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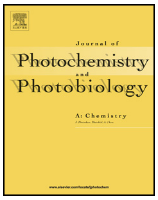

Two-electron oxidation of water to form hydrogen peroxide sensitized by di(hydroxo)porphyrin Ge^{IV} complex under visible-light irradiation

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ABSTRACT

Visible-light-induced two-electron oxidation of water to form hydrogen peroxide (H_2O_2) was investigated in a photovoltaic cell (PVC) composed of an ITO electrode coated by tetrakis-(4-carboxylphenyl) porphyrinatogermanium(IV) (**1**)-adsorbed titanium oxide (TiO_2) particles as an anode (**1**/TiO_2/ITO) and a Pt electrode as a cathode in an aqueous solution containing an electrolyte. The short-circuit photocurrent was observed under irradiation of the **1**/TiO_2/ITO anode with the light of 550 nm under aerated conditions. Simultaneously, H_2O_2 was detected only in the anode chamber. After irradiation for 6 h, the turnover number (TON) and the faradaic efficiency for the formation of H_2O_2 were estimated to be 9.0 and 92%, respectively. The action spectrum for the formation of H_2O_2 was well consistent with the absorption spectrum of **1**. These findings indicate that H_2O_2 is produced by the excitation of **1** on the anode through a quantitative process with the obtained faradaic current. It was concluded that water acted as an electron donor on the anode, while molecular oxygen acted as an electron acceptor under aerated conditions, and several different types of ions also acted as an electron acceptor under argon atmosphere on the cathode. It is suggested that the photooxidation of water to form H_2O_2 was initiated by a photoinduced electron transfer from the excited singlet state of **1** to TiO_2 to generate the porphyrin radical cation ($\mathbf{1}^{+\bullet}$), which underwent a proton dissociation from the hydroxo axial ligand to give a Ge-oxyl complex as a key intermediate for a two-electron activation of water to form hydrogen peroxide.

1. Introduction

It is most desirable to develop water oxidation systems for the construction of artificial photosynthesis [1–3]. There are many reports on the electrochemical oxidation of water to induce oxygen evolution through four-electron transfer processes using metal complexes as a catalyst [4–10]. However, there are few studies on the photochemical oxidation of water through the four-electron transfer [11]. In the photochemical process, for example, a period of time of the order of seconds is required to achieve the stepwise four-electron oxidation of a metal complex, because the photon-flux is very rarefied in natural sunlight [12]. Therefore, the unstable highly oxidized state of the metal complex must survive during the second-order timescale in order to induce the four-electron transfer with a photochemical process. It is, thus, difficult to achieve these processes under such conditions due to the short lifetime of the oxidized species, even in the one-electron-oxidized case. This problem is referred to as the "photon-flux-density problem" [12].

On the other hand, we have focused on the two-electron oxidation of water using metal complexes as an alternative pathway for water activation and found that the oxygenation of alkenes to form epoxides can be sensitized by metalloporphyrins such as di(hydroxo) porphyrininato Sb^{V} [13], Sn^{IV} complexes [14–16], or carbonyl-coordinated ruthenium porphyrin complex [17–19] in the presence of water as both an electron and oxygen atom donor. In this system, a key intermediate capable of activating the water molecule is thought to be a metal-oxo complex formed by photoinduced electron transfer (PET) to an electron acceptor and the subsequent proton dissociation of the axial hydroxo ligand. We elucidated that these reactions proceed with a two-electron oxidation process using the energy of one

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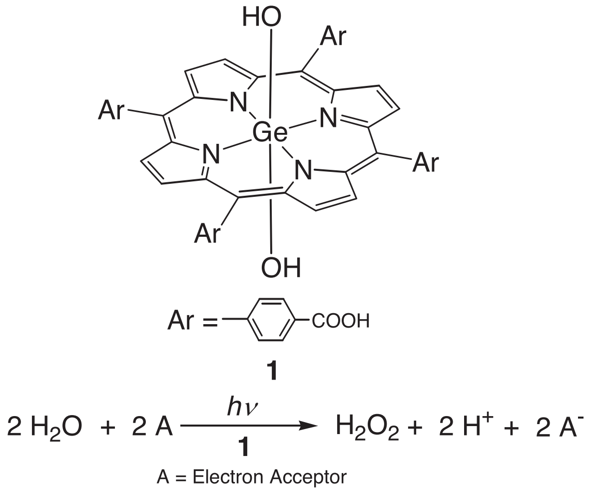
photon, so that they are free from the "photon-flux-density problem" [20]. Accordingly, it can be expected that it would be possible to achieve the two-electron oxidation of water to form hydrogen peroxide (H_2O_2), if a photochemical water oxidation system were properly fabricated using a metal complex.

