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Unexpected photo-initiated oxidation of antimony in (tetra-*tert*-butyl) phthalocyaninatoantimony(III) complex in the presence of singlet oxygen acceptors

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Abstract

The title complex cation, $[Sb(tbpc)]^+$ (where tbpc denotes tetra(*tert*-butyl)phthalocyaninate, $C_{48}H_{48}N_8{}^{2-}$), was gradually bleached under irradiation with visible light ($900 > \lambda/\mathrm{nm} > 600$) in aerated nonaqueous solvents, such as CH_2Cl_2, $CHCl_3$, benzene, chlorobenzene. On the other hand, irradiation under the same conditions but in the presence of 1,3-diphenylisobenzofuran (DPBF) caused slow oxidation of $[Sb(tbpc)]^+$ to the corresponding antimony(V) derivatives, $[Sb(tbpc)LL']^+$, (L and L′ denote monoanionic axial ligands containing oxygen as the donor atom), which was monitored by optical absorption and ESI-MS spectra of the photolyzed solutions. Both the photobleaching and oxidation have efficiently been inhibited by preliminary addition of β-carotene in photolyzed solutions, indicating that photosensitization of singlet oxygen ($^1O_2$) by $[Sb(tbpc)]^+$ itself is involved. The use of furans (except dibenzofuran) or oxazoles instead of DPBF gave rise to similar oxidation but not in the case of the other type $^1O_2$-acceptors, such as 9,10-diphenylanthracene, tetraphenylcyclopentadienone, or 2,3-dimethyl-2-butene, indicating that formation of ozonide-type *endo*-peroxide through 1,4-cycloaddition with $^1O_2$ is essential. Peroxides, such as EtOOH and H_2O_2, generated through nucleophilic attack to the ozonide by EtOH and H_2O (present in the solvent) respectively, are considered to oxidize $[Sb(tbpc)]^+$ to the antimony(V) species. Photochemistry of antimony–phthalocyanine complex has been studied for the first time of pnicogen derivatives of phthalocyanine.

Keywords: Phthalocyanine; Antimony; Singlet oxygen; Oxidative addition

1. Introduction

Photochemistry involving phthalocyanines and/or porphyrins has attracted much attention from the viewpoints of photo-induced hydrogen evolution toward fuel cells [1–3], models for natural photosynthesis and applications to artificial photosynthesis [3], and photosensitization of singlet oxygen ($^1O_2$) toward photodynamic therapy of tumors [4–10] or degradation of pollutants in wastewater [11–14]. Since phthalocyanines form complexes with essentially all metal elements [15,16], photochemistry of numbers of complexes ligating these macrocycles has so far been intensively investigated [1,4–6]. However, no photochemical study on derivatives of the group-15 elements has been done although numbers of photochemical studies on porphyrin analogues have been reported [17–23]. This is rather surprising because the presence of heavy atom like antimony or bismuth in the cavity of phthalocyanine macrocycle is expected to facilitate singlet–triplet intersystem crossing in the phthalocyanine π-system due to a metal-induced strong spin–orbit coupling [24] and hence their photochemistry could prove very intriguing. This is probably because little was known about derivatives of group-15 elements until we published the first antimony(V) and bismuth(III) complexes of phthalocyanine in 1994 [25–27]. Even today, studies on pnicogen derivatives of these macrocycles are still uncommon [25–39]. Thus, this work is the first report on photochemistry not only of antimony–phthalocyanines but also of those of the entire group-15 elements.

Another interest stems from the ease of photochemical accessibility from low- to high-valent antimony phthalocyanines

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or vice versa because antimony(III)–porphyrin analogues are known to be photosensitive and to be readily oxidized to antimony(V) derivatives upon irradiation with visible light in aerated solutions [23]. In addition, quite recently, we have prepared some antimony(V)–phthalocyanines from the corresponding antimony(III) derivatives via oxidative addition process [35,36]. Such conversion can work as a two-electrons transfer catalyst like the reaction center of cytochrome P-450 in photosynthetic system [17–23]. This work was also undertaken to ascertain if photo-induced conversion from antimony(III) to antimony(V) can occur.

2. Experimental

2.1. Materials

The synthesis of the antimony complex, $[Sb(tbpc)]I_3$ (where tbpc denotes tetra-*tert*-butyl-phthalocyaninate, $C_{48}H_{48}N_8{}^{2-}$), is described elsewhere [31]. Dihydroxo(tetra-*tert*-butyl-phthalocyaninato)antimony(V), $[Sb(tbpc)(OH)_2]^+$, was readily prepared by heating $[Sb(tbpc)]I_3$ with *tert*-butyl perbenzoate in CH_2Cl_2 at 40 °C [35,36]. Metal-free (H_2tbpc), zinc ([Zn(tbpc)]) [40], and cobalt ([Co(tbpc)]) [41] analogues were prepared according to the literature methods. Chlorobenzene of reagent grade was passed through alumina prior to its use. All the solvents used for photolyses and spectral measurements were of reagent grade and used as received unless otherwise noted. Commercially available β-carotene of reagent grade (Wako) was handled under argon atmosphere until it was added into solutions. Methylene Blue (Lancaster) and $^1O_2$ acceptors studied in this work (Fig. 1; 2,5-diphenyloxazole (Kanto Chemicals), 1,3-diphenylisobenzofuran (DPBF; Aldrich), 2,5-diphenylfuran (Lancaster), 4,5-diphenyl-2-(2-methoxyphenyl)oxazole (Aldrich), 2-methyl-4,5-diphenyloxazole (Aldrich), dibenzofuran (Tokyo Kasei), tetraphenylcyclopentadienone (Tokyo Kasei), 9,10-diphenylanthracene (Aldrich), and 2,3-dimethyl-2-butene (Tokyo Kasei)) were of reagent grade and used as received. All the other chemicals were of reagent grade and used without further purification.

