

Photochemical Epoxidation of Cyclohexene Sensitized by Tetraphenylporphyrinatoantimony(v) in the Presence of Water Acting both as an Electron and an Oxygen Donor

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Visible light irradiation of a reaction mixture involving tetraphenylporphyrinatoantimony(v) (Sb^VTPP) {[Sb^VTPP(OMe)Br]Br **1** or [Sb^VTPP(OH)₂]OH **2**}, methylviologen (MV²⁺), hydroxide ion and cyclohexene **6** in acetonitrile–water (95:5) under degassed conditions induced formation of MV^{•+} (one-electron reduced product of MV²⁺), and oxidation of cyclohexene (with cyclohexene oxide **7** and cyclohex-2-enol **8** as major products and cyclohexane-1,2-diol **9** in small amounts in the case of **1**, and cyclohexene oxide **7** as the sole product in the case of **2**). One third of the obtained diol was *cis* isomer. The oxygen atom of the water molecule in the reaction system was confirmed as being incorporated in the oxidized products of cyclohexene by an experiment using H₂¹⁸O. The overall quantum yield of the photochemical epoxidation was in the order of 10⁻³, while that of MV^{•+} production were in the order of 10⁻¹. Hydroxide ion was shown to have both a negative effect on radical anion formation by reductive quenching of the excited triplet state of Sb^VTPP, and also a positive effect by acting as an oxygen source itself for the epoxidation. A key intermediate for the epoxidation was presumed to be an antimony(vi) oxo-type porphyrin complex generated by an electron transfer to MV²⁺ from a singly and doubly deprotonated excited triplet Sb^VTPP. The different product distributions obtained for **1** and **2** are discussed in relation to the geometrical structures of the presumed key intermediate oxo-complexes.

Among recent studies of photochemical redox reactions much attention has been focused on hydrogen evolution and fixation of carbon dioxide in a suitably reductive photoredox system, the aim being artificial photosynthesis and solar energy conversion into chemical energy.¹⁻³ Such photoredox systems generally involve appropriate sacrificial electron donors, sensitizers, electron acceptors and some electron relay, such as noble metal-colloids, which lead to evolution of hydrogen. Charge separation between the resultant radical ion pair, generated either in an oxidative or a reductive electron-transfer quenching process of an excited sensitizer by an electron donor or an acceptor, has been accepted as being one of the most crucial factors which determine the total efficiency of the net electron transfer.⁴ Efficient hydrogen evolution has already been found in the presence of appropriate sacrificial electron donors.^{1,5} Attention has now focused on the possibility of replacing the sacrificial reaction of an electron donor by a terminal oxidation in a photoredox system. From the viewpoint of artificial photosynthesis, the incorporation of a water molecule as an ideal electron donor into an oxidation cycle would be most advantageous.⁶⁻¹³ To this end we chose high-valent metalloporphyrins, which are known to have rather high oxidation and reduction potentials, as a sensitizer of a photoredox system,¹⁴ though their photochemical behaviour has rarely been reported, in contrast to low-valent metalloporphyrins such as Zn porphyrins.¹⁵ We examined photoredox systems involving high-valent metalloporphyrins, such as Sb^V, P^V, Sn^{IV} and Ge^{IV} tetraphenylporphyrins as sensitizers, and various kinds of electron donors, such as alkenes and hydroxide ion equilibrated with water. Our studies showed that alkenes could be photochemically oxidized to the corresponding epoxide upon visible light irradiation in the presence of the metalloporphyrins (Fig. 1).¹⁶ Water molecules have been shown to be incorporated into the oxidation cycle and act as both an electron and an oxygen donor. This paper details the photo-

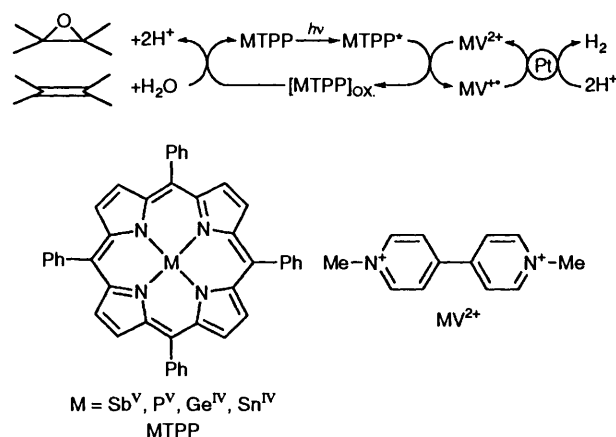


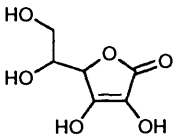



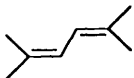
Fig. 1 Photo-redox system involving high valent metalloporphyrins as a sensitizer

chemical epoxidation of alkene sensitized by tetraphenylporphyrinatoantimony(v) (Sb^VTPP). The epoxidation proceeds without any of the strong oxidizing agents usually required in conventional epoxidations and even in model reaction systems of the enzyme P-450.¹⁷

