A Novel Photosensitizer of Palladium(II) Phthalocyanine Tetrasulfonate for Chlorophenol Oxidation under Visible Light Irradiation

Meiqin Hu, Yiming Xu,* and Zhigang Xiong
Department of Chemistry, Zhejiang University, Hangzhou, Zhejiang, 310027, P. R. China

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The title complex has been found to exhibit high quantum yield of singlet oxygen generation (0.87 in DMF), and is highly efficient and stable to initiate mineralization of cholorophenols in water under visible light irradiation.

Singlet molecular oxygen, $^1O_2$, is an active species that can attack a variety of unsaturated and/or electron-rich molecules.[1] Thus, a great deal of attention has been devoted in the last years to generation and reactions of $^1O_2$ in both the homogeneous and heterogeneous system. The important fields of its application include fine chemical synthesis, polymer science, photodynamic therapy of cancer and wastewater treatment. The most common means of $^1O_2$ generation is photosensitization. Radiation in a specific wavelength region is absorbed by a photosensitizer, and consequently the electronically excited states formed induce energy transfer to ground triplet molecular oxygen, $^3O_2$, generating $^1O_2$. Obviously, for an efficient and stable sensitizer, not only the quantum yield of $^1O_2$ formation, (Φ_Δ), has to be as high as possible, but also the electron transfer from the excited sensitizer to either $^3O_2$ or the target substrate, and the possible sensitizer oxidation by $^1O_2$ as well, should be minimized.[1a]

We report herein a novel sensitizer of palladium(II) phthalocyanine tetrasulfonate, PdPcS, which is highly active and stable for elimination of several recalcitrant pollutants, 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP), and 2,4,6-trichlorophenol (2,4,6-TCP) in water under visible light irradiation.

In comparison to other sensitizers such as porphyrins,[2] metal phthalocyanines are particularly attractive, since they can collect up to 50% of the energy available in the solar spectrum. In addition, they are extremely resistant to chemical degradation, and can be synthesized at low cost in a one-step process. Many studies thus have been made on the phthalocyanines of non-transition metal,[1,3] but little is known about transition metal complex.[4] Secondly, the complexes MPcS (M = Al, Zn, Sn, Si) examined so far are not absolutely stable during the photosensitized reactions, among which AlPcS appears to be the best in respect to both efficiency and stability in an aqueous medium.

PdPcS used in the present study was synthesized by urea process according to the procedure described by Weber and Brusch.[5] This dye, similar to other MPcS, was highly dimerized in water at pH 7 (the dimeric peak at 611 nm and the monomer at 645 nm), but could be dissociated completely into monomer in DMF, as evidenced by a substantially narrowed peak at 659 nm.[5b] In such solvent, AlPcS and ZnPcS were also presented in a monomeric species. Thus Φ_Δ was determined in DMF (25 mL) for each sensitizer (80 uM) at 606 nm using 2,5-dimethylfuran (3.7 mM) and CH_3OH (0.9 M) as a trap.[2a] The light source was a PTI Xenon lamp (75 W) equipped with an interferance filter (606 nm, half-width 14 nm), and Reineckes's salt actinometer was employed to determine the light intensity. The resulted value of Φ_Δ was 0.87 for PdPcS, 0.40 for AlPcS, and 0.70 for ZnPcS, respectively. According to our knowledge, 0.87 of Φ_Δ is the highest one reported so far for the class of phthalocyanines.[1,3,6]

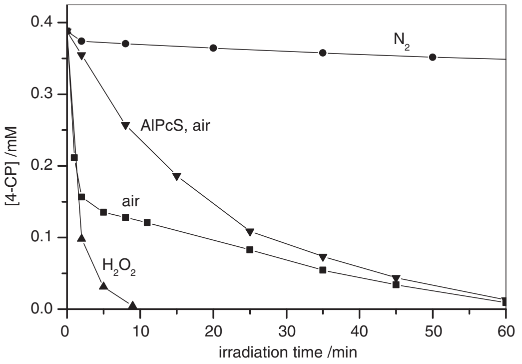

Figure 1. Photosensitized oxidation of 4-CP by PdPcS in an aqueous solution at pH 12 under air (closed square) and N_2 (closed circle) atomosphere as well as in the presence of H_2O_2 (closed triangle). The comparison run using AlPcS as a photosensitizer was performed in an air-saturated solution.

The photooxidation of chlorophenol sensitized by PdPcS (44 μM) was carried out in an open thermostatic vessel (50 mL), irradiated by a Halogen lamp (500 W) through a dichromate solution filter ($\lambda > 450$ nm). The reaction was monitored by an Agilent 8453 spectrophotometer and on a Dionex P680 HPLC (C18 reverse column, $CH_3OH:H_2O = 3:2$ by volume, 1.0 mL/min).

Figure 1 shows the photosensitized oxidation of 4-CP in an air-saturated aqueous solution at pH 12 under visible light irradiation ($\lambda > 450$ nm). It was observed that the sensitizer PdPcS exhibited very different behavior in photosensitization from AlPcS. Whereas 4-CP concentration in the presence of AlPcS decreased gradually with irradiation time, the substrate oxidation sensitized by PdPcS was very fast in the first 2 min, but then became very slow. However, both the systems gave almost the same yield of 4-CP oxidation at about 60 min. It was realized that some colored intermediates were formed from 4-CP oxidation, that competed with 4-CP for $^1O_2$. The absorbance in the range from 400 to 550 nm was increased upon irradiation, approaching a maximum at 20 min for AlPcS, but at 2 min for PdPcS. In the presence of H_2O_2, however, no such colored intermediates were seen in the spetrum, and as a result the photosenstized oxidation of 4-CP became fast. No dark reaction was observed between H_2O_2 and chlorophenol under the present conditions. The HPLC analysis showed that the reaction intermediates underwent complicated reactions, and the traces changed with time, similar to benzoquinone in an alkaline solution. Since the colored intermediate underwent very slow degradation, they accumulated much more quickly in the solution of PdPcS than in the solution of AlPcS, thus appearing an obvious inflection point at 2 min in the former. The result implies that as a photosensitizer PdPcS is more efficient than AlPcS for both 4-CP and its intermediate oxidations.