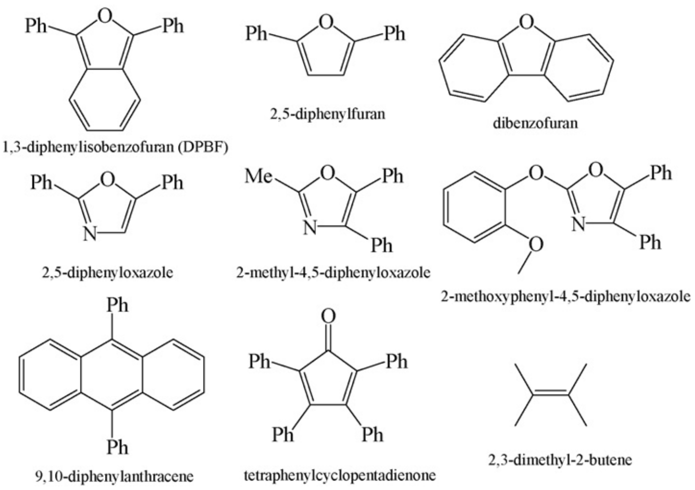

Fig. 1. Molecular structures of $^1O_2$ acceptors studied in this work.

2.2. Photochemical experiments

The experimental set-up is as follows: in a typical experiment, a 2 ml of chloroform solution containing $[Sb(tbpc)]^+$ (10^{-6}–10^{-4} M) and DPBF (10^{-5}–10^{-3} M) was introduced to a 1-cm quartz cell and then photolyzed in the Q-band region (600–900 nm) with a Schott Halogen lamp (100 mW) equipped with a 600-nm glass cut-off filter (HOYA) and cold filter were used to filter off light of shorter (<600 nm) and longer (>900 nm) wavelengths for known time. In another typical experiment, a 1.5 ml of $CHCl_3$ solution containing ca. 1×10^{-3} M of DPBF and ca. 1×10^{-5} M of the other dye (Methylene Blue, H_2tbpc, [Zn(tbpc)], or [Co(tbpc)]) was irradiated for known time, to which a 0.5 ml of $CHCl_3$ solution containing $[Sb(tbpc)]^+$ (ca. 1×10^{-5} M) was added. The power of the radiation was tuned with a variable voltage transformer so that the magnitude at the surface of the optical cell was ca. 2 mW/cm^2, which was monitored by using a HIOKI 3664 optical power meter. In some experimental runs, a 690-nm laser diode (Leonix; 35 mW) was used instead of the halogen lamp.

2.3. Measurements

All the measurements of optical absorption spectra were performed with a Shimadzu UV-160A or a Hitachi U-3500 spectrophotometer at room temperature (24 ± 1 °C). All the ESI-MS spectra were measured with a Waters Platform LCZ (ZMD) spectrometer after the reaction mixtures were diluted with acetonitrile just prior to the measurements.

3. Results and discussion

3.1. Photobleaching

Chloroform and dichloromethane solutions containing $[Sb(tbpc)]I_3$ are quite stable in the dark for a few months irrespective of the presence of oxygen. In benzene and chlorobenzene solutions, a small portion (ca. 2% based on absorption spectra) of $[Sb(tbpc)]^+$ has been found demetallated to form H_2tbpc over a few months. In any cases $[Sb(tbpc)]I_3$ is stable for a day or two and no bleaching occurred without light. It should be noted that donor solvents, such as DMF or THF, have been found unsuitable for this study because a considerable amount of the complex was demetallated within a few hours [31]. However, under visible light irradiation, $[Sb(tbpc)]I_3$ in aerated solutions has been bleached over a period of a few hours (Fig. 2). The stability of $[Sb(tbpc)]^+$ against photobleaching was evaluated by calculating the decay of the Q-band to the first-order kinetics in the concentration of the complex according to $\ln(A_t/A_0) = -k_d t$, where A_t and A_0 denote absorbance at irradiation time, t, and $t = 0$, respectively, and the k_d is the kinetic rate constant [42,43]. The k_d value obtained in this way (1.21×10^{-2} min^{-1}) is essentially the same as that for H_2tbpc under the same conditions (1.17×10^{-2} min^{-1}). On the other hand, when solutions were preliminary deoxygenated by bubbling with dry argon, such photobleaching was significantly inhibited. It is widely believed that the photosensitizer (dye)