Recently, we have found that the two-electron oxidation of methanol to formaldehyde can be sensitized by a di(hydroxo) porphyrin Ge^{IV} complex, suggesting that the oxidation proceeds through a mechanism involving hydrogen abstraction from methanol with a Ge-oxyl complex formed by PET to an electron acceptor, with the subsequent proton dissociation of the axial hydroxo ligand [21]. We have also succeeded in the generation of the Ge-oxyl complex in a photovaltaic cell (PVC) composed of an ITO electrode coated by tetrakis-(4-carboxylphenyl) porphyrinatogermanium(IV) (**1**)-adsorbed titanium oxide (TiO_2) particles (**1**/TiO_2/ITO) as an anode and a Pt electrode as a cathode. In this PVC system, it was elucidated that the short-circuit photocurrent was obtained by PET to TiO_2 from the excited singlet state of **1** to form a Ge-oxyl complex, with subsequent hydrogen abstraction from aliphatic alcohols by the Ge-oxyl complex [22]. These results indicate that the photooxidation of water with a Ge-oxyl complex can be expected to be induced by this PVC system. Here, we report the formation of hydrogen peroxide (H_2O_2) as a two-electron oxidation product from water using the **1**/TiO_2/ITO electrode in the presence of various electron acceptors (Scheme 1).



Scheme 1. **1**-sensitized oxidation of water to form H_2O_2 with various electron acceptors (A).

2. Experimental

2.1. Materials and instruments

H_2O_2 aqueous solution, L-ascorbic acid, potassium iodate, iron (III) nitrate hydrate ($Fe(NO_3)_3{\cdot}9H_2O$), ceric ammonium nitrate ($Ce(NH_4)_2(NO_3)_6$) tetraethylammonium tetrafluoroborate ($Et_4N^+BF_4^-$), germanium tetrachloride ($GeCl_4$) and organic solvents were purchased from Wako Pure Chemical Industries as guaranteed reagent grade (GR) and used without further purification. Oxo [5,10,15,20-tetra(4-pyridyl) porphyrinato]titanium(IV) (Ti-oxo porphyrin) was purchased from Tokyo Kasei as GR reagent for the quantitative analysis of the produced hydrogen peroxide. Potassium hexachloroplatinate (IV) ($K_2[PtCl_6]$) and tetraphenylporphyrin (H_2tpp) were also purchased from Aldrich as GR reagent. **1** was synthesized according to the literature [22]. UV–vis absorption of the solutions was obtained on a JASCO V-500 spectrophotometer. The short-circuit current of the PVC experiment was measured by a microammeter (8340A, ADC Corporation, Japan). Light of 550 nm (4.4 mW cm^{-2}) was isolated from the output of a 500-W Xe lamp using a monochromator (L12194, Hamamatsu Photonics K. K, Japan).

2.2. Photovoltaic cell

Transparent ITO glass electrodes (20 mm × 16 mm × 3.2 mm) coated with TiO_2 particles (0.8 cm^2 of the coating area) were purchased from Dyesol Industries Pty. Ltd. (Australia). The preparation of **1**/TiO_2/ITO was performed by a dipping TiO_2/ITO for 2 h in a methanol solution of **1**. The amount of adsorbed **1** was estimated to be 7.0×10^{-8} mol cm^{-2}. The area of **1**-modified TiO_2 electrode used for the photoreaction was 0.8 cm^2. The PVC was composed of **1**/TiO_2/ITO as an anode, Pt wire as a cathode, and aqueous solution (12 cm^3) of $Et_4N^+BF_4^-$ (0.1 M) as an electrolyte. The anode and cathode chambers were separated by a glass filter (Fig. 1).