The higher activity of PdPcS than AlPcS was further evidenced by the measurement of reaction products, chloride ions and carbon dioxide.[4b] For quantitative analysis, a solution of 4-CP at high initial concentration (1.5 mM) was employed. In both the cases, 99.7% of chloride ions were detected after 10 h of irradiation, while 55.3 and 16.6% of CO_2 was obtained in the system of PdPcS and AlPcS, respectively. If the solution was irradiated for 30 h, the yield of CO_2 formation was increased up to 99.8% for PdPcS and 38.8% for AlPcS. The data demonstrates that the photosensitization system is effiicient not only for 4-CP oxidation, but also for complete mineralization into Cl^- and CO_2, which is essential to enviromental application.

The stability of PdPcS was high. No obvious bleaching of PdPcS was found during the reactions. Nyokong and his coworkers reported that the photobleaching of AlPcS occurred via electron-transfer pathway, and became more serious when the solution pH was low and when the organic substrate present changed from phenol to 4-CP, 2,4,5-TCP, and PCP (pentachlorophenol), due to the increased strength of electron-accepting.[3b] For this concern, the reaction sensitized by PdPcS was examined for 2,4-DCP and 2,4,6-TCP in water. While the photosensitized oxidation of 2,4-DCP (Figure 2, top) or 2,4,6-TCP (Figure 2, bottom) was very efficient at pH 12, the sensitizer was quite stable, as evidenced by its monomeric absorbance at 650 nm that remained unchanged during the reaction. The direct irradiation of PdPcS aqueous solution in the absence of chlorophenol also did not lead to any change of PdPcS spectrum. But during 2,4,6-TCP oxidation at pH 7, a slightly decreased absorbance (0.02) at 657 nm was observed indeed after 70 min of irradiation. The evidence showed that while the sensitizer was highly resistant to the attack by $^1O_2$, the electron-transfer between the excited PdPcS and chlorophenol was quite slow and/or not efficient.

Singlet oxygen was the reactive species that initiated the mineralization of chlorophenols. In the N_2-degassed solution, the reaction became extremely slow, indicating that oxygen was the required reactant. The slightly decreased concentration of the substrate observed in the figures was attributed to trace amount of dissolved oxygen still in the degassed solution (note that no decrease in PdPcS absorbance was observed). In the presence of NaN_3 (0.05 M), $^1O_2$ scavenger,[3] the reaction was inhibited completely, in agreement with singlet oxygen pathway. Similar to 4-CP oxidation, some colored intermediates were also found during 2,4-DCP or 2,4,6-TCP oxidation. In the presence of H_2O_2, these intermediates disappeared and thus the rate of 2,4-DCP or 2,4,6-TCP oxidation increased significantly. From the figures, the relative reaction rate at pH 12 followed the order of 4-CP > 2,4-DCP~2,4,6-TCP, matching nearly the rate constant of $^1O_2$ reaction with phenolate anion in aqueous solution.[7] On the other hand, the photosensitized oxidation of 2,4,6-TCP in water at pH 7 was very slow (Figure 2 bottom), due to the less reactive molecular phenol toward $^1O_2$, and thus the reaction was not significantly enhanced by addition of H_2O_2.

In summary, PdPcS has been shown to be an efficient and stable photosensitizer for chlorophenol degradation in water under visible light irradiation. Although the study was made for environmental application, the high quantum yield of $^1O_2$ generation (0.87 in DMF), preserved by PdPcS, and high stablity against photobleaching would be useful to other applications in organic synthesis and biological science.

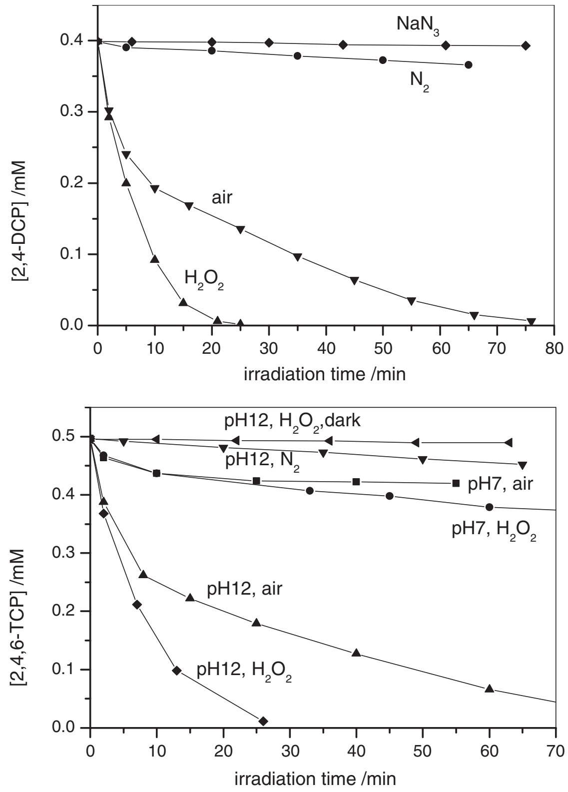

Figure 2. Photosensitized oxidation of 2,4-DCP at pH 12 (top) and 2,4,6-TCP at pH 7 or 12 (bottom) in an aqueous solution of PdPcS under various conditions.

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