Results and Discussion

Preparation of Sensitizer.—The sensitizer (Sb^VTPP) was prepared by reaction of antimony(III) tribromide and tetraphenylporphyrin in pyridine, followed by oxidation to antimony(v) by bromine. The bromine atom co-ordinated species was purified by column chromatography. The above crude product was carefully treated with hydroxide ion to give dihydroxy axial ligands. The purified porphyrin complexes were

Table 1 Quantum yield of MV^{2+} production sensitized by $[Sb^V TPP(OMe)Br]Br$ **1**

Reductant	Quantum yield ^a	
	$Sb^V TPP$	$Sb^V TPP + OH^-$ ^b
<chem>Me2CHOH</chem>	0.00	—
	0.00	—
<chem>MeCO2K</chem>	0.01	—
<chem>SEt2</chem>	0.00	—
<chem>PPh3</chem>	0.10	—
<chem>[EDTA]Na4</chem>	0.04	—
<chem>(PhCH2)3N</chem>	0.06	—
<chem>N(C2H4OH)3</chem>	0.10	—
<chem>NEt3</chem>	0.27	—
<chem>Ph-CH=CH-Ph</chem>	0.00	0.12
<chem>PhCH=CH2</chem>	0.00	0.15
	0.00	0.24
	0.00	0.16
	0.00	0.16
	0.17	0.19

^a $[1] = 1.7 \times 10^{-6} \text{ mol dm}^{-3}$; $[MV^{2+}] = 8.3 \times 10^{-3} \text{ mol dm}^{-3}$; $[Reductant] = 8.3 \times 10^{-4} \text{ mol dm}^{-3}$ in CH_3CN-H_2O (95:5).
^b $[KOH] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$.

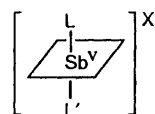
confirmed as the bromine co-ordinated $[Sb^V TPP(OMe)Br]Br$ **1** and dihydroxy co-ordinated species $[Sb^V TPP(OH)_2]OH$ **2**, (see Experimental section). The cyclic voltammogram of the complex **1** in dichloromethane and the complex **2** in acetonitrile have peak potentials of one electron oxidation to be 1.70 V *vs.* saturated calomel (reference) electrode (SCE) and one-electron reduction to be -0.70 and -0.50 V *vs.* SCE, respectively. The values are higher by almost 1 V than those of low-valent Zn and Mg porphyrins.¹⁴

Photochemical Reactions Sensitized by $Sb^V TPP$ in the Presence of Sacrificial Electron Donors.—Reaction mixtures involving $Sb^V TPP$ **1** as a sensitizer, *N,N'*-dimethyl-4,4'-bipyridinium bis(hexafluorophosphate) (methylviologen, MV^{2+}) as an electron acceptor, and the various sacrificial electron donors listed in Table 1 were irradiated by visible light of $\lambda = 420$ nm in 95:5 acetonitrile–water under degassed conditions. In most cases, the cation radical of methylviologen (MV^{2+}), the one-electron reduction product MV^{2+} , was produced upon visible

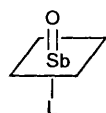
Table 2 Oxidation of cyclohexene sensitized by $[Sb^V TPP(OMe)Br]Br$ **1** upon visible light irradiation^a

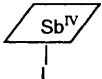
$[KOH]/10^{-4}$ mol dm^{-3}	$[MV^{2+}]/10^{-5}$ mol dm^{-3}	$(6)_{ox.}/10^{-7} \text{ mol dm}^{-3}$				$2[(6)_{ox.}]/[MV^{2+}]$
		7	8	9	10	
0.00	0.0	0.0	0	0	0	—
0.57	0.7	13.0	36	0	0	1.32
1.14	2.2	11.0	19	11	0	0.37
2.89	4.3	7.9	13	11	0	0.15
8.58	14.0	9.3	13	12	0	0.05

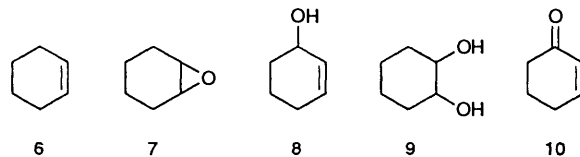
^a $[1] = 1.7 \times 10^{-6} \text{ mol dm}^{-3}$, $[MV^{2+}] = 8.3 \times 10^{-3} \text{ mol dm}^{-3}$, $[6] = 0.1 \text{ mol dm}^{-3}$ in degassed $MeCN-H_2O$ (95:5), λ 420 nm, 60 min.
^b Oxidation products of **6**.