2.3. Photoreaction

The short-circuit photocurrent was normally measured under irradiation of the anode with monochromic light (550 nm) under air or argon atmospheres in the presence of electron acceptors in the cathode chamber at 20 °C. The identification and quantitative analysis of H_2O_2 was carried out for the irradiated solution in the anode chamber by absorption spectrophotometry using a Ti-oxo porphyrin complexing reagent [23].

3. Results and discussion

3.1. Formation of H_2O_2 under aerated conditions

When the **1**/TiO_2/ITO anode was irradiated with 550-nm light in aqueous electrolyte solution under aerated conditions in the PVC system, the short-circuit current was observed to respond to on-off irradiation switching (Fig. 2). The observed photocurrent was nearly constant, even under continuous irradiation for 1 h (Fig. 3). The short-circuit current density (J_{sc}) and the incident photon-to-current conversion efficiency (IPCE) were estimated to be 5.5 μA cm^{-2} and 0.28%, respectively. After irradiation for 1 h, H_2O_2 (75 nmol) was detected only in the anode chamber, not in the cathode chamber, as shown in run 1 of Table 1. On the other hand, when the aqueous electrolyte solution was bubbled with argon gas, the J_{sc} was much smaller (IPCE = 0.05%) than that under aerated conditions. Moreover, only trace amounts of H_2O_2 (5 nmol) were detected in the anode chamber, whereas no H_2O_2 was produced in the cathode chamber (run 2). Although a larger photocurrent

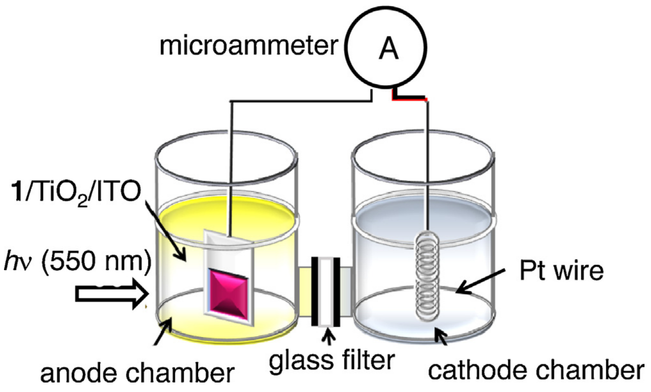


Fig. 1. Photovoltaic cell (PVC) with **1**/TiO_2/ITO and Pt wire as an anode and cathode, respectively.

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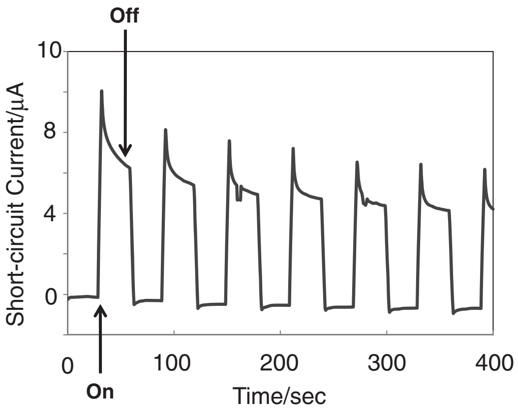

Fig. 2. Short-circuit current observed under visible light irradiation (550 nm) and in the dark in aqueous electrolyte solution. Irradiation was started at the mark "ON" and stopped at the mark "OFF".

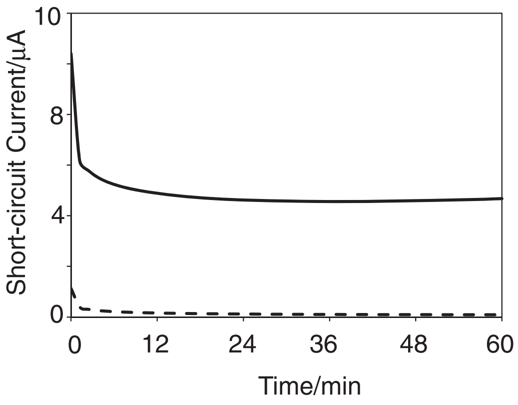

Fig. 3. Time-course plots of the short-circuit currents generated by continuous visible light irradiation (550 nm) under air (—) and argon (——) atmospheres.