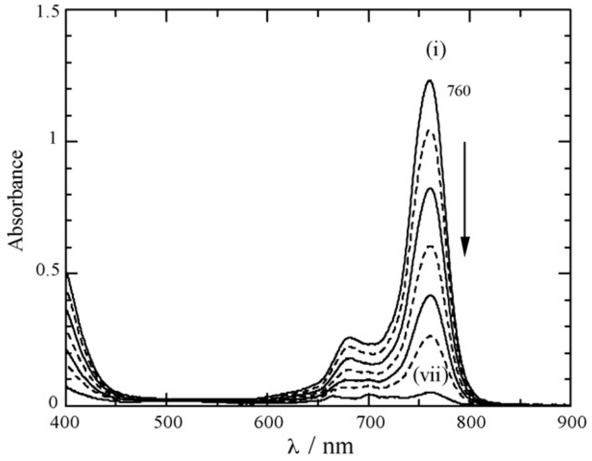

Fig. 2. Spectral changes of aerated $CHCl_3$ solution containing $[Sb(tbpc)]I_3$ (1.0×10^{-5} M) under irradiation with visible light (900 > λ/nm > 600). (i–vi) Every 36-min irradiation; (vii) after 252-min irradiation.

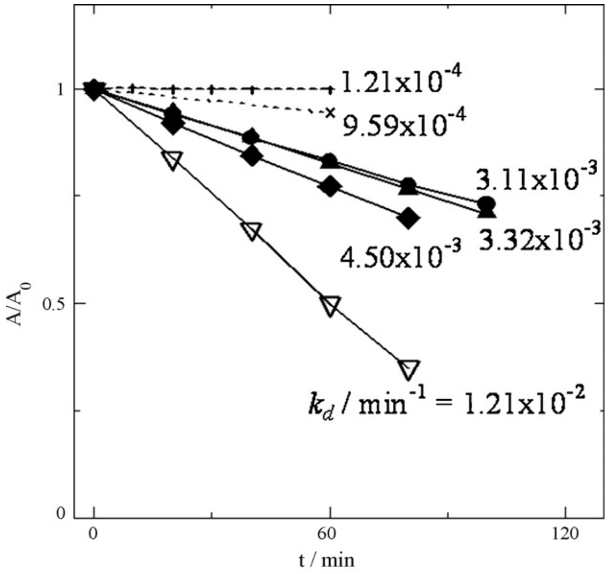

Fig. 3. Effects of β-carotene on rates of photobleaching of $[Sb(tbpc)]^+$. Open triangle; without β-carotene, closed square; [β-carotene] = 0.156 mM, closed triangle; [β-carotene] = 1.56 mM, closed circle; [β-carotene] = 15.6 mM; broken line; in the dark; dotted line in Ar-saturated solution. The k_d values were calculated assuming first-order kinetics (see text).

is excited to its triplet state (via its singlet state), and then transfers its energy to ground-state triplet oxygen ($O_2(^3\Sigma_g)$) to form excited-state singlet oxygen ($O_2(^1\Delta_g)$), through the so-called the Type II mechanism [44,45]. As the antimony(III) complex does not emit fluorescence around the Q-region at room temperature [31], it is likely that the singlet–triplet intersystem crossing has been facilitated via a metal-induced strong spin–orbit coupling. As is shown in Fig. 3, the k_d value decrease with an increase in β-carotene concentration, which is well known to physically quench $^1O_2$ [45,46],[1] indicating that generation of $^1O_2$ is involved in this photobleaching. On the other hand, as the photobleaching was little inhibited by the addition of 2,6-di-*tert*-butylphenol (radical scavenger [47,48]), contribution of O_2^- has been found insignificant. Furthermore, phthalimide derivative (4-*tert*-butylphthalimide in this case), which is known as the main product of photooxidation of phthalocyanines [49], was detected in the photolyzed solutions by ESI-MS ($m/z = 203$). Therefore, it is concluded that photosensitization of $^1O_2$ by the antimony–phthalocyanine should trigger the photobleaching[2] (contribution of I_3^- to the photochemical process has been found insignificant if any as discussed later in Section 3.2.1).

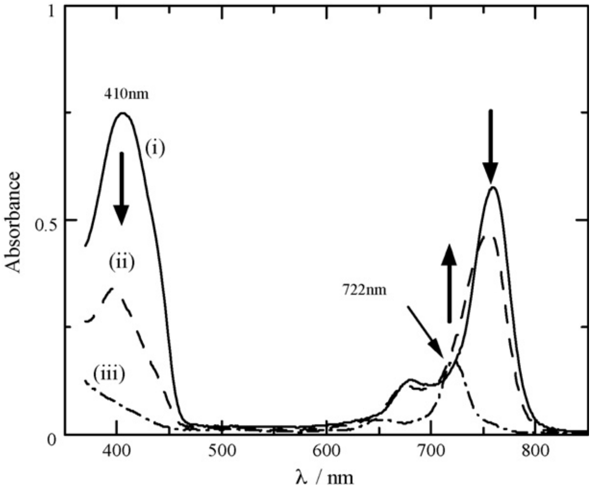

Fig. 4. Spectral changes of aerated $CHCl_3$ solution containing a mixture of $[Sb(tbpc)]I_3$ (5.0×10^{-6} M) and DPBF (3.4×10^{-5} M) (i) before irradiation, (ii) upon 6- and (iii) 12-min irradiation.