L	L'	X
Br	OMe	Br
OH	OMe	OH
OH	OH	OH



L		
OMe	3a	
OH	3b	
O ⁻	4	
		 5a



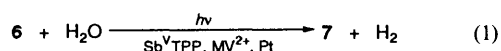
light irradiation to $Sb^V TPP$ **1**. Quantum yields of the production of MV^{2+} are tabulated in Table 1. Among the examined sacrificial electron donors, triphenylphosphine, amines and 2,5-dimethylhexa-2,4-diene exhibited rather high reactivities for the production of MV^{2+} , while monoenes and aromatic olefins had negligibly small reactivities.

Photochemical Epoxidation of Cyclohexene Sensitized by $Sb^V TPP$.—Our attention was thus focused on how monoenes could be incorporated in the photoredox reaction. Axial ligands are known to play a substantial role in the photochemical behaviour of high-valent metalporphyrins and addition of hydroxide ion as an axial ligand to the reaction system could be expected to maintain dihydroxy co-ordination to the metal complex.¹⁸ In a photoredox reaction sensitized by tin(IV) tetraphenylporphyrin involving triphenylphosphine as a sacrificial electron donor, in which the dihydroxy co-ordinated species was also proposed to be the reaction one, addition of hydroxide ion was revealed to have an enormous effect on increasing and maintaining the reactivity.¹⁸ Addition of small amount of hydroxide ion ($1 \times 10^{-3} \text{ mol dm}^{-3}$) to the present photoredox system in fact increased the production of MV^{2+} (Table 1). Inspection of the photochemical reaction product from cyclohexene as a typical case revealed that the corresponding epoxide, cyclohexene oxide **7** and cyclohex-2-enol **8** were the major products and cyclohexane-1,2-diol **9** was also detected in small amounts (Table 2). One third of the obtained diol was the *cis* isomer. Cyclohex-2-enone **10**, cyclohexanol and other oxidized material were not detected. Quantum yield of the epoxidation was 1.0×10^{-3} under the typical conditions where $[1] = 2 \times 10^{-6} \text{ mol dm}^{-3}$, $[MV^{2+}] = 8 \times 10^{-3} \text{ mol dm}^{-3}$, $[6] = 0.1 \text{ mol dm}^{-3}$ and $[KOH] = 9 \times 10^{-4} \text{ mol dm}^{-3}$ in acetonitrile–water (95:5). Absorbance and λ_{max} of the Soret

band of $\text{Sb}^{\text{V}}\text{TPP}$ in the reaction system remained constant during the photoreaction, indicating that the sensitizer was unchanged even on prolonged irradiation. Under neutral conditions no productions of MV^{2+} or the epoxide was observed. Hydroxide ion was thus supposed to play a key role in the epoxidation. Very interestingly, different product distributions were observed with the complex **2** as a sensitizer: the epoxide was found to be the major product, but cyclohex-2-enol **8**, and cyclohexane-1,2-diol **9** were produced in trace amounts (Table 3). As described later, it was proposed that the axially co-ordinated bromine atom in the complex **1** had been replaced mostly by a hydroxy group, forming $[\text{Sb}^{\text{V}}\text{TPP}(\text{OMe})(\text{OH})]$ **1'** in the reaction system. Though the different reactivity between the two complexes, **1'** and **2** is very interesting, the dihydroxy co-ordinated species (the complex **2**), was used as a sensitizer hereafter to avoid complications due to the presence of multiple light-absorbing components in the case of the complex **1**.

Formation of an epoxide involves oxygen atom incorporation into cyclohexene. Since the photoreaction was carried out under the strictly degassed conditions, the oxygen atom should come from the hydroxide ion or the water molecule itself, equilibration occurring between the two. To confirm this, a photoreaction using H_2^{18}O was examined. As is shown in Table 4, ^{18}O atom was actually incorporated in the epoxide even under aerated conditions, where autooxidation and singlet oxygen-induced oxidation of cyclohexene caused by dissolved molecular dioxygen predominated.

A platinum electrode was immersed in the photoreaction flask (the flask A) and was connected electrochemically by copper wire to another platinum electrode in a flask containing aqueous hydrochloric acid (flask B). The two flasks were also connected by a salt bridge of agar gel. Hydrogen evolution on the platinum electrode in flask B was observed upon light irradiation of the photoreaction flask (flask A). Thus, the photoredox reaction can be expressed as the chemical eqn. (1).



