Photochromic Reactions Involving Palladium(II) Octabutoxynaphthalocyanine and Molecular Oxygen

Boris D. Rihter,[†,‡] Malcolm E. Kenney,[†] William E. Ford,[§] and Michael A. J. Rodgers*[,§]

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106, and Center for Photochemical Sciences, Bowling Green State University, Bowling Green, Ohio 43403

Received April 22, 1993

Abstract: The palladium complex of 1,6,10,15,19,24,28,33-octabutoxynaphthalocyanine, $PdNc(OBu)_8$, is shown to undergo reversible addition of O_2 in benzene solution at ambient temperature (22 ± 1 °C) during steady-state photolysis with an Ar ion laser. On the basis of ^1H-NMR and electronic absorption spectral evidence, the photoadduct is postulated to be an endoperoxide which has molecular oxygen added to one of the benzene rings at the sites α to the point of fusion with the tetrapyrrole ring, *i.e.*, the positions bearing butoxy substituents. The formation of this product probably involves $O_2(^1\Delta_g)$. The photoadduct decomposes mainly back into $PdNc(OBu)_8$ by a thermal process whose first-order rate constant is $(2.6 \pm 0.2) \times 10^{-4}\ s^{-1}$ at 22 °C. This reaction is accelerated by light. Laser flash photolysis results show that the quantum efficiency for the formation of the photoadduct in O_2-saturated benzene is <0.01. The quantum efficiency for decomposition of the adduct into $PdNc(OBu)_8$ in Ar-saturated benzene is 0.035 ± 0.010 with either 355- or 532-nm light, but the value is 0.0015 ± 0.0005 with 683-nm light. $PdNc(OBu)_8$ may be the first example of a tetrapyrrole to form a metastable endoperoxide, and the latter compound appears to be the first example of an endoperoxide that is subject to photocycloreversion with visible light. It is also demonstrated that energy transfer from $O_2(^1\Delta_g)$ to $PdNc(OBu)_8$ occurs with a bimolecular rate constant of $9 \times 10^9\ M^{-1}\ s^{-1}$ to produce $PdNc(OBu)_8(T_1)$ which phosphoresces in fluid solution. This behavior suggests that the platinum group metal complexes of octaalkoxynaphthalocyanine may prove to be useful as luminescence probes for improving the detection limit of $O_2(^1\Delta_g)$.

Introduction

In recent years researchers interested in the production and properties of singlet molecular oxygen, $O_2(^1\Delta_g)$, have had the advantage of using its phosphorescence to detect its presence in fluid phases. The phosphorescent $^1\Delta_g \rightarrow {}^3\Sigma_g{}^-$ transition in the isolated molecule is strictly forbidden for electric dipole transitions, but in condensed phases solvent enhancement of the radiative rate constant, k_r, results in the quantum efficiency of phosphorescence becoming significantly greater than 0 and luminescence at 1270 nm can be observed. The consensus of recent studies[1] is that k_r is strongly solvent dependent, and values in aromatic liquids are *ca.* 10 times those in σ-bonded liquids, *e.g.*, alcohols (and presumably water). This information, coupled with a value of $k_r = 1.5\ s^{-1}$ in benzene,[2] leads to the conclusion that the value of k_r in aqueous media will be on the order of $0.1-0.2\ s^{-1}$. In such media in the absence of added quenching species the deactivation of $O_2(^1\Delta_g)$ is dominated by the nonradiative processes, and the resulting observed lifetime (τ_Δ) in water is 4 μs; hence, the quantum efficiency of luminescence therein is on the order of 5×10^{-7}. Thus, only about 500 molecules per billion of $O_2(^1\Delta_g)$ undergo radiative decay. In biological milieux, where the value of τ_Δ is lower than its neat water value owing to the presence of reactive biosubstrates, an even lower number of molecules undergo the radiative process, and current instruments are no longer able to detect 1270-nm luminescence from biological systems undergoing singlet oxygen photosensitization.[3]

The above considerations indicate that the limiting factor in our inability to detect singlet molecular oxygen is its k_r value. One possible way to overcome this limitation would be to transfer the excitation from oxygen to a molecule that would have a significantly higher value of radiative rate constant than does oxygen. A molecule with a low-lying triplet state could be a candidate for the acceptor system. Spin forbiddenness of the $T_1 \rightarrow S_0$ transition puts k_r values of phosphorescence of aromatic π-systems near 1 s^{-1} or less,[4] which is hardly an improvement, but platinum metal complexes of such π-systems exist where k_r values exceeding $10^2\ s^{-1}$ pertain to the $T_1 \rightarrow S_0$ transition.[5] Thus, the possibility exists that if the electronic energy of $O_2(^1\Delta_g)$ could be donated to another compound with higher k_r, then it should be possible to monitor emission from the acceptor under conditions where the oxygen emission was too weak. Under certain conditions this could improve the detection limit for singlet oxygen.

The logic that guided the design of the molecular system that would have the desired properties derived from our recent studies of phthalocyanine and naphthalocyanine derivatives.[6] Significant red shifts are induced in the absorption spectra of the basic

---

[†] Case Western Reserve University.

[‡] Present address: Aldrich Chemical Company, Stains and Dyes Division, 1001 West Paul Avenue, Milwaukee, WI 53233.

[§] Bowling Green State University.

(1) (a) Gorman, A. A.; Hamblett, I.; Lambert, C.; Prescott, A. L.; Rodgers, M. A. J.; Spence, H. M. *J. Am. Chem. Soc.* **1987**, *109*, 3091–3097. (b) Scurlock, R. D.; Ogilby, P. R. *J. Phys. Chem.* **1987**, *91*, 4599–4602. (c) Losev, A. P.; Byteva, I. M.; Gurinovich, G. P. *Chem. Phys. Lett.* **1988**, *143*, 127–129. (d) Gorman, A. A.; Krasnovsky, A. A.; Rodgers, M. A. J. *J. Phys. Chem.* **1991**, *95*, 598–601.