Table 1
Production of H_2O_2 with various electron acceptors in **1**-sensitized PVC system.[a]

Run	Acceptor	H_2O_2 (nmol)	FE (%)[b]	IPCE (%)
1	O_2[c]	75	92	0.28
2	O_2[d]	5	30	0.05
3	Ce^{4+}	51	88	0.20
4	Fe^{3+}	55	92	0.21
5	IO_3^-	48	91	0.15
6	$[PtCl_6]^-$	54	99	0.19

[a] Under argon atmosphere.
[b] Faradaic efficiency.
[c] Under air atmosphere.
[d] Low concentration of O_2 in aqueous electrolyte solution under argon atmosphere.

($J_{sc} = 130\ \mu A\ cm^{-2}$) was obtained using L-ascorbic acid as an electron donor in the anode chamber, H_2O_2 was not detected at all in the cathode chamber under argon atmosphere. These results strongly suggest that water acted as an electron donor on the anode and molecular oxygen acted as an electron acceptor as a consequence of the four-electron reduction to water on the Pt cathode. Fig. 4 shows the action spectrum for the production of H_2O_2 under aerated conditions. The action spectrum is well consistent with the absorption spectrum of **1**; this consistency strongly indicates that the observed production of H_2O_2 was induced by the photochemical sensitization of **1**.

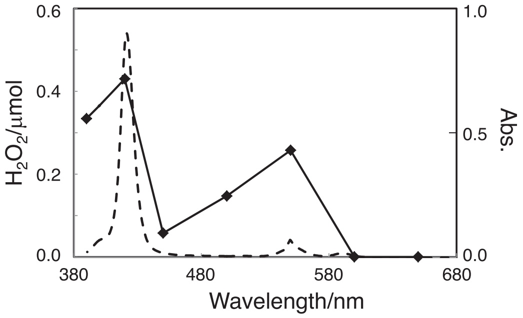

Fig. 4. Action spectrum for the formation of H_2O_2 (◆) along with absorption spectrum of **1** (——).

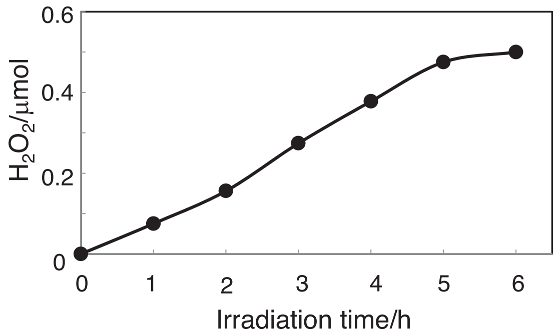

Fig. 5. Time-course plot for the formation of H_2O_2 in **1**-sensitized PVC system.

Fig. 5 shows the time-course plot for the production of H_2O_2 from water in the PVC system. H_2O_2 was produced in amounts that increased nearly linearly vs. irradiation time, without an induction period. The turnover number (TON) for the formation of H_2O_2 was estimated to be 9.0 after 6 h of visible light irradiation. Furthermore, the faradaic efficiency (FE) for the production of H_2O_2 was estimated to be 92 % (run 1 of Table 1). These results indicate that the production of H_2O_2 should proceed with both a catalytic cycle of **1** and a nearly quantitative process for the obtained faradaic currents. After irradiation for 6 h, however, **1** was decomposed and desorbed from TiO_2. The decomposition of **1** was not occurred with backward reactions of formed H_2O_2, because the formation of H_2O_2 was observed even in the presence of small amount of H_2O_2 (0.5 μmol) using new **1**/TiO_2/ITO anode under the irradiation.

