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Photooxidation of phenol derivatives using μ-(dihydroxo)dipalladium(II) bisporphyrin complex

Yuko Takao*[a◊], **Toshinobu Ohno**[a], **Kazuyuki Moriwaki**[a], **Fukashi Matsumoto**[a] and **Jun-ichiro Setsune***[b◊]

[a] *Osaka Municipal Technical Research Institute, Joto-ku, Osaka 536-8553, Japan*
[b] *Department of Chemistry, Graduate School of Science, Kobe University, Nada-ku, Kobe 657-8501, Japan*

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ABSTRACT: μ-(dihydroxo)dipalladium(II) complex with N^{21},N^{22}-etheno bridged tetraphenylporphyrin ligand was employed in the catalytic photooxidation of phenol derivative in aerated homogeneous solution with visible light irradiation. The Pd complex promoted the degradation of *p*-*tert*-butylphenol as well as Cu phthalocyanine under basic conditions and it worked as a photosensitizer even in neutral conditions in contrast with Cu phthalocyanine. Some phenol derivatives afforded corresponding quinones selectively in this photooxidation. The present Pd complex coordinated by the bidentate porphyrin ligand showed higher photosensitizing ability than tetraphenylporphyrin free-base and ordinary tetradentate tetraphenylporphyrin palladium(II) complex for photooxidation of 2,6-di-*tert*-butylphenol. This bidentate Pd complex showed higher light durability even under the conditions where photodegradation of porphyrin free-base and tetradentate Pd porphyrin were observed by extensive irradiation.

KEYWORDS: bridged porphyrin, μ-(dihydroxo)dipalladium complex, photooxidation, phenol derivative.

INTRODUCTION

Palladium complexes with weakly coordinating anions have been known to activate substrates in organic transformations [1]. As an example, μ-(dihydroxo) and μ-(dialkoxo)dipalladium(II) complexes have been drawing much interest and their usage as catalyst for substitution, carbonylation and Mannich-type reactions is known [2]. We have reported the synthesis and the reactions of unique μ-(dihydroxo) dipalladium(II) bisporphyrin (**2**) that was obtained by the reaction of dicationic bis(aqua) Pd(II) complexes of N^{21},N^{22}-etheno bridged porphyrin (**1**) with NaOH or triethyamine (Scheme 1) [3]. Since palladium(II) porphyrin is a coordinatively saturated metal complex having a tetradentate ligand, it is not useful for metal-catalyzed reactions that require coordination sites for substrates. By using N^{21},N^{22}-etheno bridged porphyrin as a bidentate ligand, we have been investigating the coordination chemistry and organometallic chemistry of palladium porphyrin complexes [4], and showed that the N^{21},N^{22}-bridged porphyrin ligand strongly coordinated to Pd and influenced the dynamic behavior of the coexisting ligand [5, 6]. It is of interest to make use of N^{21},N^{22}-bridged porphyrins considering a role of palladium catalysts with bidentate ligands in modern organic synthesis, though there is concern about palladium porphyrins with regard to their photophysical and electrochemical properties [7].

In this paper we report the application of the μ-dihydroxo complex of dimeric palladium(II) porphyrin for photooxidation of phenol derivatives. Though the oxidation of several substrates with porphyrin analogs as photosensitizers have been developed [8, 9], the oxidation of phenol derivatives is of special interest because the oxidized products of phenol derivatives such as quinone derivatives are known to be important chemicals in the pharmaceutical and dye industries [10], and because some phenol derivatives such as chlorinated or *p*-alkylated phenols are known to be pollutants that accumulate in the environment and thus sustainable methods