The water molecule is serving both as an oxygen atom and electron donor in the photoredox reaction; here, $\text{Sb}^{\text{V}}\text{TPP}$ -sensitized water splitting occurs upon irradiation by visible light. Although this is potentially the type of photoredox system

Table 3 Oxidation of cyclohexene sensitized by $[\text{Sb}^{\text{V}}\text{TPP}(\text{OH})_2]\text{OH}$ **2** upon visible light irradiation^a

$[\text{KOH}]/10^{-4}$ mol dm ⁻³	$[\text{MV}^{2+}]/10^{-5}$ mol dm ⁻³	$(6)_{\text{ox}}/(10^{-7} \text{ mol dm}^{-3})$				$2[7 + 8]/$ $[\text{MV}^{2+}]$
		7	8	9	10	
1.0	0.8	10.1	0.0	0.0	0.0	0.240
5.0	11.9	8.4	0.0	0.0	5.5	0.014
10.0	12.7	1.7	0.1	0.0	4.6	0.003

^a Experimental conditions as in footnote to Table 2 except $[\mathbf{2}] = 1.7 \times 10^{-6} \text{ mol dm}^{-3}$.

Table 4 Photosensitized oxidation products of cyclohexene under aerobic conditions^a

$[\text{KOH}]/10^{-4}$ mol dm ⁻³	$(6)_{\text{ox}}/10^{-7} \text{ mol dm}^{-3}$							
	^{18}O incorporated products				^{16}O incorporated products			
	^{18}O -7	^{18}O -8	^{18}O -10	$^{18/16}\text{O}, ^{18}\text{O}$ -9	7	8	10	9
1	36	0	0	0	0	4194	5338	0
10	77	2	36	0	114	5211	3152	31
100	76	2	6	0	219	213	238	67

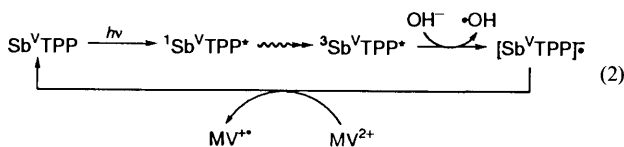
^a Experimental conditions as in footnote to Table 3 except in degassed $\text{MeCN}-\text{H}_2^{18}\text{O}$ (98%) (95:5), for 8 h.

which could incorporate a useful oxidation, the quantum yield of the epoxidation is insufficiently high. Attention is further focused on factors which could control the photochemical epoxidation and how the reactivity could be increased. Since formation of the major oxidation products (**7**, **8** and **9**) are all two-electron processes and formation of the reduction product MV^{2+} is a one-electron reduction, the net result of two cycles of the reduction should correspond to one cycle of the oxidation at both termini of the photoredox system. Comparison of the two-fold quantum yield of the epoxidation with the quantum yield of MV^{2+} formation indicates that at lower hydroxy concentrations the oxidation (epoxidation) and reduction cycles (MV^{2+} formation) are comparable, while at higher concentrations of OH^- formation of MV^{2+} exceeds that of epoxidation (Tables 2 and 3). These results strongly suggest that a reaction producing MV^{2+} other than epoxidation, operates at higher concentrations of OH^- .

Reductive Quenching by Hydroxide Ion to produce the Radical Anion of $\text{Sb}^{\text{V}}\text{TPP}$.—When only the complex **2** and hydroxide ion ($1 \times 10^{-3} \text{ mol dm}^{-3}$) in acetonitrile–water (95:5) were irradiated ($\lambda = 420 \text{ nm}$) under degassed conditions, the radical anion of **2** was produced with high efficiency (quantum yield 0.13). Sharp isosbestic points were observed at 406 and 425 nm during the irradiation. The λ_{max} values (427, 706 and 804 nm) in the visible absorption spectrum* and ESR measurements ($g = 2.000$) clearly indicated the formation of the radical anion of **2**. The radical anion produced was very stable under the reaction conditions, but reverted completely to the starting complex **2** upon introduction of air after the irradiation. When MV^{2+} was added to the reaction mixture of complex **2** and KOH in acetonitrile–water (95:5) and the mixture was irradiated with visible light under the degassed conditions, efficient production of MV^{2+} ($\Phi = 0.11$), without any accumulation of the radical anion of **2**, was observed. These results indicate that MV^{2+} is reduced to MV^{2+} by the radical anion generated in the reductive quenching of the excited **2** by hydroxide ion, to regenerate compound **2** [eqn. (2)]. Since the fluorescence intensity of **2** was not affected by hydroxide ion at this concentration ($1 \times 10^{-3} \text{ mol dm}^{-3}$), the excited state for the reaction should be the lowest excited triplet state of **2**. The electron transfer from hydroxide ion would produce hydroxide radical $\cdot\text{OH}$ which is known as a strong oxidizing agent. In the presence of cyclohexene the hydroxide radical presumably attacks the alkene, effecting its oxidation. The results in Tables 2 and 3, however, clearly exclude this possibility. The oxidation of cyclohexene was somewhat suppressed at the high concentration of hydroxide ion where efficient reductive quenching operates. The hydroxide radical produced is thus presumed