3.2. *Oxidation of the central antimony*

3.2.1. *Contribution of $^1O_2$*

Our attempts to determine the $^1O_2$ quantum yield for $[Sb(tbpc)]^+$ by using DPBF and the other acceptors were unsuccessful due to the occurrence of unexpected oxidation of the central antimony(III) as described below. Fig. 4 shows typical spectral changes in aerated solution containing $[Sb(tbpc)]^+$, which was photolyzed in the presence of DPBF. The 410-nm band due to DPBF disappeared with the elapse of time under irradiation, but at the same time the 760-nm Q-band of $[Sb(tbpc)]^+$ diminished more rapidly than in the absence of DPBF (it should be noted that $[Sb(tbpc)]^+$ does not react with DPBF in the dark at least for 24 h). Surprisingly, in addition to that, a new absorption band appeared at around 720 nm when the solutions were irradiated for 12 min, which is character-

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[1] Attempts to quench $^1O_2$ with 1,8-diazabicyclooctane (DABCO) and tetrabutylammonium azide, which are also known as $^1O_2$ quenchers [44,45], were unsuccessful because $[Sb(tbpc)]^+$ was readily demetallated upon the addition of the reagents into the solution.

[2] Attempts to detect luminescence at around 1270 nm, which is emitted from $O_2(^1\Delta_g)$ [44,45], by irradiating aerated $CHCl_3$ solutions containing $[Sb(tbpc)]^+$, H_2tbpc, [Zn(tbpc)], or Methylene Blue using a 690-nm laser diode (ca. 10 mW at the surface of the optical cell) were unsuccessful. It should be noted that sharp luminescence centered at 1272 nm was detected when the same Methylene Blue solutions were irradiated under the same conditions but by using an Ar-laser (514.5 nm, 17 mW) instead and hence the instrumentation was considered done properly.

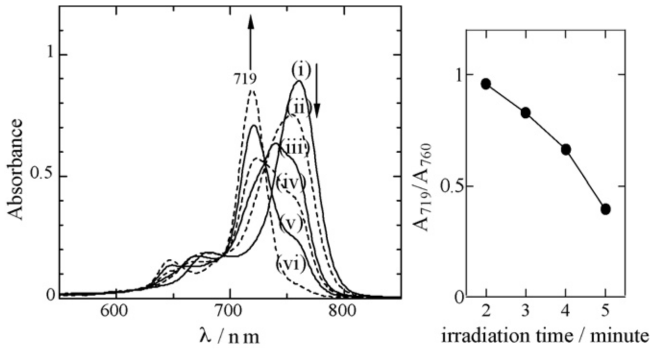

Fig. 5. (Left) Spectral changes aerated $CHCl_3$ solution containing $[Sb(tbpc)]I_3$ (1.5×10^{-5} M) and DPBF (7.2×10^{-4} M) after 2-min irradiation; (i) before irradiation; (ii) just after irradiation, (iii) 5, (iv) 10, (v) 15, and (vi) 60 min later in the dark; (Right) plots of the yields of antimony(V) derivatives (vs. $[Sb(tbpc)]^+$) as A_{719}/A_{760} against irradiation time.

istic of antimony(V)–phthalocyanines [25,29,30,32,33,35–37]. Prolonged irradiation has decreased the yield of the new species.

In order to investigate this unexpected oxidation of antimony, which was triggered by irradiation of visible light, we have photolyzed aerated solutions containing a mixture of $[Sb(tbpc)]^+$ and DPBF for known time and then monitored the spectral changes in the dark at regular time intervals. A typical experimental result is shown in Fig. 5 (left). Although the spectral difference between before and just after the irradiation was negligibly small, the 760-nm Q-band of the initial species decreased in intensity with elapse of time and incidentally a new band appeared at the blue flank of the Q-band. This new band (730–740 nm) grew in intensity over several minutes until another new band began to grow around 720 nm. The final spectrum is essentially the same as that of $[Sb(tbpc)(OH)_2]^+$ [35,36]. Essentially the same spectral changes were observed when a 690-nm laser diode was used instead of the halogen lamp. Similar oxidation process was also observed in CH_2Cl_2, benzene, and chlorobenzene. Mass spectra (Fig. 6) of the photolyzed solutions show some pairs of twin peaks attributable to phthalocyanine complexes containing one antimony ion per molecule based on their isotope patterns (resulting from the presence of ^{121}Sb and ^{123}Sb). The most intense four pairs at around *m/z* = 857&859, 919&921, 947&949, and 993&995 are, respectively, assigned as $[Sb(tbpc)]^+$ (the starting material), $[Sb(tbpc)(OH)(OEt)]^+$, $[Sb(tbpc)(OEt)_2]^+$, and $[Sb(tbpc)(salc)]^-$ (where salc denotes salicylate, $C_7H_4O_3{}^{2-}$). When the irradiation time was shorter (1 min.), the 993&995 pair was the most intense. On the other hand, this pair diminished and hence the 919&921 and 947&949 pairs became more prominent when the irradiation was prolonged (over 5 min.). This suggests that the species showing the 993&995 pair is the intermediate species that appears in the spectral changes during the oxidation (λ_{max} = ca. 735 nm) as discussed later in Section 3.2.3. Therefore, the species showing the 720-nm band has been found a mixture of antimony(V) complexes with axial ligands containing oxygen as the donor atom. The yields of the antimony(V) derivatives versus the starting $[Sb(tbpc)]^+$ for respective experimental run have been evaluated as the ratio of the absorbance of the oxidation product at 719 nm (when it has reached to the maximum) to that of the initial species at 760 nm (i.e., the Q-band of $[Sb(tbpc)]^+$), of which