(2) Schmidt, R.; Afshari, E. *J. Phys. Chem.* **1990**, *94*, 4377–4378.

(3) Gorman, A. A.; Rodgers, M. A. J. *J. Photochem. Photobiol., B* **1992**, *14*, 159–176.

(4) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley: New York, 1970.

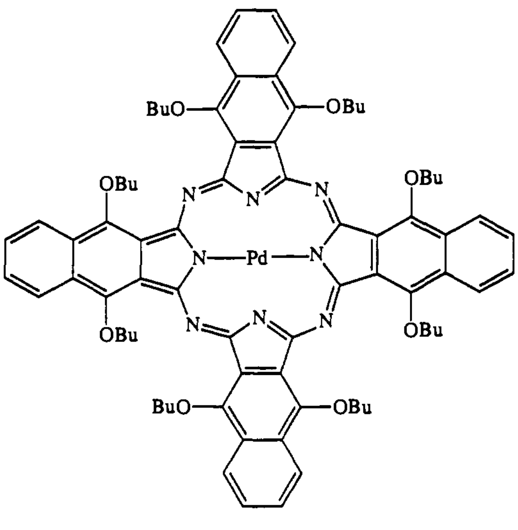
(5) (a) Becker, R. S. *Theory and Interpretation of Fluorescence and Phosphorescence*; Wiley Interscience: New York, 1969; pp 190–199. (b) Gouterman, M. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. III, Part A, pp 1–165. (c) Ferraudi, G. In *Phthalocyanines: Properties and Applications*; Leznoff, C. C., Lever, A. B. P., Eds.; VCH Publishers: New York, 1989; pp 291–340. (d) Serpone, N.; Jamieson, M. A. *Coord. Chem. Rev.* **1989**, *93*, 87–153. (e) Kalyanasundaram, K. *Photochemistry of Polypyridine and Porphyrin Complexes*; Academic Press: London, 1992.

(6) (a) Firey, P. A.; Ford, W. E.; Sounik, J. R.; Kenney, M. E.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1988**, *110*, 7626–7630. (b) Rihter, B. D.; Kenney, M. E.; Ford, W. E.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1990**, *112*, 8064–8070. (c) Ford, W. E.; Rodgers, M. A. J.; Schechtman, L. A.; Sounik, J. R.; Rihter, B. D.; Kenney, M. E. *Inorg. Chem.* **1992**, *31*, 3371–3377.

0002-7863/93/1515-8146$04.00/0

phthalocyanine π-system by either expansion of the number of condensed benzene rings at the molecular periphery, as in the 2,3-naphthalocyanines, or substitution of alkoxy residues at the eight positions α to the point of fusion with the tetrapyrrole ring.[6,7] Each of these constitutional changes leads to red shifts of up to 100 nm from the unsubstituted phthalocyanine values. These red shifts are accompanied by concomitant lowering of the energy of T_1, and in fact, the T_1 states of certain of these compounds have been demonstrated to be populated by energy transfer from singlet oxygen.[6] It was predicted from these results that the platinum metal complexes of octaalkoxynaphthalocyanine could have $S_0 \rightarrow T_1$ energy gaps below the $^3\Sigma_g^- \rightarrow {}^1\Delta_g$ energy gap in molecular oxygen (22.5 kcal/mol) and a phosphorescence quantum efficiency much higher than that of singlet oxygen.

To this end the palladium complex of 1,6,10,15,19,24,28,33-octabutoxynaphthalocyanine, PdNc(OBu)$_8$, was prepared and its photoproperties were examined. In what follows we report the extent to which the aims outlined above have been achieved. During the course of the investigation, we observed that this compound exhibits a tendency to form an oxygen adduct that undergoes thermal reversion and photoreversion with visible light. In view of the ongoing interest in photooxygenation reactions[8] and the novelty of the present system, the photochemistry of PdNc(OBu)$_8$ and its oxygen adduct was investigated and is also reported below.



PdNc(OBu)$_8$

Experimental Section

Materials. 1,4-Dihydroxy-2,3-dicyanonaphthalene. 1,4-Dihydroxy-2,3-dicyanonaphthalene was prepared from 2,3-dichloro-1,4-naphthoquinone by the method of Reynolds and VanAllen.[9]

1,4-Dibutoxy-2,3-dicyanonaphthalene.[7] Under Ar, a mixture of 1,4-dihydroxy-2,3-dicyanonaphthalene (2.40 g), 1-iodobutane (4.0 mL), K_2CO_3 (10 g), and acetone (70 mL) was refluxed with stirring for 24 h, cooled, filtered, and evaporated to dryness with a rotary evaporator (40 °C). The residue was suspended in toluene (60 mL), and the suspension was filtered. The filtrate was chromatographed (Al_2O_3 III, 1:1 toluene–ethyl acetate), and a selected portion of the eluate was concentrated to a small volume (*ca.* 15 mL), diluted with hexane (50 mL), chilled on ice, and filtered. The solid was washed with hexane and dried (1.70 g, 45%): NMR ($CDCl_3$) δ 8.24 (m, 6,7-Ar H), 7.77 (m, 5,8-Ar H), 4.45 (t, 1-CH_2), 2.11 (m, 2-CH_2), 1.65 (m, 3-CH_2), 1.03 (t, CH_3).