It is expected that the production of H_2O_2 strongly depends on the change of pH in the aqueous electrolyte solution, because two protons are released in the production of one H_2O_2 from two water molecules in an overall oxidation (Scheme 1). In fact, it was observed that the production of H_2O_2 in the PVC system tended to decrease with the increase of proton concentration (Fig. 6). This result indicates that the production of H_2O_2 can be induced by the

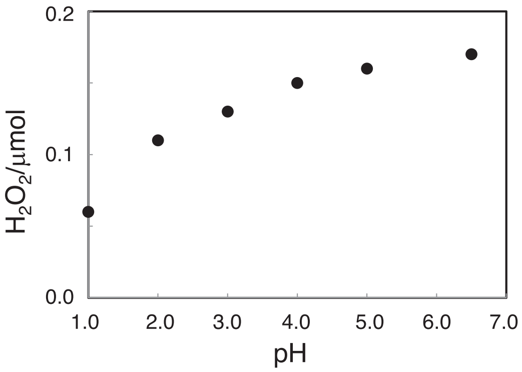

Fig. 6. pH effect upon the formation of H_2O_2 in **1**-sensitized PVC system.

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oxidation of water. Although an enhancement of H_2O_2 production was expected for irradiation under basic conditions, the desorption of **1** from TiO_2 was accelerated under at pH > 8, resulting in the complete absence of formation of H_2O_2 under basic conditions. The observed desorption may be rationalized by the repulsive force between the carboxylate anion group of **1** and the anionic TiO_2 surface under basic conditions.

3.2. Formation of H_2O_2 in the presence of various electron acceptors under argon atmosphere

The production measurements of H_2O_2 from water were performed in the presence of various electron acceptors except molecular oxygen under argon atmosphere in the PVC system (runs 3–6 of Table 1). When Ce^{4+}, Fe^{3+}, IO_3^- and $[PtCl_6]^-$, which are well known as typical effective electron acceptors, were used in the cathode chamber, H_2O_2 was produced in the anode chamber for all cases. Their IPCE and FE values were nearly the same as those for the case of molecular oxygen as an electron acceptor. In particular, FE reached 99% in the case of $[PtCl_6]^-$. However, the catalytic reaction of **1** at the anode can be rate-determining in the PVC system, since the production of H_2O_2 did not depend on the type of electron acceptor in general. These results again strongly suggest that the oxygen source of H_2O_2 is water molecules themselves, because H_2O_2 was obtained even in the absence of molecular oxygen.

*3.3. DFT calculation of the one-electron oxidized species of **1***

The generation of the photocurrent induced by the excitation of **1** adsorbed on the TiO_2 nanoparticles clearly indicates that there is an electron injection from the excited state of **1** into the conduction band of TiO_2 to form the one-electron oxidized form of **1**. As we had already reported, a Ge-oxyl complex (one-electron-oxidized radical form) was presumed to be the key intermediate in the photochemical C-H activation sensitized by **1** [21] and the photochemical fuel cell device by **1** [22]. In the current PVC system of forming H_2O_2, the one-electron-oxidized radical form, Ge-oxyl complex, is also supposed to be the key intermediate. To rationalize this hypothesis, the electronic structure of the one-electron oxidized form of **1** was estimated by theoretical analysis with DFT calculations (Gaussian09 UB3LYP/6-31G* SCRF (PCM, solvent = water). Taking the axial ligands of **1** to be dihydroxo groups, the DFT calculation of the one-electron-oxidized Ge complex (cation radical: **I**) in water indicates that the electron spin density is mostly delocalized on the porphyrin ring, while its deprotonated species (**II**) has a dominant spin population on the axial ligand oxygen, as shown in Figs. 7a and b, where the spin population was expressed by the size of the blue lobe on each atom by use of the Jmol software package [24]. Species **II** thus has mostly oxygen radical character in its axial ligand (Fig. 7b), and the hydrogen abstraction from a proper hydrogen atom donor would be rationalized by the electronic structure, as presumed [21]. Here, it should be the pointed out that there is a question as to whether or not the formation of H_2O_2 is feasible in the expected process between the Ge-oxyl radical and the hydroxide ion. To obtain deeper insight into this point, each heat of formation before and after the reaction of the Ge-oxyl complex (**II**) with the hydroxide ion was calculated. Very interestingly, the reaction of Ge-oxyl radical (**II**) with hydroxide ion to form Ge-hydroperoxy complex (**III**) is fairly exothermic, with $\Delta H = -31.41$ kcal/mol. The formation of hydroperoxy complex (**III**) is thus well rationalized. Another curious point would be how the formation of H_2O_2 actually proceeds on the anode. The electronic structure analysis should provide crucial information about this. As shown in Fig. 7c, the Ge-hydroperoxy complex (**III**) generated through the reaction of Ge-oxyl complex (**II**) has still be in a doublet state with a spin. The spin in complex **III** is indicated to be delocalized on the porphyrin ring, but mostly on the meso-position of the ring (~20% population); specifically, complex **III** has an electronic structure as the radical anion of the porphyrin. This strongly suggests that the Ge-hydroperoxy complex (**III**) as the radical anion of the porphyrin can readily inject the second electron to the conduction band of TiO_2. As a conclusion, the sensitized one-electron injection from the excited state of **1** to the conduction band of TiO_2 can initiate the reaction with the hydroxide ion to form Ge-hydroperoxy complex (**III**) in the form of the radical anion on the porphyrin ring. The complex (**III**) would subsequently inject the second electron to TiO_2, leading to a two-electron activation of water to form H_2O_2, as discussed below.

