very suggestive information was obtained by varying the method of detection of oxygenated products. For precise measurements of the amount of epoxide, the irradiated reaction mixture was normally hydrolyzed by the addition of *p*-toluenesulfonic acid. The epoxide was converted to cyclohexane-1,2-diol by the procedure. Potassium hydroxide was further added to the mixture for protecting GC column in the measurements. The amount of epoxide produced in the photoreaction was estimated from the difference of the diol content before and after the hydrolysis procedure (see Experimental Section). Table 3 shows the effect of hydrolysis procedure on the amount of **6** and cyclohexenones (**4**, **5**) in the irradiated reaction mixture. Even an addition of neutral water to the irradiated reaction mixture caused an increase of both **6** and cyclohexenones (**4**, **5**). A striking increase was observed by the addition of *p*-toluenesulfonic acid and potassium hydroxide in excess amount. Obviously the major portion of both **6** and cyclohexenones was not directly produced by the photoreaction. The results strongly suggest that some intermediate is formed during the photoreaction and the oxygenated products are formed by the hydrolysis of the intermediate in the dark.

When only 1 (2×10^{-6} M) and PPh_3 (1×10^{-3} M) in acetonitrile–water (95:5) were irradiated by the light of λ = 420 nm under the degassed condition, efficient formation of the radical anion of **1**[12] was observed (ϕ = 0.51) (Figure 2) and subsequently Sb(III)TPP was formed. In the presence of MV^{2+} under the same conditions of the light irradiation, $MV^{\bullet+}$ was effectively produced (ϕ = 0.43) without any formation of the reduced species of **1**. The formation of $MV^{\bullet+}$ was obviously caused by an electron transfer from the porphyrin radical anion to MV^{2+}.

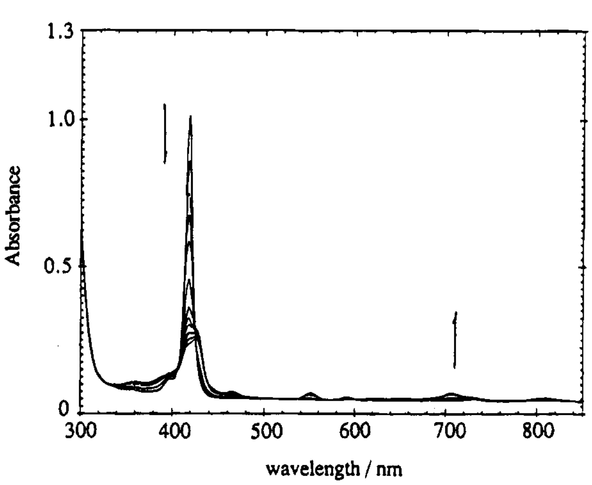
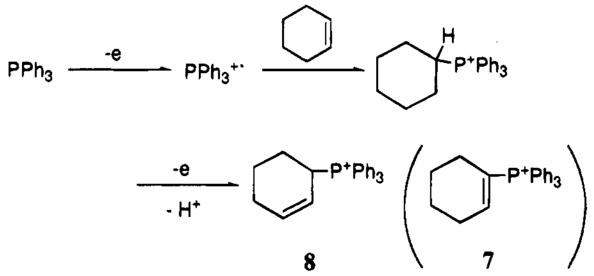


Figure 2. UV–vis spectral change when visible light (λ = 420 nm) was irradiated to the reaction mixture involving **1** (2×10^{-6} M) and PPh_3 (1.0×10^{-3} M) under the degassed conditions.

Scheme 1



Fluorescence of **1** was slightly quenched by PPh_3; the Stern–Volmer constant of the fluorescence quenching was 11.8 M^{-1}. Under the typical conditions of [PPh_3] = 1.0×10^{-2} M, the quenching efficiency ϕ is only 0.12 which is much smaller than the quantum yield of the photoreduction (ϕ = 0.51). Thus, the photoreduction should proceed mostly from the excited triplet state of porphyrin, though the excited singlet state may partly responsible for the reaction. This strongly suggests that the cation radical of PPh_3 ($PPh_3^{\bullet+}$) is obviously produced by reductive quenching of an electron transfer to the excited porphyrin triplet and participates in the oxidation of **2**.