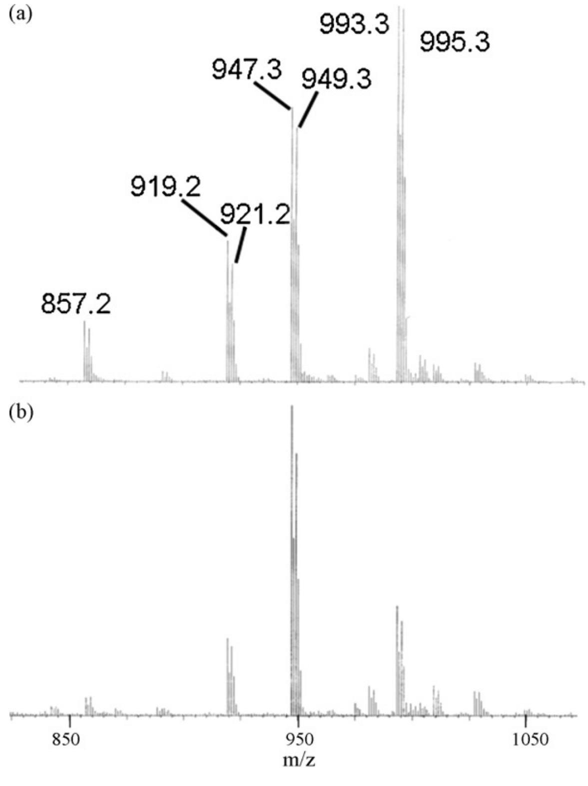

Fig. 6. The ESI-MS spectra of the photolyzed $CHCl_3$ solutions containing $[Sb(tbpc)]I_3$ (1.5×10^{-5} M) and DPBF (7.2×10^{-4} M) after (a) 1-min and (b) 5-min irradiation.

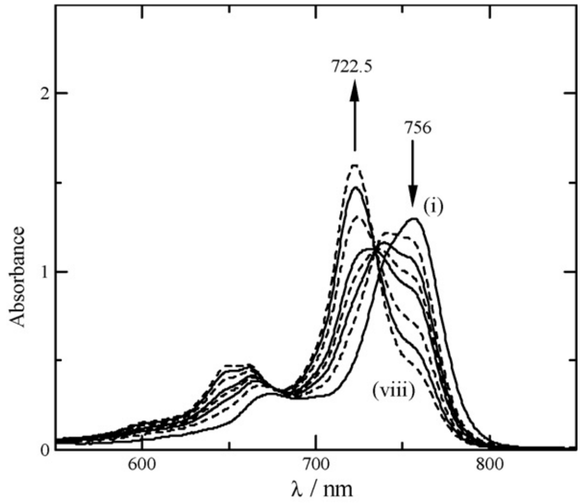

Fig. 7. Spectral changes in $CHCl_3$ solution containing $[Sb(tbpc)]^+I_3{}^-$ (1.8×10^{-5} M), DPBF (7.5×10^{-4} M), and Methylene Blue (1.3×10^{-5} M). $[Sb(tbpc)]^+$ was added into the photolyzed solution containing DPBF and Methylene Blue after the solution was irradiated for 20 min. (i) 10, (ii) 20, (iii) 30, (iv) 50, (v) 70, (vi) 90, (vii) 110, (viii) 130 min after the addition of $[Sb(tbpc)]^+$ solution.

the value is represented as A_{719}/A_{760}.[3] As shown in Fig. 5 (right), the A_{719}/A_{760} value decreased as the irradiation was prolonged, indicating that the oxidation of antimony is not a photochemical process although it is photochemically triggered. The oxidation was efficiently inhibited by β-carotene that was preliminarily added to the photolyzed solutions, as is the case for photobleaching of $[Sb(tbpc)]^+$. Therefore, this oxidation is likewise initiated by photosensitization of $^1O_2$.

This has been further confirmed by the following experiments using other dyes instead of $[Sb(tbpc)]^+$. That is, $CHCl_3$ solutions containing DPBF and either H_2tbpc, [Zn(tbpc)], or Methylene Blue were photolyzed for known time, to which a $CHCl_3$ solution containing $[Sb(tbpc)]^+$ was added and then spectral changes were monitored in the dark. In any case, similar spectral changes have been reproduced as is shown in Fig. 7 (Methylene Blue was used in this case). It should be noted that the addition of $[Sb(tbpc)]^+$ to photolyzed solutions containing DPBF alone under the same conditions did not cause detectable spectral changes for at least 1 h. Similar spectral changes occurred when H_2tbpc and [Zn(tbpc)] was used in place of Methylene Blue, but the use of [Co(tbpc)] did not cause either photolysis of DPBF or oxidation of $[Sb(tbpc)]^+$. This is quite reasonable assuming that photosensitization of $^1O_2$ triggers the oxidation of antimony, because it is well known that metal-free and zinc–phthalocyanines as well as Methylene Blue photosensitize $^1O_2$ while cobalt(II)–phthalocyanines do not [44,45,50,51]. It is noteworthy that these experimental results also indicate that the contribution of I_3^- (the counter anion of $[Sb(tbpc)]^+$) to the photochemical process is negligible if any.