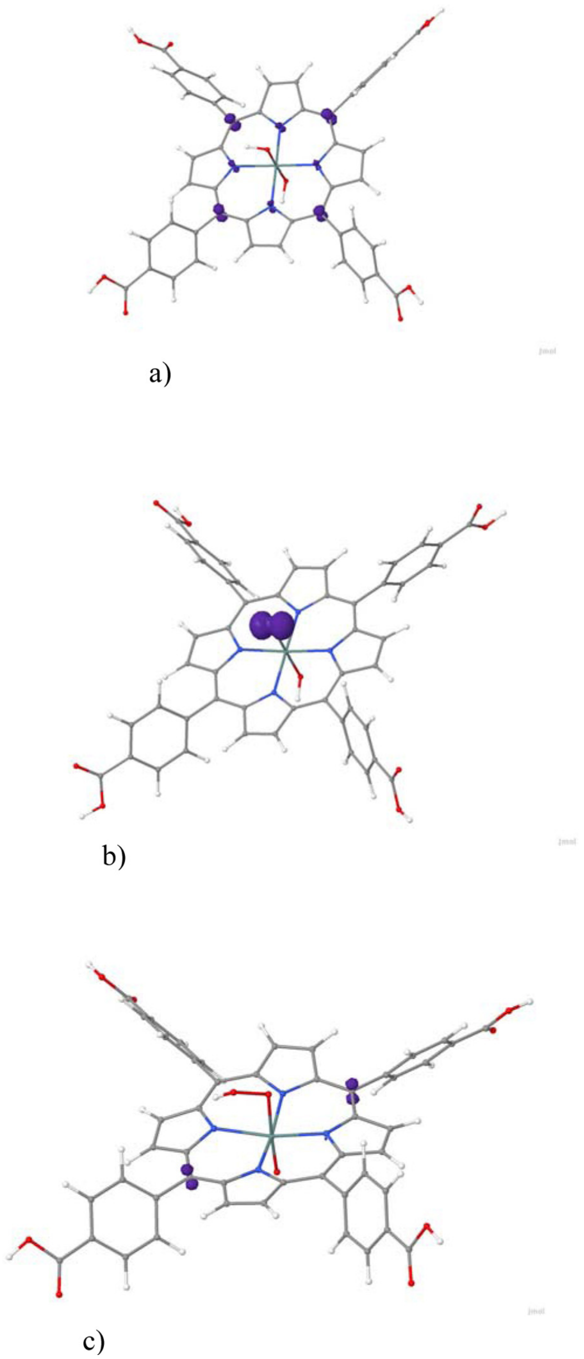

Fig. 7. Electronic structures and spin densities of (a) the one-electron oxidized form of **1** (Intermediate **I**), (b) the deprotonated form of **I** (Intermediate **II**), and (c) the reaction product between **II** and hydroxide ion (Intermediate **III**).