Since $PPh_3^{\bullet+}$ has been reported to produce an adduct with alkene,[13] the adduct is readily presumed to be the intermediate which produces **6** and cyclohexenones (**4**, **5**) upon hydrolysis. We further examined the possibility of the formation of **6** and cyclohexenones (**4**, **5**) from the adduct by hydrolysis. The adduct was synthesized by electrolysis according to the method reported by Ohmori et al.[13] (Scheme 1).

The isolated adduct was revealed to be (2-cyclohexen-1-yl)triphenylphosphonium ion **8** in contrast to the above report which described a formation of (1-cyclohexen-1-yl)triphenylphosphonium ion **7** by electrolysis (see Experimental Section). The hydrolysis of **8** in the dark within 1 h at ambient temperature produced **4** and **6**

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(12) The UV–vis spectrum (λ_{max} = 427, 706, and 804 nm) of one electron reduced species of Sb(V)TPP upon electrolysis was completely the same with that observed in the photoreaction. The spectrum and the ESR signal (g = 2.000) were almost the same with those of other metalloporphyrins.[17,18]

(13) Ohmori, H.; Takanami, T.; Masui, M. *Tetrahedron Lett.* **1985**, *26*, 2199.

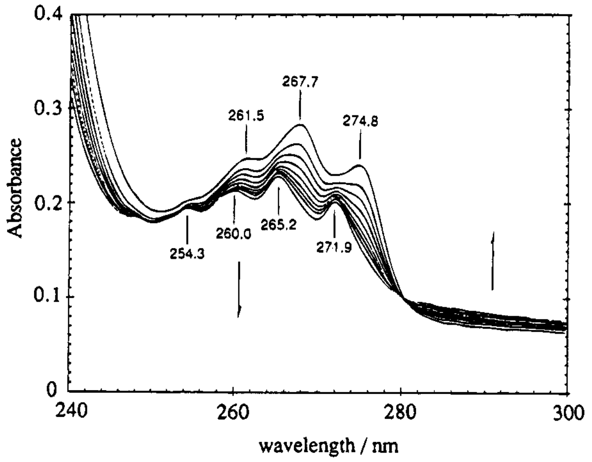

Figure 3. UV−vis spectral change under hydrolysis of **8** under the conditions of [**8**] = 6.2 × 10^{-4} M and [KOH] = 6 × 10^{-3} M in acetonitrile−water (91:9).

Table 4. The Concentration Effect[a] of 8 on the Hydrolysis Affording 4 and 6

8 (10^{-4} M)	yield (%)	
	4	**6**
1.7	39.6	0.08
6.8	26.2	0.07
34	16.6	0.11

[a] [KOH] = 10^{-2} M, CH_3CN/H_2O (95/5), 30 min, under air.

(Table 4) under the conditions in alkaline aqueous acetonitrile ($[OH^-] = 1 \times 10^{-2}$ M in $MeCN-H_2O$ (95:5)). A sharp isosbestic point was observed in the UV−vis spectral change during the hydrolysis (Figure 3).

As the concentration of **8** became higher, the yield of **4** became lower while that of **6** was almost constant (Table 4). This might be caused by the reaction between **8** and **4**. Under the basic conditions **8** would readily form the corresponding ylide by a deprotonation to react with ketones. In fact, when **8** and **4** were treated in the alkaline aqueous acetonitrile, **4** was monotonically disappeared. Though alkenyltriphenylphosphonium salts are known to be hydrolyzed to afford the corresponding phosphine oxide and benzene,[14] formation of carbonyl compounds as observed in the present case have not been reported. The reason might be due to the high reactivity of ylide toward carbonyl compounds. Under the usual synthetic conditions, phosphonium salts in rather high concentration may trap the carbonyl compounds once generated by the hydrolysis of phosphonium salt itself. A rather low concentration (around 10^{-4} M) of phosphonium salt might render it possible to detect the carbonyl compounds in the present case and also in the photochemical reaction system.