H_2Nc(OBu)$_8$.[7] Under Ar, freshly cut Li wire (250 mg) was added in portions to a warmed solution of 1,4-dibutoxy-2,3-dicyanonaphthalene (1.00 g) and 1-butanol (10 mL), and the resulting suspension was refluxed for 1 h and cooled. The suspension formed was diluted with glacial acetic acid (10 mL), and the acidified suspension was stirred for 4 h and evaporated to dryness with a rotary evaporator (80 °C). The residue was dissolved in a CH_2Cl_2–pyridine solution (3:1, 70 mL), and the solution was washed with water, dried ($MgSO_4$), and evaporated to dryness with a rotary evaporator (60 °C). In succession, the residue was chromatographed (Al_2O_3 III, toluene), washed with methanol, and vacuum dried (60 °C) for 5 h (428 mg, 43%). UV–vis (λ_{max} (nm)) (CH_2Cl_2): 862. NMR ($CDCl_3$): δ 8.97 (m, 1,4-Nc H), 7.88 (m, 2,3-Nc H), 5.15 (t, 1-CH_2), 2.44 (s, NH), 2.23 (m, 2-CH_2), 1.66 (m, 3-CH_2), 1.03 (t, CH_3).

PdNc(OBu)$_8$. Under Ar, a solution of H_2Nc(OBu)$_8$ (61 mg) and dimethylformamide (12 mL) was refluxed for 3.5 h while being treated with $Pd(P(C_6H_5)_3)_2Cl_2$ in portions (300 mg total). The resulting mixture was cooled and evaporated to dryness with a rotary evaporator (45 °C), and the residue was chromatographed (Al_2O_3 III, toluene), washed with methanol, and vacuum dried (60 °C) for 8 h (51 mg, 77%). UV–vis (λ_{max} (nm), ϵ (M^{-1} cm^{-1})) (benzene): 323, 101 000; 467, 24 000; 732, 51 000; 828, 279 000. NMR ($CDCl_3$): δ 8.97 (m, 1,4-Nc H), 7.88 (m, 2,3-Nc H), 5.20 (t, 1-CH_2), 2.25 (m, 2-CH_2), 1.66 (m, 3-CH_2), 1.04 (t, CH_3). MS-HRFAB exact mass, *m/z*: calcd for $C_{80}H_{89}N_8O_8Pd$ $(M + H)^+$, 1395.5868; found, 1395.5817, 1395.5831.

Steady-State Photolysis. These experiments were performed with an Ar ion laser (Coherent, Innova 90) as the light source. Typically, a *ca.* 7 μM solution of PdNc(OBu)$_8$ in benzene was bubbled with O_2 gas while being irradiated with 458-nm laser light with an output power of 200 mW. The laser beam diameter was *ca.* 1.5 mm, and the solution was contained in a standard 1 × 1 cm quartz cuvette; the gas bubbles served to mix the solution during the photolysis. Five minutes of irradiation was sufficient to effect complete conversion of PdNc(OBu)$_8$ into its O_2-adduct. The 514-nm line of the Ar ion laser was used instead for excitation of samples containing porphyrin as sensitizer. UV–visible absorption spectra were measured within 2 min after the photolysis was terminated. Irradiation times were 2 min when it was necessary to restore a partially decomposed solution of the adduct after flash photolysis studies.

Photoproperties. The instrumentation and techniques employed in the determination of the photophysical properties of the octabutoxynaphthalocyanines were the same as those described in earlier publications.[6] An H_2 gas Raman shifter was used for obtaining the first Stokes line (683 nm) derived from the 532-nm output of the Nd:YAG laser.

The quantum efficiency of the laser-induced decomposition of the O_2-adduct was estimated as follows. A *ca.* 7 μM solution of PdNc(OBu)$_8$ in benzene was divided between two cuvettes (1 × 1 cm). One of these samples was subjected to steady-state photolysis to convert the PdNc(OBu)$_8$ into its O_2-adduct (see above). This sample was bubbled with Ar gas during the flash photolysis phase of the experiment. It was exposed to no more than three laser pulses during the flash photolysis measurement before being subjected to steady-state photolysis again to regenerate the adduct that had decomposed. The other sample was used as a solution actinometer during flash photolysis. The absorbance change at 650 nm immediately after pulsed laser excitation, $\Delta A(650)$, in the actinometer solution was due almost entirely to the formation of PdNc(OBu)$_8$(T_1) (see below) for which the product $\phi_T\Delta\epsilon_T$ equals (5.1 ± 0.9) × 10^4 M^{-1} cm^{-1}. This signal is related to $\phi_T\Delta\epsilon_T$ and to the ground-state absorbance of the solution at the excitation wavelength, $A(\lambda)$, according to eq 1,

$$\Delta A(650) = c(1 - 10^{-A(\lambda)})\phi_T\Delta\epsilon_T \qquad (1)$$

where c is a parameter that is proportional to the intensity of the laser pulse. For the solution containing the O_2-adduct, the absorbance change was monitored at 828 nm, where the $\Delta\epsilon$ value associated with the decomposition of the adduct, $\Delta\epsilon_D$, is 2.5 × 10^5 M^{-1} cm^{-1} (see below), so that the observed signal is

$$\Delta A(828) = c(1 - 10^{-A(\lambda)})\phi_D\Delta\epsilon_D \qquad (2)$$

where ϕ_D is the quantum efficiency for the decomposition of the O_2-adduct into PdNc(OBu)$_8$. The shot-to-shot intensity of the laser pulse varied by less than 5%, so that c was taken to be the same in eqs 1 and 2. The value of $A(\lambda)$ for the sample containing the O_2-adduct was assumed to be the value expected if *ca.* 100% of the PdNc(OBu)$_8$ was converted

---

(7) Cook, M. J.; Dunn, A. J.; Howe, S. D.; Thomson, A. J.; Harrison, K. J. *J. Chem. Soc., Perkin Trans. 1* **1988**, 2453–2458.

(8) (a) Kearns, D. R.; Khan, A. U. *Photochem. Photobiol.* **1969**, *10*, 193–210. (b) Kearns, D. R. *Chem. Rev.* **1971**, *71*, 395–427. (c) Saito, I.; Matsuura, T. In *Singlet Oxygen*; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979; Chapter 10, pp 511–574. (d) Frimer, A. A. In *The Chemistry of Functional Groups, Peroxides*; Patai, S., Ed.; Wiley: Chichester, 1983; Chapter 7, pp 201–234. (e) Brauer, H.-D.; Schmidt, R. In *Photochromism; Molecules and Systems*; Durr, H., Bonas-Laurent, H., Eds.; Elsevier: Amsterdam, 1990; Chapter 15, pp 631–653.