3.2.2. Effects of $^1O_2$ acceptors

We have photolyzed solutions containing $[Sb(tbpc)]^+$ in the presence of various $^1O_2$ acceptors (Fig. 1) to investigate the mechanism of the photo-initiated oxidation of antimony. Similar $Sb^{III/V}$ conversion occurred when the other furan- or oxazole-derivatives (such as 2,5-diphenylfuran, 2,5-diphenyloxazol, 2-methyl-4,5-diphenyloxazole, 2-(2-methoxyphenyl)-4,5-diphenyloxazole) instead of DPBF. Only dibenzofuran was exceptional and no reaction (apart from photobleaching of $[Sb(tbpc)]^+$) was observed under irradiation. Contribution from autooxidation process of the furan-derivatives, which has been reported for DPBF [52,53], to the oxidation of antimony(III) has been found insignificant because similar oxidation occurred in the presence of 2,5-diphenylfuran (except that intermediate species showing 735-nm band was not observed in spectral changes during the oxidation as described in Section 3.2.3). It is known that 2,5-diphenylfuran is stable against autooxidation [54]. On the other hand, the use of 9,10-diphenylanthracene, tetraphenylcyclopentadienone, or 2,3-dimethyl-2-butene as $^1O_2$ acceptors [55] did not give rise to such oxidation. Furan- and oxazole-derivatives are well known to accept $^1O_2$ through 1,4-cycloaddition to form ozonide-type *endo*-peroxides (Scheme 1a) [44,45]. The *endo*-peroxide generated in this way is further attacked by nucleophiles present in the solution (EtOH and H_2O in this case) to liberate peroxides like EtOOH and H_2O_2, respectively.[4] The peroxides are considered to oxidize the $[Sb(tbpc)]^+$ to the corresponding antimony(V) species (Scheme 1b) because we have recently reported that $[Sb(tbpc)]^+$ is converted to antimony(V) derivatives by treating it with perbenzoates in CH_2Cl_2 at room temperature [35,36]. This is further supported by experimental evidence that free iodide (as $^n Bu_4N^+I^-$) was readily oxidized to liberate iodine as I_3^- ($\lambda_{max} = 294$ and 364 nm [56]). With this mechanism taken into consideration, it is quite understandable that dibenzofuran does not contribute to the oxidation of antimony because 1,4-cycloaddition of $^1O_2$ with the furan-skeleton will disrupt the π-conjugation systems of the fused benzene rings and hence this compound is unlikely to work as a $^1O_2$ acceptor.

3.2.3. The intermediate species that appears in the spectral changes

During the process of the oxidation of $[Sb(tbpc)]^+$, a new absorption band appeared around 730–740 nm and then disappeared as another band around 720 nm grew in intensity, as mentioned in Section 3.2.1. When the irradiation time was short (e.g. for 1 min), similar spectral changes to the first process were observed, but any further spectral change due to the oxidation to $[Sb(tbpc)L_2]^+$ was not observed as shown in Fig. 8 (left). The final spectrum little changed over 3 h in the dark until the solution was again irradiated. Upon irradiation for more 30 s, spectral changes ascribable to the oxidation of antimony(III) took place (Fig. 8 right). We have obtained clearer spectrum of the possible intermediate by photolyzing $[Sb(tbpc)]^+$ solutions under the same conditions but by photolyzing solutions containing a lower concentration of DPBF (Fig. 9). The product showed an absorption band characteristic of antimony(III)–phthalocyanine complex [31,35,36]. By monitoring the photo-generated products by ESI-MS, we have found that a pair of peaks at $m/z = 993$ and 995 were prominent in the early stage of the photolysis while they got less intense under prolonged irradiation (Fig. 6). Therefore, this species is considered the intermediate species. We have studied the reaction of $[Sb(tbpc)]^+$ with salicylate in $CHCl_3$ solutions because the formulae weight of dianion of salicylic acid (136) is identical with the difference between the intermediate ($m/z = 993$ and 995) and the initial species ($m/z = 857$ and 859). Although salicylic acid (H_2salc) did not react with $[Sb(tbpc)]^+$ for at least 3 h, its tetrabutylammonium salt ($^n Bu_4N$(Hsalc)) has rapidly reacted upon its addition at room temperature, forming new species that shows a Q-band-like absorption band at 735 nm (Fig. 9).[5] Therefore, we may conclude the intermediate species should be salicylato complex, $[Sb(tbpc)(salc)]^-$. The salicylate