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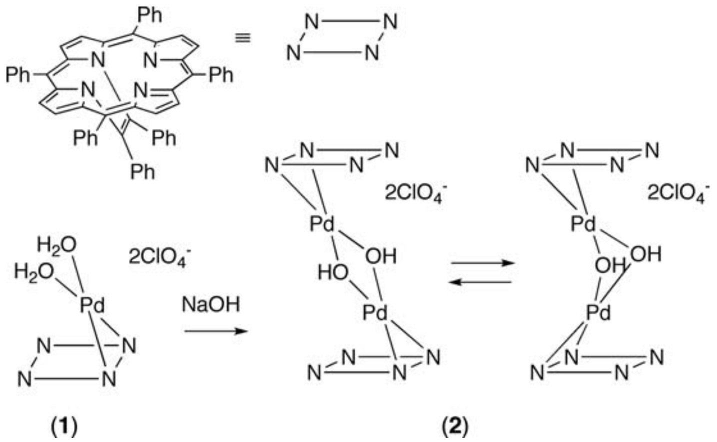
◊SPP full member in good standing

*Correspondence to: Yuko Takao, email: yuktakao@omtri.or.jp, fax: +81 06-6963-8049 and Jun-ichiro Setsune, email: setsunej@kobe-u.ac.jp, fax: +81 078-803-5770



Scheme 1. Preparation of μ-(dihydroxo)dipalladium(II) complex with N^{21},N^{22}-(diphenyletheno) bridged porphyrin dimer

for their decomposition are needed [11–13]. So oxidation of several phenol derivatives has been studied using porphyrins or phthalocyanines in the presence of various oxidants, for example, oxygen [8b, 14], hydrogen peroxide [11, 12, 15] or potassium monoperoxysulfate [11, 15]. Furthermore, photooxidations using a singlet oxygen photosensitizer are regarded as a friendly process for environment by considering minimum usage of toxic chemicals, use of oxygen from air and visible light which has the largest energy density in solar radiation as unlimited natural resources. A number of examples have been reported for the use of classic dyes such as Methylene Blue and Rose Bengal as photosensitizers in these reactions. However, there is a problem of photodegradation of sensitizer upon extensive irradiation. Thus it is important to develop efficient and stable photosensitizers [10, 16]. With this purpose in mind, effective photooxidations using new phthalocyanine and porphyrin derivatives have been developed [8, 13, 17].

Here, the photooxidations of some phenol derivatives using μ-dihydroxo complex of dimeric palladium(II) porphyrin are described, and the oxidation activity and photostability of the bidentate porphyrin complex are compared with those of a tetradentate normal metal porphyrin and a free-base porphyrin.

EXPERIMENTAL

Materials and synthesis

μ-(dihydroxo)dipalladium(II) complex with N^{21},N^{22}-(diphenyletheno) bridged TPP (tetraphenylporphyrin) dimer (**2**) was prepared by the reaction of dicationic bis(aqua)Pd(II) complexes of N^{21},N^{22}-etheno bridged porphyrin with NaOH or triethyamine according to the previously reported procedures [3]. Bis(perchlorato)bis(aqua) palladium(II) complex of N^{21},N^{22}-(diphenyletheno) bridged TPP (**1**) was also prepared according to a previously reported procedure [4]. Tetradentate (tetraphenylporphyrinato)Pd(II) [(TPP)Pd] was prepared as follows: A solution of tetraphenylporphyrin [$TPPH_2$] (0.1 mmol) in $CHCl_3$ (14 mL) was added to a solution of $Pd(OAc)_2$ (0.2 mmol) in propionic acid (10 mL). The mixture was refluxed for 6 h, then evaporated, followed by column chromatography on silica gel with dichloromethane. The product was recrystallized from dichloromethane and *n*-hexane to afford (TPP)Pd as a red solid (yield: 71%). Solvents were purified prior to use by conventional methods. Cupper(II) phthalocyanine-3,4′,4″,4‴-tetrasulfonic acid, tetrasodium salt [(Pc)Cu] and other chemicals were of reagent grade. $CDCl_3$ was passed through basic Al_2O_3 before use.

Measurement

^{1}H NMR spectra were recorded on JEOL AL-300 spectrometer. Chemical shifts were referenced with respect to $(CH_3)_4Si$ (0 ppm) as an internal standard. Gas chromatography was carried out using a HiCap-CBP1 (25 m × 0.53 mm × 1 μm) Shimadzu capillary column on a Shimadzu-14B chromatography. GC analysis was run at 140°C; detector temperature 250°C, injector temperature 250°C. Absorption spectra were measured on Shimadzu UV-3100B instrument.