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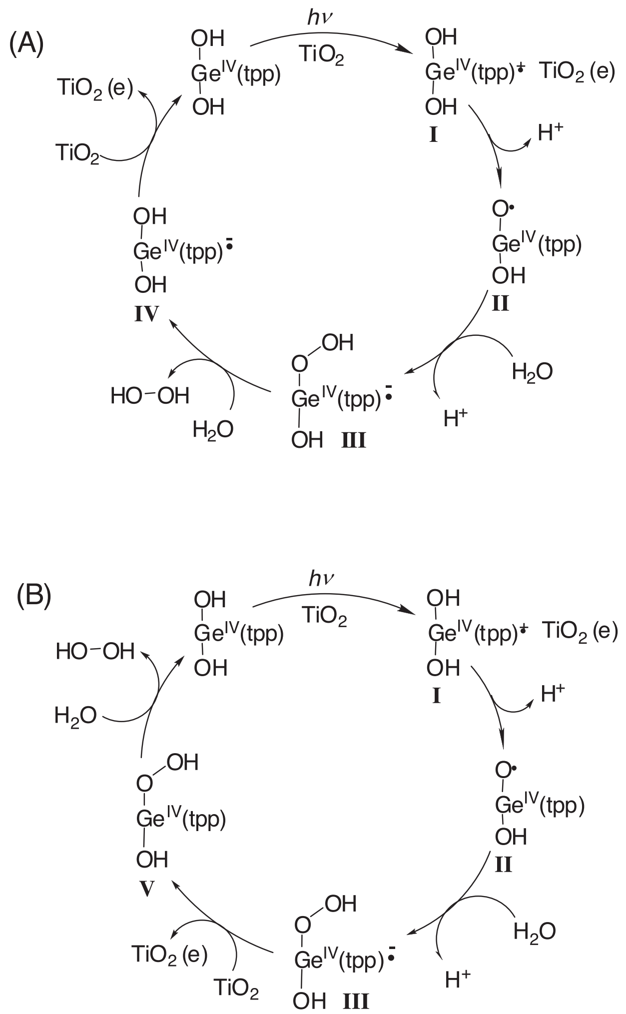
3.4. Plausible reaction mechanism of water oxidation to H_2O_2

On the basis of the experimental results and theoretical analysis, a plausible reaction mechanism is shown in Scheme 2. Upon visible light irradiation, an electron transfer process from the excited singlet state of **1** to TiO_2 takes place to form the radical cation of **1** (intermediate **I**), which is followed by deprotonation to give a Ge-oxyl complex (intermediate **II**). A nucleophilic attack of water to complex **II** proceeds to form the intermediate **III**, which has the character of a porphyrin radical anion, as analyzed above. After the formation of complex **III**, there may be two probable routes leading to the formation of H_2O_2. One of the processes would be that the axial hydroperoxo ligand of **III** is exchanged with a hydroxo ligand to form intermediate **IV**, resulting in the release of H_2O_2. The intermediate **IV** returns to the original state of **1** by electron transfer from **IV** to TiO_2 (route of A). The other pathway would be an electron transfer from **III** to TiO_2 at first to form Ge-hydroperoxy complex (**V**) followed by substitution of the ligand with water to recover the starting complex **I** (route of B). As discussed above, the electron injection into TiO_2 proceeded via the route of B preferently. The electrons injected into TiO_2 can move to the Pt cathode through the external circuit to reduce the electron acceptor ions or molecular oxygen, resulting in the short-circuit photocurrent.



Scheme 2. Two plausible mechanisms (routes of A and B) of water oxidation to H_2O_2 in **1**-senstized PVC system.

4. Conclusion

It was elucidated that the photochemical two-electron oxidation of water to H_2O_2 could be selectively induced by using a Ge-oxyl complex generated by PET from **1** to TiO_2 under visible light irradiation in a PVC system. The strong electrophilicity of the Ge-oxyl complex can induce the activation of water, leading to the production of H_2O_2 through a stepwise two-electron transfer to TiO_2. This is the first example of a water oxidation by a photochemical process using a Ge^{IV}-porphyrin complex. Among the studies on water oxidation, either transition metal-complexes [8,10] or noble metal complexes [7,9] have been nearly always been employed as the catalyst. Therefore, this study, in which water oxidation was achieved by using a non-transition metal (main group element) complex, may be significant from the viewpoint of an "elemental strategy " in photocatalysis.

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