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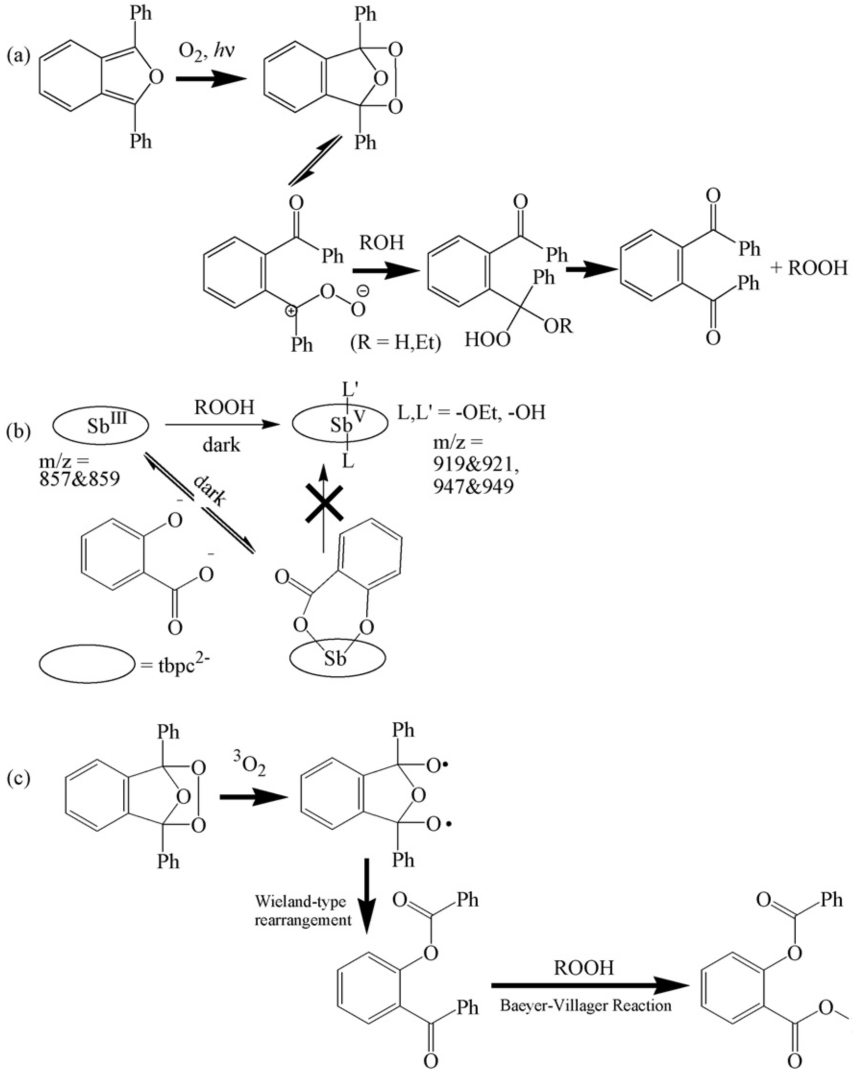
[3] Assuming that all the generated $[Sb(tbpc)L_2]^+$ species have essentially the same molar extinction coefficients to that of $[Sb(tbpc)(OH)_2]^+$ ($\varepsilon = 1.79 \times 10^5\ M^{-1}\ cm^{-1}$ in CH_2Cl_2 [36]) and that $[Sb(tbpc)]^+$ has the same ε value in CH_2Cl_2 ($\varepsilon = 1.27 \times 10^5\ M^{-1}\ cm^{-1}$ in CH_2Cl_2 [31]) and in $CHCl_3$, 68% of antimony(III) species was converted to antimony(V) species. This value seems reasonable because the yields of $[Sb(tbpc)(OH)_2]^+$ were in a range of 65–75% vs. $[Sb(tbpc)]^+$ [36].

[4] Generally, commercially available chloroform contains ethanol as stabilizer.

[5] It is known that the Q-band of $[Sb(tbpc)]^+$ blue-shifts in the presence of donor [31,32].



Scheme 1. The mechanism proposed for the photo-initiated oxidation of $[Sb(tbpc)]^+$ to antimony(V) species. (a) Photooxidation of DPBF. The process from the zwitter ion to dibenzoylbenzene is based on the literature [53]. (b) Oxidation of $[Sb(tbpc)]^+$ to antimony(V) derivatives and formation of dead-end antimony(III) species. (c) Speculated mechanism for the formation of salicylate derivative [52].

is considered to be produced from *endo*-peroxide of DPBF, the photooxidation product of DPBF, through thermal rearrangement of the phenyl groups to the oxygen atoms (Scheme 1c) [52,53]. This is because formation of such intermediate species was not observed when 2,5-diphenylfuran, which is not subject to autooxidation unlike DPBF [54], was used as the $^1O_2$ acceptor and hence the starting material and the oxidation products (antimony(V) species) were detected in the spectral changes during the oxidation as mentioned in Section 3.2.2. As the reaction between $[Sb(tbpc)]^+$ and salicylate is so rapid and terminates within a few seconds, the slow formation of the intermediate may be due to slow formation of salicylate.

It is not certain if this intermediate formation is essential to the oxidation of antimony at present. This is because we have found that oxidation of $[Sb(tbpc)]^+$ with *tert*-butyl perbenzoate isosbestically proceeded without such intermediate formation [34,35], indicating that $[Sb(tbpc)]^+$ can be directly converted to the corresponding antimony(V) species. Furthermore, attempts to oxidize the salicylato complex by *tert*-butyl perbenzoate to form antimony(V) species were unsuccessful and only degradation of the complex occurred. Therefore, the intermediate is likely to be dead-end species and hence unlikely to contribute to the oxidation of antimony.

3.2.4. Contribution of superoxide ion (the Type I mechanism)

As some dyes are known to photosensitize superoxide ion (O_2^-) as well as $^1O_2$ through the Type I mechanism [44,45], we have also investigated on the possibility of contribution of O_2^- in the photobleaching and the oxidation of antimony. Neither reaction was inhibited by the addition of 2,6-di-*tert*-butylphenol, which is known as radical scavenger [47,48], and hence superoxide is unlikely to be involved in both the reactions. In addition to that, we have photolyzed solutions containing $[Sb(tbpc)]^+$ in the presence of *tert*-butyl-benzoate, which would be converted to perbenzoate through nucleophilic attack by O_2^- [44,57].