Detection of the Intermediate in the Actual Reaction System. Detection of the intermediate **8** in the actual reaction system was further examined. In order to avoid the hydrolysis of the intermediate during the photoreaction, visible light (λ = 420 nm) was irradiated to the reaction mixture involving **1** (2 × 10^{-6} M), MV^{2+} (8.3 × 10^{-3} M), PPh_3 (1.0 × 10^{-3} M), and **2** (0.1 M) in dry acetonitrile (5 mL) under the degassed condition without hydroxide ion. Chloroform (10 mL) was added to the irradiated reaction mixture to precipitate MV^{2+} which was removed by filtration and the filtrate was evaporated to a few mL. The obtained sample was analyzed by GPC (column; K-2001 Shodex, 20 mm i.d. × 600 mm, eluent; $CHCl_3$). The chromatogram had a peak at the same retention time of **8** and the collected fraction had the same λ_{max}'s (275, 268, 262 nm in acetonitrile) with those of **8** obtained in the electrolysis. Moreover, an addition of alkali to the collected fraction induced the same change of the UV−vis spectrum with the case of **8**. These results clearly indicate that **8** is actually formed in the photoreaction mixture. The direct detection of **8** strongly supports the postulate of Scheme 2: (1) the adduct **8** is formed between **2** and $PPh_3^{\bullet+}$ generated by the reductive quenching of excited triplet **1** by PPh_3, and (2) the adduct is further hydrolyzed and oxidized to form cyclohexenones. Though the detailed reaction mechanism of the hydrolysis and further oxidation is not yet clear, detections of benzene by ^{1}H-NMR, cyclohexenyldiphenylphosphine oxide, and triphenylphosphine oxide by FAB-MS in the reaction mixture and the fact that the amount of **4** is almost equal to that of benzene strongly suggest the similar mechanism to the hydrolysis of phosphonium salts[14] (Scheme 3). Attack of hydroxide ion to the phosphonium center induces a cleavage of C−P bonds. The cleavage of the P−cyclohexenyl bond affords triphenylphosphine oxide. Another cleavage of the P−phenyl bond produces benzene and cyclohexenyldiphenylphosphine oxide. The phosphine oxide is further attacked by hydroxide ion and oxidized to lead to formation of **4** and diphenylphosphine oxide. Since MV^{2+} is known to be a rather efficient oxidizing agent, it may participate in the subsequent oxidation processes. The obtained results mostly support the Schemes 2 and 3. The quantum yield of photoreduction of Sb(V)TPP by PPh_3 in the absence of **2** (ϕ = 0.51) and the formation of **4** in the presence of **2** (ϕ = 0.14) indicates that ca. 27% (0.14/0.51) of $PPh_3^{\bullet+}$ generated in the photoreduction induced the formation of **4**. The ratio is almost comparable with those in Table 4 where 26−40% is found for the hydrolysis of **8** derived from $PPh_3^{\bullet+}$ at the initial concentration being 6.8−1.7 × 10^{-4} M. This strongly suggests that the formation of adduct **8** from $PPh_3^{\bullet+}$ is almost quantitative in the photoreaction system. Since the hydrolysis of **8** mostly proceeds in the aftertreatment procedures of the irradiated reaction mixture (Table 3), only the formation of **8** by two-electron processes is considered to proceed during the photoreaction. The redox balance in Table 1, thus, should be modified into $[\mathbf{2}]_{ox.} \times 2/[MV^{\bullet+}]$. The modified value 5.7 in the case of PPh_3 still indicates that the formation of $[MV^{\bullet+}]$ is much less than the oxidation. Though the reason of poor redox balance is not clear, there should be some processes of reoxidizing $MV^{\bullet+}$ into MV^{2+} among the dark processes. Formation of **5** in addition to **4** in the photoreaction might also look puzzling. The hydrolysis of the authentic **8** afforded only **4**, but the isomer **5** was not detected at all (Table 4). The puzzling could be rationalized by a presumption that **7**, isomer of **8**, is also formed in the photochemical reaction system and **7** affords **5** upon hydrolysis. Further study including a detection of **7** in the photoreaction system is required to clarify the point.

Conventional photochemical hydrogen evolution system requires sacrificial electron donor such as amines, and only decomposition of an electron donor proceeds at the oxidative terminal end. In the present photoredox system, PPh_3 acts as an electron donor, and also induces oxygenation reaction of **2** with rather high efficiency. Since $MV^{\bullet+}$ can be easily coupled with hydrogen evolution