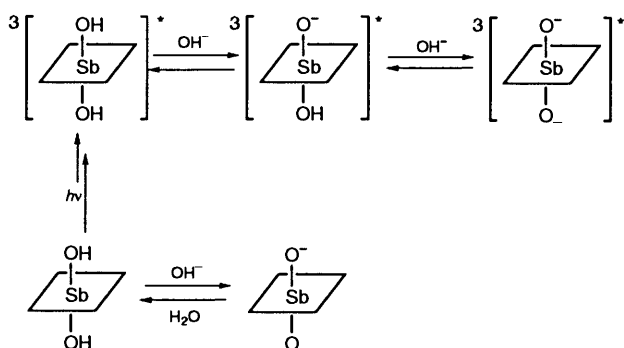
* One electron reductive electrolysis of **2** at -0.3 V vs. NHE in acetonitrile containing tetrabutylammonium perchlorate as a supporting electrolyte afforded the radical anion of **2** (λ_{max} 427, 706 and 804 nm).

to be inactivated by a hydrogen abstraction from the solvent acetonitrile to produce a water molecule.



Axial Coordination Chemistry in the Ground and Excited States.—Since the photochemical behaviour of high-valent metalloporphyrins is known to be very sensitive to the axial ligands of the complex,¹⁸ the co-ordination chemistry of the complexes **1** and **2** was investigated. Addition of neutral water (0–10% v/v) to the dry acetonitrile solution of complex **1** ($\lambda_{\text{max}} = 424 \text{ nm}$) induced a rather slow blue shift of the Soret band to 417.5 nm, an isosbestic point occurring at 422 nm. FAB–MS analysis clearly indicated that complex **1** ($M^+ = 847, 845$ and 843) was converted into the hydroxy coordinated species $[\text{Sb}^{\text{V}}\text{TPP}(\text{OMe})(\text{OH})]$ (**1'**) ($M^+ = 783$ and 781) by the axial ligand substitution of a bromine atom by a hydroxide ion upon being refluxed in aqueous acetonitrile. Though the equilibrium constant of the axial ligand exchange could not be determined due to the very slow coordination at ambient temperature, at least two light-absorbing species such as **1** and **1'** must be present in the reaction system when the bromine coordinated complex **1** is employed in the reaction. Phosphorus octaethylporphyrin, which bears a hydroxide ion as an axial ligand, has been reported to suffer deprotonation of the axial ligand under alkaline conditions.¹⁹ The sensitizer **2**, $[\text{Sb}^{\text{V}}\text{TPP}(\text{OH})_2]\text{OH}$, is also expected to suffer the similar deprotonation. As is shown in Fig. 2 the Soret band of the sensitizer in acetonitrile–water (95:5) exhibited a red shift upon addition of hydroxide ion. A sharp isosbestic point was observed at 420 nm. Since the starting sensitizer **2** is confirmed as $[\text{Sb}^{\text{V}}\text{TPP}(\text{OH})_2]\text{OH}$, the red shift could be explained as a single-step deprotonation of the axial ligand hydroxide. The $\text{p}K_{\text{a}}$ value was estimated to be 10.9, being a rather weak acid. Thus, most of the sensitizer **2** $[\text{Sb}^{\text{V}}\text{TPP}(\text{OH})_2]\text{OH}$ (88.5%) remains protonated with $[\text{OH}^-] = 1 \times 10^{-4} \text{ mol dm}^{-3}$ as typical reaction conditions, and the major light-absorbing species must, therefore, be the starting sensitizer $[\text{Sb}^{\text{V}}\text{TPP}(\text{OH})_2]\text{OH}$.