(9) Reynolds, G. A.; VanAllen, J. A. *J. Org. Chem.* **1964**, *29*, 3591–3593.

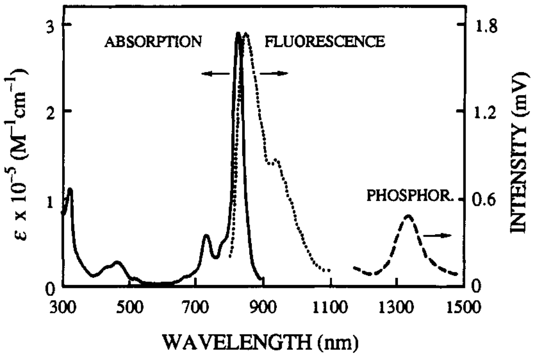


Figure 1. Absorption, fluorescence, and phosphorescence spectra of PdNc(OBu)$_8$ in benzene at 22 °C. The emission spectra were obtained with an N_2-saturated solution containing 7.2 μM PdNc(OBu)$_8$, an excitation wavelength of 458 nm (Ar ion laser, 200-mW output power), and monochromator slit widths of 2 mm.

into the adduct (see Figure 4). The value of ϕ_D was calculated from eqs 1 and 2 and the experimentally determined parameters.

^{1}H-NMR Analysis of the Photoadduct. A benzene-d_6 solution of PdNc(OBu)$_8$ (3.6 mM) contained in a 5-mm NMR tube was bubbled with O_2 while it was being irradiated with an all-lines Ar ion laser beam (5-mm diameter, 1.6 W) (Coherent Innova 100) for 5 min. The NMR tube was jacketed with a water bath during the irradiation to avoid heating the sample. The irradiated solution was frozen (dry ice), transported to an NMR spectrometer, and thawed. Proton NMR spectra were taken with a 400-MHz spectrometer (USA Bruker Instruments MSL-400) periodically over the next 26 h.

Results

Photoproperties of PdNc(OBu)$_8$. Steady-State Absorption and Luminescence. The Q(0,0) and B absorption band maxima of PdNc(OBu)$_8$ in benzene solution are located at 828 and 323 nm, respectively. The extinction coefficient at 828 nm is (2.8 ± 0.1) × 10^5 M^{-1} cm^{-1}. Luminescence spectra obtained in N_2-saturated benzene have maxima at 850 and 1335 nm, which are attributed to fluorescence and phosphorescence, respectively. These absorption and emission spectra are shown in Figure 1. The S_1–T_1 gap estimated from these spectra is 12.7 kcal/mol, which is 0.3 kcal/mol less than the value for the phthalocyanine analogue, PdPc(OBu)$_8$.[6b]

Introduction of O_2 into the benzene solution of PdNc(OBu)$_8$ results in quenching of the emission at 1335 nm and the concomitant appearance of phosphorescence from the singlet oxygen molecule, $O_2(^1\Delta_g)$, at 1270 nm. A comparison of the steady-state luminescence signals, L, due to O_2 ($^1\Delta_g \rightarrow {}^3\Sigma_g^-$) in the O_2-saturated solution, L_Δ, and due to PdNc(OBu)$_8$ ($T_1 \rightarrow S_0$) in the N_2-saturated solution, L_T, under constant laser fluence allows an estimate of the radiative rate constant, k_r^T, of the T_1 state to be made as follows. The response of the instrument to the emission from singlet oxygen is given by

$$L_\Delta = bI_a\phi_\Delta k_r^\Delta\tau_\Delta \qquad (3)$$

where b is an instrument parameter that accounts for light gathering and detector sensitivity, I_a is the rate of photon absorption by PdNc(OBu)$_8$, ϕ_Δ is the quantum efficiency of $O_2(^1\Delta_g)$ production, k_r^Δ is the radiative rate constant of $O_2(^1\Delta_g)$ emission, and τ_Δ is the lifetime of $O_2(^1\Delta_g)$ in the solution.[3] The corresponding expression for phosphorescence from PdNc(OBu)$_8$(T_1) is

$$L_T = bI_a\phi_T k_r^T\tau_T \qquad (4)$$

where ϕ_T is the quantum efficiency of production of the triplet state of radiative rate constant k_r^T, and τ_T is its lifetime in N_2-saturated benzene. When the rate of photon absorption is held constant in the O_2-saturated and N_2-saturated solutions, the ratio of the emission signals is