Photoreactivity study

The solution containing a substrate and a sensitizer was placed into a 1 cm optical cell with external water cooling and filled with oxygen gas, and then irradiated by a 500 W xenon lamp through cut-filters ($350 \text{ nm} < \lambda < 800 \text{ nm}$). In the case of measurement by GC, 3 mL of acetonitrile solution containing substrate (0.5 mM) and a sensitizer (5×10^{-5} M) was irradiated. A 0.05 mL amount of the solution was diluted 3.5 times and passed through a little silica gel, and then analyzed. In the case of observation by ^{1}H NMR spectrometry, a mixture of a substrate (3 mM) and a sensitizer (0.03–0.3 mM) in a deuterated solvent was irradiated. A 0.5 mL amount of sample solution was analyzed and content of product was calculated from integral values of signals.

Photostability study

To study the photostability of sensitizers, 0.3 mL of the CH_2Cl_2 solution containing a sample (2.5×10^{-5} M) was placed into a 1 mm optical cell with external cooling, and irradiated by a xenon lamp. The intact optical cell was set in the spectrophotometer, and the absorbance at the Soret band was measured to monitor the change of concentration of samples.

RESULTS AND DISCUSSION

The photocatalytic activities of the compound **1**, **2**, (TPP)Pd, $TPPH_2$ and copper phthalocyanine ((Pc)Cu) were examined in the photooxidation of some phenol derivatives such as **3** and **5** as shown in Scheme 2. At first, the solution of *p*-*tert*-butylphenol (**3a**; 0.5 mM) in 3:5 (*v*/*v*) water-acetonitrile binary mixture containing photosensitizers (0.05 mM) was irradiated by a xenon lamp (350 nm < λ < 800 nm). The concentration of **3a** was measured by GC analysis to monitor the photodegradation of **3a** (Fig. 1).

Addition of complex **2** without photoirradiation resulted in little change in the concentration of **3a** after 3 h (filled square, Fig. 1). But under photoirradiation the concentration of **3a** decreased rapidly, especially in the presence of NaOH (open circle, Fig. 1). The efficiency of complex **2** was compared with that of (Pc)Cu and they similarly promoted photodegradation of **3a** under basic conditions (open triangle, Fig. 1). On the other hand, it is noteworthy that complex **2** showed 94% of photodegradation of **3a** (filled circle, Fig. 1) though (Pc)Cu showed only 20% of photodegradation (filled triangle, Fig. 1) after 3 h under neutral conditions. This result means that **2** works as a photosensitizer without adding some bases and is suitable for water treatment; *e.g.* photodegradation of phenols in normal water.

In the case of photooxidation of **3a** oxidized products were of complex mixtures, while in the photooxidation of 2,6-di-*tert*-butylphenol (**3b**) the conversion of substrate to products was confirmed by monitoring with ^1H NMR spectroscopy. Figure 2 shows the ^1H NMR spectrum on the photooxidation process of **3b** in acetonitrile after 15 min irradiation in the presence of **2**. Then it was proved that almost single product was formed selectively as an initial product under such conditions. Although 2,6-di-*tert*-butyl-1,4-benzoquinone (**4b**) and 3,3′,5,5′-tetra-*tert*-butyl-4,4′-diphenoquinone were formed as oxidized products in thermal oxidation of **3b** with porphyrin complexes [13], only one product was formed in this photooxidation and identified as **4b** by comparing the chemical shifts of the product with those of the standard 2,6-di-*tert*-butyl-1,4-benzoquinone. The influence of the amount of complex **2** as a photosensitizer on the conversion of **3b** to **4b** was also examined after 60 min of irradiation in acetonitrile. When **2** was added to the solution of **3b** in the molar ratio of 0.1, 0.01 and 0.001 to **3b**, the formation of **4b** was 94%, 73% and 25%, respectively.