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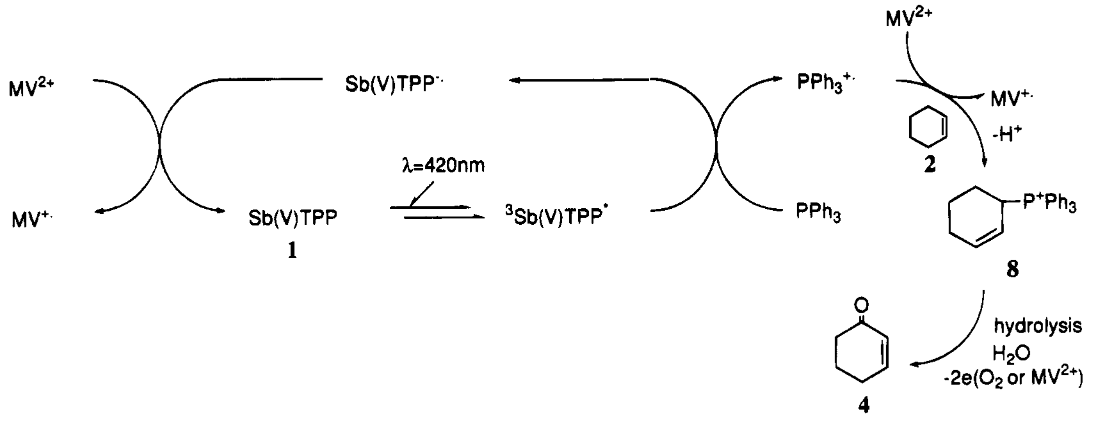
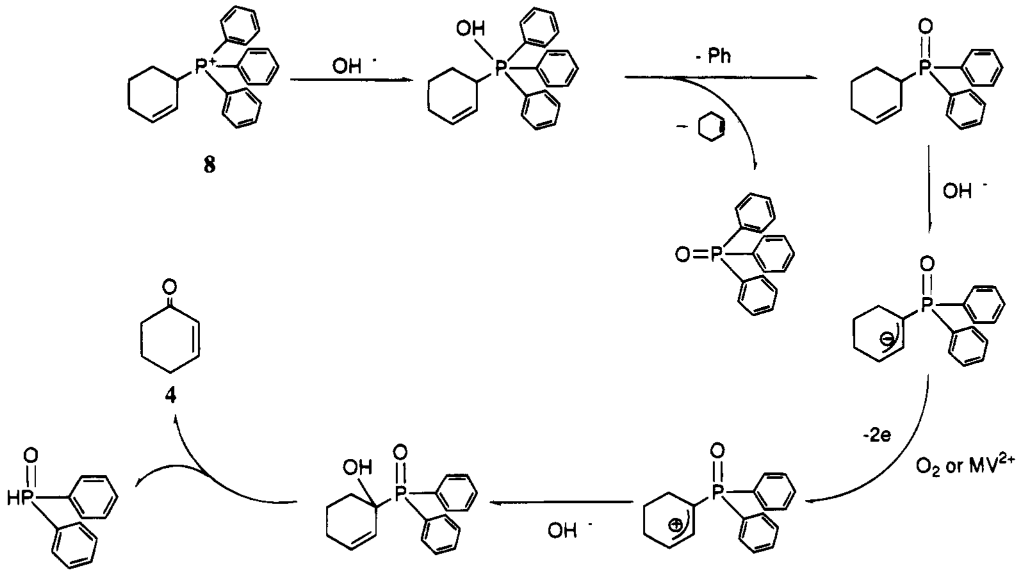
[14] Saleh, G.; Minami, T.; Ohshiro, Y.; Agawa, T. *Chem. Ber.* **1979**, *112*, 335.

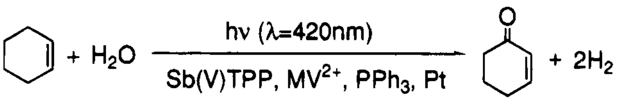
Scheme 2



Scheme 3



Scheme 4



system using platinum electrode or colloidal platinum, the net chemistry of the present photoredox system could be depicted as Scheme 4 where water molecule is split into hydrogen and oxygen atom in cyclohexenone.

Experimental Section

Materials. Acetonitrile was purified by refluxing over P_2O_5 and fractional distillation followed by further fractional distillation over K_2CO_3 under a nitrogen atmosphere. Cyclohexene **2** (Tokyo Kasei Co. Gr. grade) was distilled either in vacuo or under a nitrogen atmosphere before use. Methylviologen (MV^{2+}) was prepared by treatment of 4,4′-bipyridine with, methyl bromide in methanol at ambient temperature followed by repeated treatment with ammonium hexafluorophosphate for ion exchange.[9] *p*-Toluenesulfonic acid (Gr. grade) was purchased from Tokyo Kasei Co. and used as received. Potassium hydroxide was purchased from Kanto Chemical Co. and used as received. Tetraphenylporphyrinatoantimony(V)([Sb(V)TPP$(OH)_2$]Br) **1** was prepared according to a procedure described elsewhere.[9] Triphenylphosphine (PPh_3) (Tokyo Kasei Co. Gr. grade) was recrystallized from ethanol.