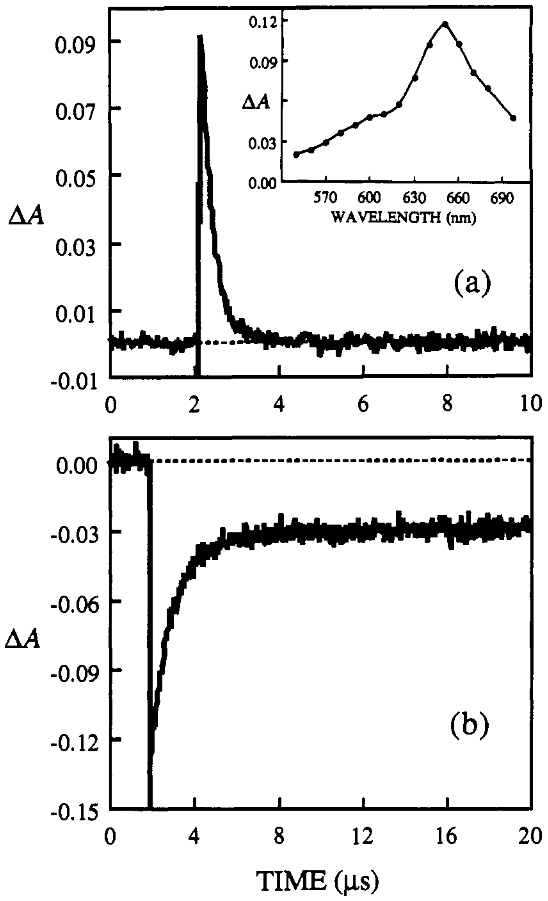


Figure 2. Time profiles of the absorbance changes at 698 nm following 532-nm laser excitation (single shot) of benzene solutions of (a) PdNc(OBu)$_8$ and (b) its O_2-adduct. The solutions were saturated with either (a) O_2 or (b) Ar. Inset: Triplet–triplet difference absorption spectrum of PdNc(OBu)$_8$.

$$L_T/L_\Delta = (\phi_T k_r^T\tau_T)/(\phi_\Delta k_r^\Delta\tau_\Delta) \qquad (5)$$

The parameter b cancels out in the ratio because there is practically no change in the sensitivity of the detector over the range 1120–1360 nm.[10] Furthermore, PdNc(OBu)$_8$(T_1) is the precursor to $O_2(^1\Delta_g)$, so that ϕ_Δ can be replaced with the product $\phi_T P_{tr} S_\Delta$, where P_{tr} is the probability of T_1 quenching by O_2, and S_Δ is the fraction of these quenching events that lead to production of $O_2(^1\Delta_g)$. Thus, under the conditions of constant laser fluence, eq 5 becomes

$$L_T/L_\Delta = (k_r^T\tau_T)/(P_{tr}S_\Delta k_r^\Delta\tau_\Delta) \qquad (6)$$

The value of k_r^Δ in benzene is known to be 1.5 s^{-1},[2] and the value of S_Δ is probably close to 1, as it is for a variety of diamagnetic metal phthalocyanines and naphthalocyanines.[6] On the basis of the ratio of emission intensities determined from the steady-state measurements and the lifetimes determined from flash photolysis measurements (see below), the value of k_r^T is found to be 65 ± 10 s^{-1}. The phosphorescence quantum efficiency, $\phi_P = k_r^T\tau_T$, is thus (6 ± 1) × 10^{-5}.

Characterization by Flash Photolysis. Flash photolysis of benzene solutions of PdNc(OBu)$_8$ with either 355-, 532-, or 683-nm laser light produces a transient whose difference absorption spectrum has a maximum at 650 nm, which is assigned to the triplet (T_1) state of the compound. The inset in Figure 2a shows the difference spectrum in the range 550–700 nm. The triplet-minus-ground-state extinction coefficient, $\Delta\epsilon_T$, at 650 nm was determined by the total depletion method to be (6.7 ± 0.6) × 10^4

---

(10) Schmidt, R. *Chem. Phys. Lett.* **1988**, *151*, 369–374.

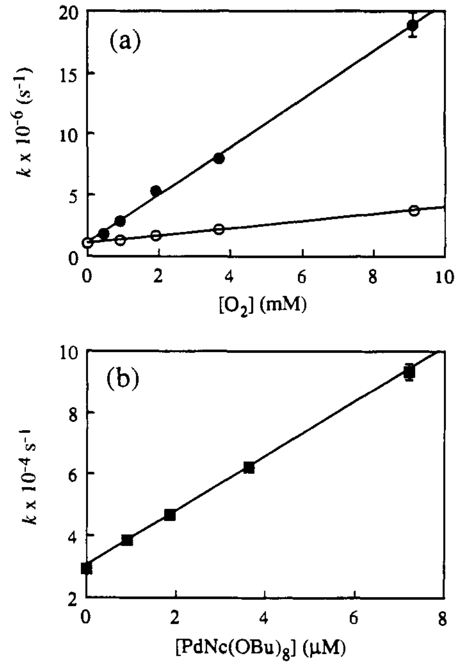


Figure 3. (a) Plots of the first-order rate constant for decay of the triplet state of PdNc(OBu)$_8$ (open circles) and its O$_2$-adduct (closed circles) versus the concentration of O$_2$ in benzene solution. (b) Plot of the first-order rate constant for decay of O$_2$($^1\Delta_g$) as a function of the concentration of PdNc(OBu)$_8$ in benzene solution. The formation of O$_2$($^1\Delta_g$) was photosensitized with protoporphyrin-IX dimethyl ester (532-nm laser excitation).

M^{-1} cm^{-1}; this method provides a lower limit for the true value.[11] Actinometry with a solution of bis(tri-*n*-hexylsiloxy)silicon 2,3-naphthalocyanine in benzene as standard ($\phi_T\Delta\epsilon_T$ = (1.65 ± 0.22) × 10^4 M^{-1} cm^{-1} at 590 nm)[6] gives a value for $\phi_T\Delta\epsilon_T$ of (5.1 ± 0.9) × 10^4 M^{-1} cm^{-1} at 650 nm, so that ϕ_T has an upper limit of 0.76 ± 0.20.

The lifetime of PdNc(OBu)$_8$(T$_1$) in deaerated benzene solution is 950 ± 10 ns. The decay of T$_1$ in the presence of O$_2$ deviated slightly from single exponential, but this deviation was only evident at higher concentrations of O$_2$, *e.g.*, O$_2$-saturated benzene, and when the concentration of PdNc(OBu)$_8$ exceeded *ca.* 5 μM. Double-exponential fits of these decay profiles typically gave slower decay components having lifetimes of 10–30 μs and constituting *ca.* 2–3% of the total T$_1$ population. This behavior is probably a consequence of reversible energy transfer (see below). Figure 2a shows an example of the nearly monoexponential decay of T$_1$ for an O$_2$-saturated solution containing 4 μM PdNc(OBu)$_8$, and Figure 3a shows the linear dependence of rate constant on O$_2$ concentration. The derived bimolecular rate constant for quenching of T$_1$ by O$_2$($^3\Sigma_g^-$) is $k_{T\Sigma}$ = (2.9 ± 0.2) × 10^8 M^{-1} s^{-1}.