On the other hand, laser flash photolysis studies revealed that complex **2** in its excited triplet state suffers successive two-step deprotonations within 100 μs which are considerably accelerated under alkaline conditions (see Scheme 1).²⁰ This



Scheme 1 Deprotonation of $\text{Sb}^{\text{V}}\text{TPP}$ in the ground and excited triplet states

means that both the photochemical epoxidation and also the reductive quenching by hydroxide ion could possibly proceed through the three individual excited species, the protonated

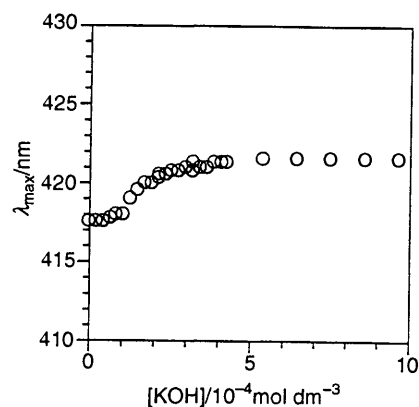


Fig. 2 Shift of the Soret band of $[\text{Sb}^{\text{V}}\text{TPP}(\text{OH})_2]\text{OH}$ **2** in acetonitrile–water (95:5) under alkaline conditions

excited sensitizer, the singly deprotonated excited species and the doubly deprotonated excited one.

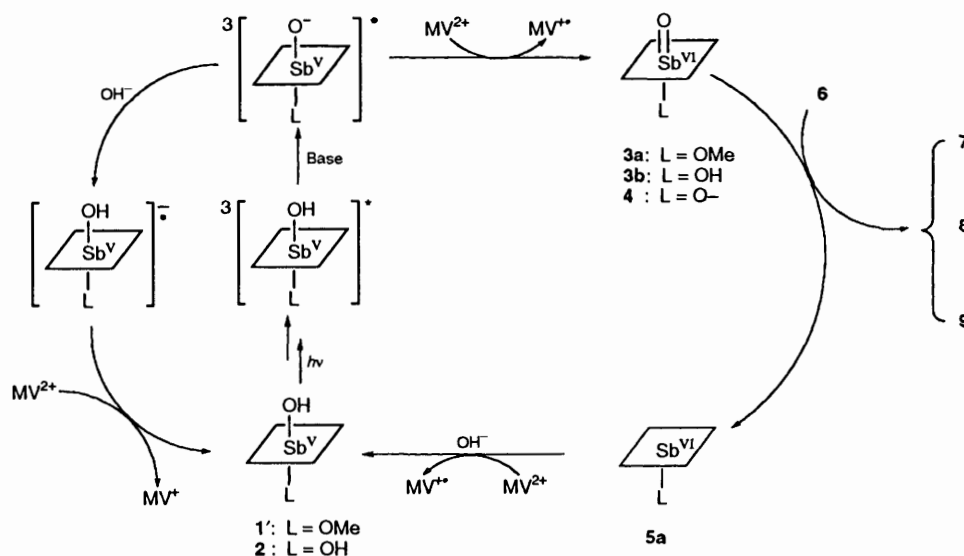
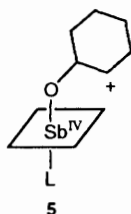
Reaction Scheme for the Photochemical Epoxidation.—The results shown in Tables 2 and 3 apparently suggest that the reductive quenching of the excited triplet state of the sensitizer by hydroxide ion competes with the photochemical epoxidation process. Since the epoxidation of alkene was only observed in the presence of MV^{2+} and an oxidative quenching of the excited triplet state of the complex **2** by MV^{2+} producing $\text{MV}^{\cdot+}$ has actually been observed in laser flash photolysis studies,²⁰ the photochemical epoxidation is proposed to be induced by an oxidative electron transfer to MV^{2+} from complex **2** in its triplet excited state. One-electron oxidation of the singly deprotonated excited triplet state and the doubly deprotonated one by MV^{2+} could conceivably produce oxo-type metal complexes **3** and another oxo-type complex **4**. The photochemical epoxidation could most plausibly be explained as proceeding through oxo-type complexes in a similar manner to that reported in the epoxidation of P-450 model reaction systems.¹⁷ Cyclohexene oxide and cyclohex-2-enol are well known products in the P-450 model reaction systems.¹⁷ The reaction scheme for the photochemical epoxidation thus could be depicted as Scheme 2. Interaction of cyclohexene with the metal oxo complexes **3** and **4** would give products **7**, **8** and **9**. Though the detailed mechanism of the formation of the diol is not yet clear, formation of the *cis*-diol in the case of the complex **1** (Table 2) strongly suggest involvement of a stereo-regulative attack of the second hydroxide ion on an intermediate such as **5** proposed in the P-450 model reaction systems.¹⁷