Photochemical Oxygenation of 2 Sensitized by 1. A reaction mixture (5 mL) in an optically transparent rectangular quartz cell (10 × 10 × 45 mm) was degassed by repeated freeze–thaw procedures under reduced pressure $<10^{-3}$ Pa and then sealed off. The sample was irradiated with visible light (λ = 420 nm) from a 500 W Xe lamp; Ushio UXL 500DKO) through an interference filter KL-42 (Toshiba) and a sharp-cut filter L-39 (Toshiba). Visible absorption spectra were recorded on a Shimadzu UV 210 spectrophotometer.

Analysis of Oxygenated Products. The light irradiated sample was analyzed by GC–MS (JEOL DX-300) according to the following procedures. The products were identified by coincidence of fragmentation patterns and retention times with those of the authentic samples. Quantitative analysis was carried out by SIM (selected ion monitoring method) detection mode. GC columns were G-300 (Chemicals Inspection & Testing Institute) 75 cm plus G-450 (Chemicals Inspection & Testing Institute) 40 m at the column temperature of 125 °C. The light irradiated samples (2 mL) were treated with aqueous solution of *p*-toluenesulfonic acid (0.1 M, 0.5 mL) to convert the epoxide into the diol and aqueous solution of hydroxide ion (0.6 M, 0.1 mL) for neutralization to protect the column. Quantitative analysis of **5** was according to the following procedure. Mixture of **4** and **5** was prepared from 1-methoxy-1,3-cyclohexadiene according to the literature.[15] On the basis of the ratio of **4** to **5** in the obtained mixture determined by ^{1}H-NMR analysis, the sensitivity of **5** on GC−MS was determined by the comparison of the authentic **4**.

Synthesis of Adduct between $PPh_3^{\bullet+}$ and 2.[10] The electrolytic synthesis of adduct between $PPh_3^{\bullet+}$ and **2** was carried out according to the literature.[13] A mixture of PPh_3 (1.57 g), **2** (3.0 mL), K_2CO_3 (6.0 g), and lutidinium tetrafluoroborate (3.26 g) was electrolyzed in dichrolomethane (8 mL) at the constant current of 20 mA for 19 h under nitrogen atmosphere. The obtained reaction mixture was filtered and evaporated to ca. 4 mL. The solution was diluted with water to 20 mL and extracted with $CHCl_3$ (10 mL) repeatedly for four times. The extracts was dried with $MgSO_4$ over one night. After filtration, the solution was evaporated to ca. 1 mL. The concentrated solution was dropped into diethyl ether (20 mL) to precipitate a crystal. The procedures were repeated three times and a slightly yellow powder was obtained (1.31 g, yield 51%). ^{1}H-NMR ($CDCl_3$): 1.5−2.4 (6H, m), 4.6 (1H, m), 5.6 (1H, m), 6.1 (1H, m), and 7.6−7.9 (15H, m) ppm. ^{13}C-NMR ($CDCl_3$): 20.3 (d, J_{CP} = 11 Hz), 22.9 (s), 24.1 (s), 31.1 (d, J_{CP} = 50 Hz), 117.2 (d, J_{CP} = 83 Hz), 117.7 (d, J_{CP} = 6 Hz), 130.6 (d, J_{CP} = 11 Hz), 133.9 (d, J_{CP} = 9 Hz), 135.2 (d, J_{CP} = 4 Hz), and 136.6 (d, J_{CP} = 11 Hz) ppm. ^{31}P-NMR ($CDCl_3$): 24.6 (s) ppm (H_3PO_4 as a standard). Anal. Calcd for $C_{24}H_{24}PBF_4$-$0.5H_2O$: C, 65.63; H, 5.74. Found: C, 65.39; H, 5.47. IR (KBr): 1430, 1100, and 1000 cm^{-1}. FAB-MS: 343 ((M − BF_4)$^+$). The structure of the obtained adduct was revealed to be different from that reported.[13] The structure of the adduct was further confirmed by comparison with the authentic sample obtained in the reaction of 3-bromocyclohexene with PPh_3.[16]

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