The phosphorescence measurements cited above place the energy of PdNc(OBu)$_8$(T$_1$) at 21.4 kcal/mol above the ground state, so that energy transfer from O$_2$($^1\Delta_g$) to PdNc(OBu)$_8$ is exergonic by 0.9 kcal/mol (eq 7). The bimolecular rate constant

$$O_2(^1\Delta_g) + PdNc(OBu)_8(S_0) \rightarrow O_2(^3\Sigma_g^-) + PdNc(OBu)_8(T_1) \quad (7)$$

for the quenching of O$_2$($^1\Delta_g$) by PdNc(OBu)$_8$ was determined by generating O$_2$($^1\Delta_g$) via the T$_1$ state of protoporphyrin-IX dimethyl ester (532-nm laser excitation) and measuring the time dependence of the near infrared luminescence as a function of increasing concentration of PdNc(OBu)$_8$. When the concentration of PdNc(OBu)$_8$ was nonzero, the observed luminescence was from both O$_2$($^1\Delta_g$) and PdNc(OBu)$_8$(T$_1$). Biexponential kinetics was observed for the luminescence decay in these samples because PdNc(OBu)$_8$(T$_1$) was produced by direct photoexcitation as well as via eq 7. The rate constant for the slower decay component was linearly dependent on the concentration of PdNc(OBu)$_8$ and gave a bimolecular rate constant for quenching of O$_2$($^1\Delta_g$) of (8.8 ± 0.5) × 10^9 M^{-1} s^{-1}. These results are presented in Figure 3b.

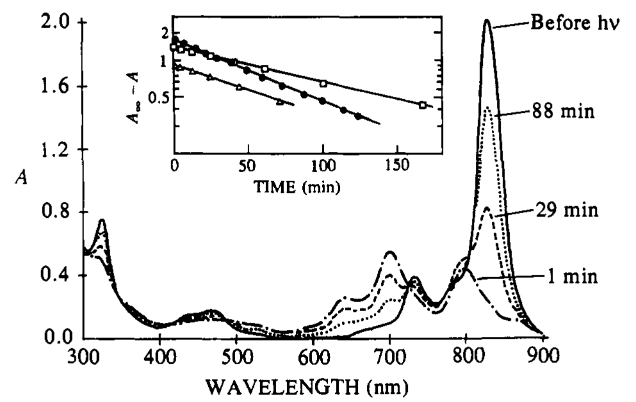


Figure 4. Absorption spectra of PdNc(OBu)$_8$ (7.2 μM) in benzene before and after photoconversion to its O$_2$-adduct. The spectrum labeled "1 min" was recorded within 1 min after the conversion to the adduct was completed. The other two spectra were recorded 29 and 88 min after the photoconversion and show the thermal (22 ± 1 °C) reversion of the adduct back into PdNc(OBu)$_8$. Inset: Plot of log(A_∞–A) versus time after the photoconversion, where the absorbances refer to the values at 828 nm. The data shown are for benzene (solid circles), cyclohexane (open squares), and dichloromethane (open triangles) as the solvents.

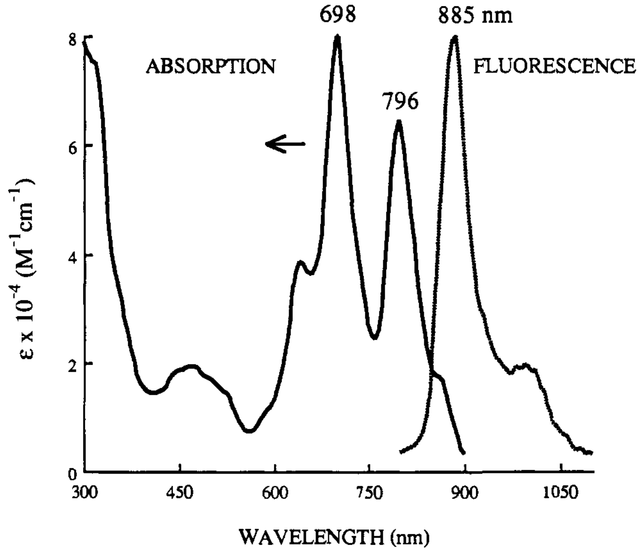


Figure 5. Absorption and fluorescence spectra of the O$_2$-adduct of PdNc(OBu)$_8$ in benzene. The fluorescence spectra was obtained with an O$_2$-saturated solution containing *ca.* 1 μM of the adduct, an excitation wavelength of 476 nm (Ar ion laser, 150-mW output power), and monochromator slit widths of 1.5 mm.

Photochemical Reaction with O$_2$. Ground State Absorption Spectral Changes. Steady-state photolysis of PdNc(OBu)$_8$ at room temperature in O$_2$-saturated benzene with an Ar ion laser results in a change in the color of the solution from olive to emerald green. The absorption spectra of the solution before and after this conversion are shown in Figure 4. The photoproduct has absorption maxima at 698 and 796 nm. Continued photolysis under these conditions has no further effect on the spectrum. Assuming complete conversion, the extinction coefficient of the product at 698 nm is 8.0 × 10^4 M^{-1} cm^{-1} (Figure 5). This transformation requires O$_2$ since photolysis of N$_2$-saturated solutions has no effect on the absorption spectrum. When solutions of the photoproduct are kept in the dark at room temperature (22 ± 1 °C), the absorption spectrum reverts into the original one

---

[11] Carmichael, I.; Hug, G. L. *J. Phys. Chem. Ref. Data* **1988**, *15*, 1–250.

with isosbestic points near 345, 415, 487, and 742 nm (Figure 4); these same isosbestic points are seen in spectra taken at intermediate stages of the photolysis. The absorbance at 828 nm recovers to 50% of its original value after 45 min, but the recovery is only 95% complete after 25 h. This result indicates that the reaction is not completely reversible. The inset in Figure 4 is a semilogarithmic plot of the absorbance at 828 nm versus time, which shows that the first-order rate constant for recovery of the 95% reversible portion is $k = (2.6 \pm 0.2) \times 10^{-4}\ \mathrm{s}^{-1}$.