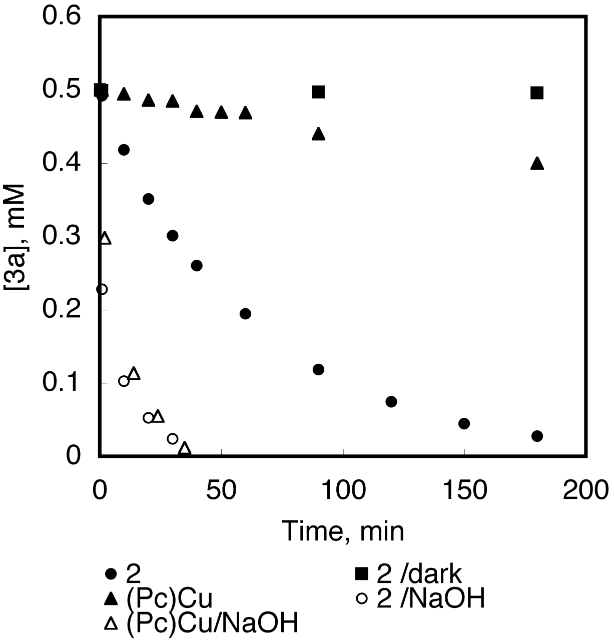


Fig. 1. GC analysis of photosensitized degradation of **3a** (5×10^{-4} M) in MeCN-H_2O with irradiation with a 500 W xenon lamp at 80 cm distance. [photosensitizer] = 5×10^{-5} M; [NaOH] = 5×10^{-3} M

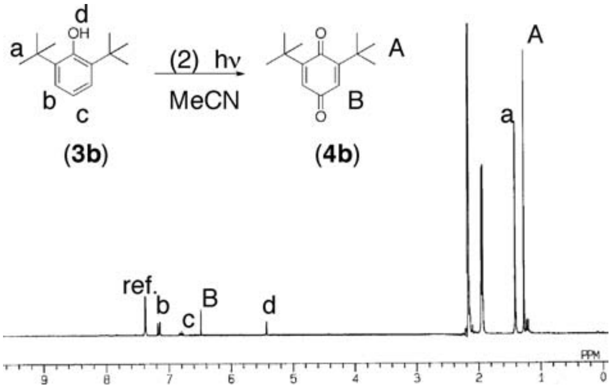
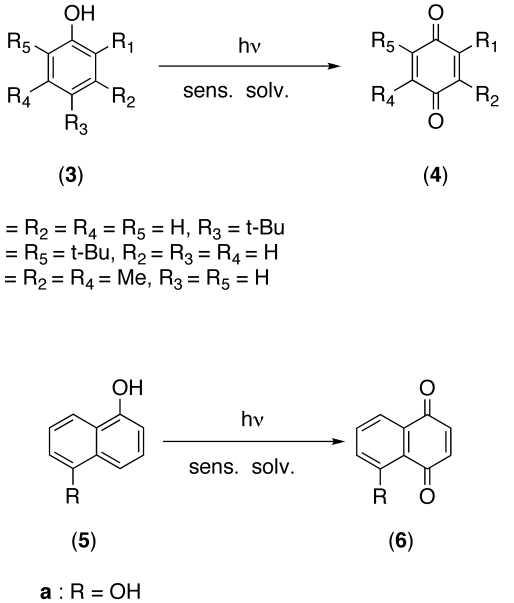


Fig. 2. ^1H NMR spectrum in CD_3CN of the reaction mixture after irradiating **3b** (3×10^{-3} M) with a 500 W xenon lamp for 15 min in acetonitrile in the presence of **2** (0.1 molar equiv.)



a : $R_1 = R_2 = R_4 = R_5 = H$, R_3 = t-Bu
b : $R_1 = R_5$ = t-Bu, $R_2 = R_3 = R_4 = H$
c : $R_1 = R_2 = R_4$ = Me, $R_3 = R_5 = H$

a : R = OH
b : R = H

Scheme 2. Photooxidation of some phenol derivatives

The photooxidation efficiency of sensitizers was evaluated by the measurement of formation of **4b** in the photooxidation of **3b**. Table 1 shows the yield of **4b** determined