Oxygen transfer from the oxo-type complexes to alkenes results in the 'vacant Sb^{IV} species' **5a** in which the axial site is vacant. The vacant species would be rapidly co-ordinated by hydroxide ion and oxidized by MV^{2+} into the starting $\text{Sb}^{\text{V}}\text{TPP}$ with formation of $\text{MV}^{\cdot+}$. Throughout the photochemical epoxidation route two molecules of $\text{MV}^{\cdot+}$ are thus produced, along with one molecule of the two-electron oxidized products such as **7**, **8** and **9**, respectively. The different product distribution afforded by the complexes **1** and **2** (Tables 2 and 3) might reflect differences in the electronic and geometric structures of the oxo-type complexes **3** and **4** with another axial ligand ($L = \text{OMe}$ **3a**, OH **3b** and O^- , respectively). The metal atom in many porphyrin complexes has been known to shift in the axial direction from the central position of the porphyrin plane²¹ and the chemical reactivity of the complexes has been proposed to depend upon the degree of shift of the central metal atom.²² In this respect we observed very interesting effects on the reaction upon addition of additives (Table 5). Addition of 2,6-lutidine as a base molecule induced drastic changes in the product distribution; at higher concentrations of lutidine

Table 5 Oxidation products of cyclohexene sensitized by $[\text{Sb}^{\text{V}}\text{TPP}(\text{OH})_2]\text{OH}$ **2** upon visible light irradiation

Reaction conditions ^a	$[\text{MV}^{2+}]/10^{-5}$ mol dm^{-3}	$(\mathbf{6})_{\text{ox.}}/10^{-7} \text{ mol dm}^{-3}$			
		7	8	9	10
$[\text{KOH}] = 1 \times 10^{-4} \text{ mol dm}^{-3}$	0.8	10.1	0.0	0.0	0.0
$[\text{Lut.}] = 1 \times 10^{-1} \text{ mol dm}^{-3}$ ^b	1.5	14.8	6.1	0.0	4.0
$[\text{Lut.}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$ ^c	1.9	0.0	18.0	0.0	0.0
$[\text{LiBr}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$ ^d	1.3	0.0	110.0	0.0	—

^a Experimental conditions as in footnote to Table 3. ^b 2,6-Dimethylpyridine (Lut.) was added; irradiated for 8 h. ^c Irradiated for 5 h. ^d KOH ($2 \times 10^{-4} \text{ mol dm}^{-3}$) was involved.

**Scheme 2** Reaction scheme for photochemical epoxidation

($1 \times 10^{-1} \text{ mol dm}^{-3}$) the epoxide **7** was the major oxidation product, while at lower concentrations of lutidine ($1 \times 10^{-3} \text{ mol dm}^{-3}$) only the enol **8** was observed. In the presence of lutidine at high concentration the deprotonations of the excited $\text{Sb}^{\text{V}}\text{TPP}$ are enhanced and the doubly deprotonated excited species plays a major role.²⁰ The oxo complex **4** having O^- as the other axial ligand derived from the doubly deprotonated form would be the key intermediate in this case. On the other hand, lutidine at low concentration would induce insufficient deprotonation of the excited $\text{Sb}^{\text{V}}\text{TPP}$ to produce the singly deprotonated excited form. Consequently, the oxo complex **3b** having OH as another axial ligand would be the major species in this case. The different product distribution with varying concentrations of lutidine thus might be ascribed to the oxo complexes **3b** and **4** having a different sixth axial ligand (OH and O^-) which would give rise to different geometry around the central metal. Addition of bromide ion to the reaction system also induced a drastic change in the product distribution (Table 5), epoxidation being completely suppressed and only the enol **8** being observed. The result also strongly suggests co-ordination of the added bromide ion to the central metal atom of the complex; the co-ordination would also affect the reactivity of the oxo complex. Further study on reaction mechanism is now in progress.

In conclusion, hydroxide ion equilibrated with water in the reaction system in addition to having a negative effect also plays three major roles in the photochemical epoxidation: (1) the negative effect of the radical anion formation by the reductive quenching of the excited triplet $\text{Sb}^{\text{V}}\text{TPP}$, competing with the epoxidation process; (2) enhancement of the deprotonations of the excited triplet $\text{Sb}^{\text{V}}\text{TPP}$ to produce the doubly deprotonated excited species which leads to the key intermediate, oxo-type complex, by an electron transfer to MV^{2+} ; (3) regeneration of the active starting complex **2** by rapid co-ordination to the co-ordination unsaturated species (vacant species); (4) acting as an oxygen atom source for the epoxidation through the co-ordination to the central metal.

Epoxidation of alkenes usually requires strong oxidizing agents either in thermal²³ or photochemical methods.^{24,25} The present photochemical epoxidation requires only light energy, sensitizer $\text{Sb}^{\text{V}}\text{TPP}$, electron acceptor MV^{2+} and hydroxide ion and it is the first example of epoxidation without molecular dioxygen or strong oxidizing agents. For preparation of active oxygen from molecular dioxygen, the P-450 model systems in most cases adopt the two electron reduced form derived from molecular dioxygen, such as molecular dioxygen with reducing agents,^{26,27} peroxides,²⁸ iodosylbenzene,²⁹ and other oxidizing agents.³⁰⁻³² The present photochemical epoxidation provides novel approach to activation of oxygen on metalloporphyrins through the total photoredox reaction route *via* two-electron oxidation of hydroxide ion which could be derived by four-electron reduction of molecular dioxygen.