The recovery of $PdNc(OBu)_8$ from the photoproduct is accelerated by light. Thus, steady-state photolysis of the solutions with the same light conditions that are used to produce the photoproduct enhances its rate of decomposition when the resulting solutions are purged with N_2 rather than O_2 (data not shown). This process was examined quantitatively by flash photolysis (see below).

NMR Analysis of the Product. Irradiation with all lines of an Ar ion laser of an O_2-saturated solution of $PdNc(OBu)_8$ having a concentration (3.6 mM) sufficient for ^{1}H-NMR analysis resulted in the same color change (olive to emerald green) that was observed with much less concentrated solutions, indicating the conversion of $PdNc(OBu)_8$ into the photoproduct. From the NMR spectrum taken within 10 min after thawing, it is concluded that the light–O_2 treatment leads to the formation of a monoendoperoxy naphthalocyanine in which the endoperoxy oxygen bridges one of the pairs of carbon atoms bearing butoxy groups. The positions and resonances of the latter spectra indicate that this endoperoxide mainly reverts back to $PdNc(OBu)_8$, although other unidentified product(s) are also evident.

Involvement of Singlet Oxygen. The requirement for O_2 in the photochemical transformation of $PdNc(OBu)_8$ and the fact that O_2-quenching of $PdNc(OBu)_8(T_1)$ generates $O_2(^1\Delta_g)$ suggest that the latter species may be involved in the reaction. This hypothesis was tested by generating $O_2(^1\Delta_g)$ independently via photosensitization with protoporphyrin-IX dimethyl ester (PPDME) and examining the effect of added 2,5-dimethylfuran, which quenches $O_2(^1\Delta_g)$.[12] The lifetime of PPDME(T_1) is sufficiently shortened by its energy-transfer reaction with $O_2(^3\Sigma_g^-)$ that the possibility of triplet energy transfer to $PdNc(OBu)_8$ can be ignored. In the sensitization experiment, the concentration of PPDME was such that it absorbed 83% of the incident 514-nm laser light at the start, the remainder being absorbed by $PdNc(OBu)_8$. The concentration of 2,5-dimethylfuran employed, 0.010 M, was sufficient to intercept *ca.* 98% of the $O_2(^1\Delta_g)$ being generated.[12] The results of these experiments are shown graphically in Figure 6. The furan inhibits both self-sensitized and photosensitized processes. These data clearly implicate the participation of $O_2(^1\Delta_g)$ in the photochemical reaction of $PdNc(OBu)_8$.

Estimated Upper Limit of Quantum Efficiency. The photochemical reaction of $PdNc(OBu)_8$ with O_2 should be detectable by laser flash photolysis since it results in distinct spectral changes (see Figure 4). The reaction results in a net increase or decrease in absorbance, depending on the wavelength being monitored, which is practically permanent on the time scale of microseconds to milliseconds. The kinetic trace in Figure 2a shows that $PdNc(OBu)_8(T_1)$ observed at 698 nm decays exponentially nearly to the base line. The positive absorbance change at 698 nm due to formation of the photoproduct (Figure 4) apparently contributes no more than 1% of the total signal. The $\Delta\epsilon$ values at this wavelength for conversion of $PdNc(OBu)_8$ into $PdNc(OBu)_8(T_1)$ and the photoproduct are estimated as $\geq 2.7 \times 10^4$ and 5.8×10^4 $M^{-1}\ cm^{-1}$, respectively. Thus, the transient absorption result in Figure 2a indicates that quantum efficiency for formation of the photoproduct (532-nm excitation) has an upper limit of 0.01. The same conclusion is reached on the basis of measurements made at 650 and 823 nm[13] with excitation wavelengths of either 355 or 532 nm.

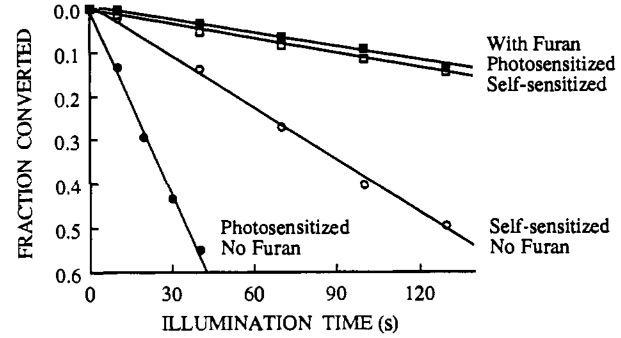


Figure 6. Plot of the fraction of $PdNc(OBu)_8$ photoconverted to its O_2-adduct versus the total time of illumination in benzene solution under four sets of conditions. Open circles: self-sensitized and in the absence of 2,5-dimethylfuran. Open squares: self-sensitized and with 2,5-dimethylfuran added as a quencher of $O_2(^1\Delta_g)$. Closed circles: photosensitized and in the absence of 2,5-dimethylfuran. Closed squares: photosensitized and with 2,5-dimethylfuran added. Each solution contained 8.4 μM $PdNc(OBu)_8$, and the excitation wavelength was 514 nm (100-mW Ar ion laser output power). The photosensitized solutions contained 20 μM protoporphyrin-IX dimethyl ester. The concentration of 2,5-dimethylfuran used was 0.010 M.