Table 1. Dependence of the photooxidation efficiency on the sensitizer and solvent[a]

Por.	Molar ratio (Por./**3b**)	Solvent	Yield of **4b**, %[b]
2	0.05	CH_3CN	90
2	0.005	CH_3CN	68
2	0.005	$CH_3CN(7\%CHCl_3)$	56
(TPP)Pd	0.01	$CH_3CN(7\%CHCl_3)$	39
$TPPH_2$	0.01	$CH_3CN(7\%CHCl_3)$	24
1	0.01	$CH_3CN(7\%CHCl_3)$	44
2 [c]	0.05	$CH_3CN(20\%H_2O)$	0
2 [d]	0.05	$CH_3CN(33\%CHCl_3)$	0

[a] [**3b**] = 3 × 10^{-3} M, irradiation with a 500-W xenon lamp at 80 cm distance, [b] after 40 min, [c] NaN_3 was added, [d] [**3b**] = 1 × 10^{-3} M, β-carotene was added.

Table 2. Photooxidation of some phenol derivatives[a]

Substrate	Solvent	Time, min	Product yield, %
3b	MeCN	40[b]	3
3b	MeCN	40[c]	0
3b	MeCN	60	96
3b	$CHCl_3$	120	48
3b	DMSO	40	6
3c	MeCN	40	15
3c	$CHCl_3$	120	13
3c	DMSO	120	0
5a	MeCN	5	96
5b	DMSO	120	25

[a] [Substrate] = 3 × 10^{-3} M, [**2**] = 1.5 × 10^{-4} M, irradiation with a 500 W xenon lamp at 80 cm distance, [b] not irradiated [c] no sensitizer.

by ^{1}H NMR spectrum after 40 min irradiation. The best result was obtained (90%) under the conditions in which 10 mol.% of Pd atom in the form of **2** was added into acetonitrile solution. For the purpose of comparison of the photooxidation efficiency with other related porphyrin derivatives, the molar ratio of the sensitizers to **3b** was decreased to 0.01 and chloroform was added to the solution (7%) by considering the solubility of other sensitizers such as $TPPH_2$. The conditions resulted in decrease of yield of **4b** from 56% by using **2** to 39, 24, and 44% yield by using (TPP)Pd, $TPPH_2$ and **1**, respectively, while **3b** did not react in the absence of sensitizers under otherwise the same conditions. When aqueous NaN_3 or β-carotene was added to the acetonitrile solution as a singlet oxygen scavenger, the photooxidation of **3b** was inhibited. These experiments might suggest that singlet oxygen is involved in the present oxidation reactions.

The photooxidation of some other phenol derivatives such as 1,2,4-trimethylphenol (**3c**) and naphthols (**5**) were also carried out because the corresponding quinones **4c** and **6** are regarded as intermediates for the syntheses of biochemicals, physiologically active substances or starting materials for preparing antiviral and antitumor agents [10a]. The results of photooxidation in the presence of 5 mol.% of **2** under some conditions are shown in Table 2. The oxidation products, **4c**, **6a** and **6b**, were identified on the basis of the reported spectroscopic data [10]. These photooxidation yields were dependent on the structures of substrates and reaction solvents. It was found that reactions in MeCN were much faster than those in $CHCl_3$ and DMSO by monitoring with ^{1}H NMR spectroscopy, while **3b** did not react in the absence of sensitizers in both MeCN and $CHCl_3$ under the same irradiation conditions. **3b** and **5a** could be converted to the corresponding quinones in excellent yields (96%) though the conversion of **3c** and **5b** was low.