Experimental

Materials.—Acetonitrile was purified by refluxing over and fractional distillation from P_2O_5 followed by further fractional

distillation over K_2CO_3 under a nitrogen atmosphere. Cyclohexene (Tokyo Kasei Co. Gr. grade) was distilled either *in vacuo* or under a nitrogen atmosphere before use.

N,N'-Dimethyl-4,4'-bipyridinium bis(hexafluorophosphate) (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. 2,6-Dimethylpyridine (lutidine) was purchased from Tokyo Kasei Co. and was purified by refluxing with potassium hydroxide and fractional distillation under a reduced pressure of nitrogen. Toluene-*p*-sulfonic acid was purchased from Tokyo Kasei Co. and used as received. Tetraphenylporphyrin (Tokyo Kasei Co.) was purified by column chromatography (SiO_2 ; dichloromethane as an eluent). Antimony(III) tribromide was purchased from Nakarai Chemical Co. and used as received. $H_2^{18}O$ (98% content; CEA France) was used as received.

Tetraphenylporphyrinatoantimony(v).—Tetraphenylporphyrin (501 mg) and antimony(III) tribromide (3.53 g) were allowed to react in refluxing pyridine (50 cm³) under a nitrogen atmosphere for 30 h. After the reaction mixture had cooled to room temperature, bromine (0.5 cm³) was added to it and the whole was stirred for several hours to oxidize the antimony(III) to antimony(v). Addition of hexane to the reaction mixture precipitated the Sb^VTPP which was then purified by repeated re-precipitation from dichloromethane solution with hexane. The crude Sb^VTPP was passed through silica gel column with methanol-chloroform (1:15) as eluent. The purple fraction was collected and identified as $[Sb^VTPP(OMe)Br]Br$ **1** (161 mg, 21%); FAB-MS 847, 845 and 843; ν_{max}/cm^{-1} 266 (Sb-Br); $\delta_H(CDCl_3)$ -2.03 (3 H, s), 7.95-8.02 (12 H, m), 8.37 (8 H, m) and 9.59 (8 H, s); $\lambda_{max}(CH_2Cl_2)/nm$ 429 (log ϵ 5.53), 560 (4.22) and 602 (4.08).

A dichloromethane solution (100 cm³) of the crude Sb^VTPP (443 mg) was washed well with water and then carefully washed with aqueous alkali until the absorption maximum of the Soret band exhibited a blue shift (to 421 nm from 429) which is characteristic of the bromine co-ordinated species, and then purified by column chromatography (see above). The purple crystalline solid was identified as $[Sb^VTPP(OH)_2]OH$ **2** (yield 112 mg, 36%); FAB-MS 769 and 767; $\delta_H(CDCl_3)$ -2.28 (2 H, br s), 7.82-7.91 (12 H, m), 8.41 (8 H, m) and 9.40 (8 H, s); $\lambda(CH_2Cl_2)/nm$ 421 (log ϵ 5.68), 550 (4.11) and 590 (3.78).

Photoreaction.—A reaction mixture (5 cm³) 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 ($\lambda = 420$ nm) emitted 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 Shimadzu UV 210 spectrophotometer.

Analysis.—The irradiated sample was analysed by GC-MS (JEOL DX-300), the products being 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. Two kinds of GC column were used; (1) OV-1 with the column temperature of 90 °C for analyses of cyclohexene oxide **7**, cyclohex-2-enol **8**, and cyclohex-2-enone **10** and OV-1 with the column temperature of 180 °C for *cis* and *trans*-cyclohexane-1,2-diol **9** in the reaction mixture which was extracted by diethyl ether and treated with a trimethylsilylating reagent TMS-HT (Tokyo Kasei; mixture of hexamethyldisilazane and trimethylchlorosilane) before analyses and (2) G-300 (Chemicals Inspection and Testing Institute) with the column temperature

of 165 °C for compounds **7**, **8**, **9** and **10**, with the sample being treated with toluene-*p*-sulfonic acid to convert the epoxide into the diol, and hydroxide ion for neutralization to protect the column.

Cyclic voltammetry and electrolysis were conducted with a potentiostat (Hokuto Denko HA-101) equipped with a function generator (Hokuto Denko HB-104). Tetrabutylammonium perchlorate was used as a supporting electrolyte, flat platinum (2 mm ϕ) as working electrode, platinum mesh as counter electrode, and SCE as reference electrode, respectively.

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