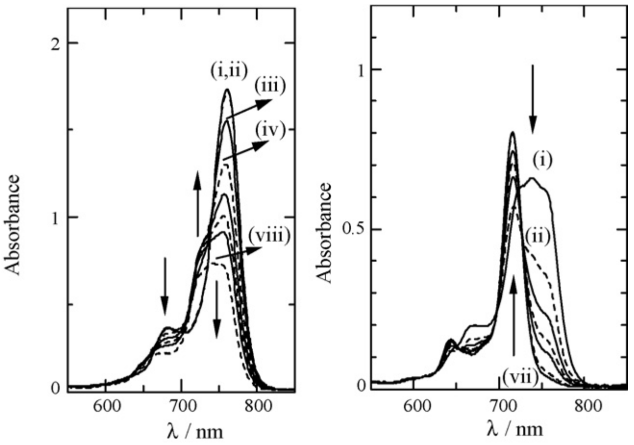


Fig. 8. Spectral changes of aerated $CHCl_3$ solution containing a mixture of $[Sb(tbpc)]I_3$ (1.5×10^{-6} M) and DPBF (7.2×10^{-4} M); (Left) (i) before irradiation, (ii) upon 1-min irradiation, (iii) 10, (iv) 20, (v) 30, (vi) 40, (vii) 50, (viii) 60 min later in the dark; (Right) (i) 1 h after the initial irradiation (identical with the spectrum (viii) in the left figure), (ii) 5, (iii) 10, (iv) 15, (v) 20, (vi) 40, (vii) 60 min after the second irradiation (30 s).

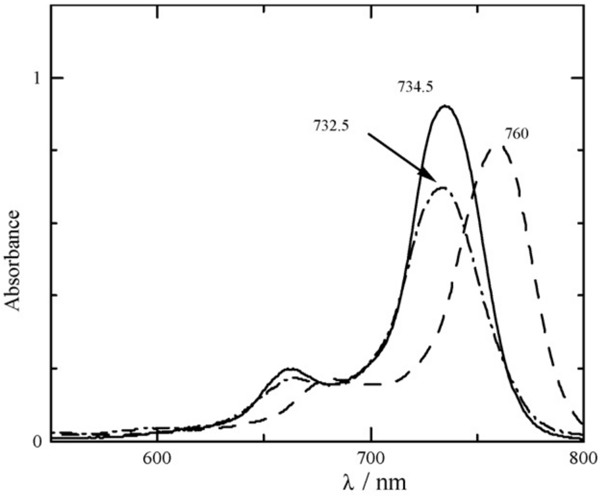


Fig. 9. The absorption spectrum (dot-dash line; absorbance in arbitrary unit) of $CHCl_3$ solution containing $[Sb(tbpc)]^+I_3^-$ (6.4×10^{-6} M) and DPBF (1.0×10^{-4} M) that was photolyzed for 15 min and measured 10 min after the photolysis. The broken and solid line show spectra of $CHCl_3$ solution containing $[Sb(tbpc)]^+I_3^-$ (6.4×10^{-6} M) before and after the addition of tetrabutylammonium salicylate (29 mM), respectively.

Hence photolysis of $[Sb(tbpc)]^+$ in the presence of benzoate ester should give rise to spectral changes due to $Sb^{III/V}$ conversion if contribution of O_2^- is significant because we have quite recently reported that perbenzoic acids and its ester are capable to oxidize $[Sb(tbpc)]^+$ even at room temperature [35,36]. However, since no such spectral change was observed, we conclude that contribution of O_2^- in the reactions is negligible, if any.

4. Conclusions

Photochemical behaviors of antimony(III) derivative of phthalocyanine under visible light irradiation has been studied for the first time. Contrary to the expectation, photo-initiated $Sb^{III/V}$ conversion did not occur by photolyzing aerated solutions containing the title complex alone but only photobleaching of the complex due to $^1O_2$ photosensitized by the complex itself was observed. However, photo-initiated $Sb^{III/V}$ oxidation has been found to occur in the presence of $^1O_2$ acceptors like DPBF. The over-all mechanism proposed for the $Sb^{III/V}$ conversion can be rationalized by considering the following stages; i.e., (i) the initial species, $[Sb(tbpc)]^+$, photosensitizes $^1O_2$ (which also decomposes the photosensitizer itself); (ii) the $^1O_2$ generated in this way undergoes a 1,4-cycloaddition with DPBF to form ozonide-type *endo*-peroxide, which decomposes by nucleophilic attack of EtOH and H_2O present in the solvent to generate peroxides, such as EtOOH and H_2O_2, respectively; (iii) the peroxides oxidize $[Sb(tbpc)]^+$ to antimony(V) derivatives, $[Sb(tbpc)LL']^+$, ligating axial ligands containing oxygen as donor atoms; (iv) the new Sb^{III}Pc-like species that appeared in the spectral changes during the $Sb^{III/V}$ conversion is likely to be a dead-end species and unlikely to contribute to the oxidation.

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