The photostability of porphyrin sensitizers was evaluated by measuring the relative absorbance at the Soret band with irradiation time. The decreasing of the relative absorbance of **2** by irradiation was also compared with those of $TPPH_2$ and (TPP)Pd under the same conditions. As shown in Fig. 3, complex **2** was the most photostable and remained unchanged after 100 min irradiation, while $TPPH_2$ was almost completely photodecomposed under the same conditions. This remarkable difference in the photostability among **2**, $TPPH_2$ and (TPP)Pd was not reflected in the photoactivity examined in Table 1, because the yield data were taken while photosensitizers are alive.

Thus, the photooxidation of phenol derivatives proceeded under mild conditions in neutral solution at room temperature using complex **2**. It is noteworthy that it works without a base as a photosensitizer probably because the OH ligand of the $Pd_2(OH)_2$ core of **2** acted as a base, which was confirmed from previous experiments that **2** reacted with an acidic substrate such as methyl 3-butenoate to give (*p*-methoxycarbonylallyl)Pd complexes by deprotonation under neutral conditions [3].

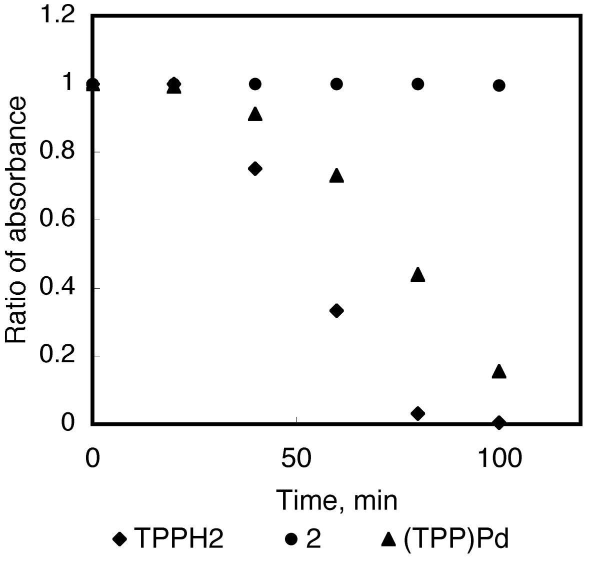


Fig. 3. The change in the absorbance at the Soret bands of porphyrins (2.5 × 10^{-5} M) with time through irradiation with a 500 W xenon lamp at 80 cm distance in CH_2Cl_2

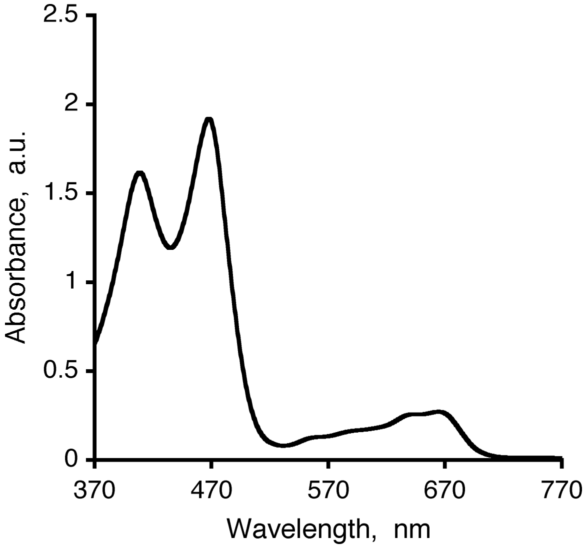


Fig. 4. UV-vis absorption spectrum of **2** in MeCN

Photooxidation of phenol derivatives was promoted by the Pd complex of the bidentate porphyrin using visible light energy. Moreover, complex **2** showed a slightly more superior efficiency and much higher photodurability as a photosensitizer than tetradentate (TPP)Pd and free-base $TPPH_2$. The UV-vis absorption spectrum of **2** in Fig. 4 shows split Soret bands and absorption bands extending to 700 nm in the Q-band region. This spectral pattern is very different from those of $TPPH_2$ and (TPP)Pd and the photophysical properties should be of interest in relation to the present photooxidation reactions. We are planning to study the photophysical properties of **2**.

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