Photoproperties of the Product. Steady-State Luminescence. The fluorescence maximum of $PdNc(OBu)_8$ in O_2-saturated benzene shifts from 850 to 885 nm during the first few minutes of excitation with Ar ion laser light under conditions known to give essentially complete conversion to the photoproduct. The fluorescence spectrum of the photoproduct is shown in Figure 5. The shoulder near 880 nm in the absorption spectrum is apparently the 0,0 transition for the observed fluorescence.

Characterization by Flash Photolysis. Pulsed laser excitation of benzene solutions containing predominantly the photoproduct generates a transient whose extinction coefficient at 698 nm is less than that of the ground state, *i.e.*, the absorbance change at 698 nm is negative, opposite to that observed for $PdNc(OBu)_8(T_1)$ (Figure 2a). An example of these data is shown in Figure 2b. Most of the bleaching signal decays within a few microseconds, but a portion of it is permanent. We tentatively assign the faster of these two kinetically resolved components to the triplet state of the photoproduct. The lifetime in the absence of O_2 is 970 ± 20 ns, which is close to that of $PdNc(OBu)_8(T_1)$, but the bimolecular rate constant for quenching by O_2, $k_{T\Sigma} = (1.9 \pm 0.1) \times 10^9\ M^{-1}\ s^{-1}$, is significantly higher (Figure 3a).

The spectrum of the long-time (>20 μs) absorption change in solutions of the photoproduct is compared to the photoproduct-minus-$PdNc(OBu)_8$ difference spectrum in Figure 7. The good correspondence between these two difference spectra identifies the permanent product as $PdNc(OBu)_8$, so that the process being monitored is the decomposition of the photoproduct back into $PdNc(OBu)_8$.

Estimation of Quantum Efficiency. The quantum efficiency of the laser-induced decomposition of the photoproduct was estimated by monitoring the absorbance change at 828 nm, where $\Delta\epsilon$ for the reaction is $2.5 \times 10^5\ M^{-1}\ cm^{-1}$. The inset in Figure 7 shows a kinetic trace obtained by a single shot with 532-nm laser light. The efficiency obtained with either 355- or 532-nm excitation was the same within experimental uncertainty, 0.035 ± 0.010 (see Experimental Section). The value obtained with 683-nm excitation was smaller by an order of magnitude, 0.0015 ± 0.0005. These values were obtained with Ar-saturated solutions. The replacement of Ar with O_2 resulted in less than 20% quenching of the quantum efficiency (355- or 532-nm excitation). By

---

(12) Gorman, A. A.; Lovering, G.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1979**, *101*, 3050–3055.

(13) This wavelength was selected because it is a maximum in the output of the Xe-arc monitoring lamp of the nanosecond laser flash photolysis apparatus.

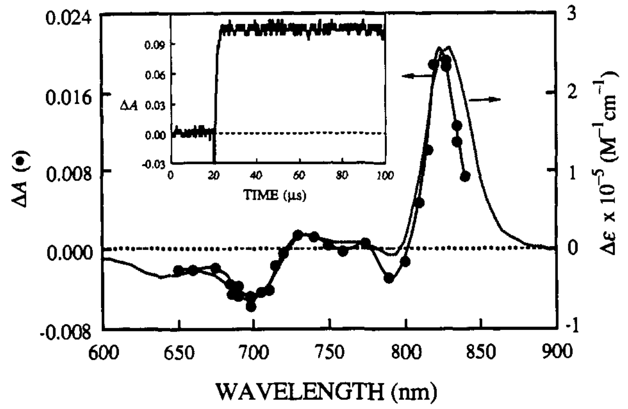


Figure 7. The difference absorption spectrum for the permanent product of photolysis of the O_2-adduct of $PdNc(OBu)_8$ (solid circles) in benzene solution is compared to the difference spectrum that is obtained by subtracting the ground-state spectrum of the adduct from that of $PdNc(OBu)_8$ (dotted line). Inset: An example of the signal observed at 828 nm following 532-nm laser excitation (single shot) of a benzene solution of the O_2-adduct.

contrast, this replacement results in *ca.* 95% quenching of the T_1 state of the photoproduct.

Other Solvents. The steady-state photolysis of $PdNc(OBu)_8$ in O_2-saturated cyclohexane and dichloromethane solutions at room temperature generated the photooxygenated product as in benzene solution. The absorption spectra of $PdNc(OBu)_8$ and its oxygen adduct in these two solvents closely resemble the spectra in benzene except for shifts in the maxima of several nanometers. As with benzene, the adduct reverted back into $PdNc(OBu)_8$ in these other solutions when they were kept in the dark at 22 °C, but there were differences in the rate constant and reversibility of the reaction. With dichloromethane as solvent, only 50% of the original $PdNc(OBu)_8$ was recovered after 16 h. The first-order rate constant for the 50% reversible portion was $(2.1 \pm 0.2) \times 10^{-4}$ s^{-1}, which is slightly less than the value in benzene. With cyclohexane as solvent, the reaction was probably close to 100% reversible and the first-order rate constant was $(1.4 \pm 0.2) \times 10^{-4}$ s^{-1}. The first-order plots for these reactions are shown in the inset in Figure 4.

Related Compounds. Two compounds that are closely related to $PdNc(OBu)_8$ were examined for possible photoreactivity with O_2 in benzene. One of these was $PdPc(OBu)_8$,[6b] the phthalocyanine analogue of $PdNc(OBu)_8$, and the other was $H_2Nc(OBu)_8$, the metal-free derivative of $PdNc(OBu)_8$. O_2-saturated solutions of these compounds were submitted to steady-state photolysis with the Ar ion laser under conditions (rate of light absorption and time of exposure) in excess of those required for complete conversion of $PdNc(OBu)_8$ to its photoproduct. There was no spectroscopic evidence of change in the solutions of $PdPc(OBu)_8$ and $H_2Nc(OBu)_8$. A repeat of the experiment with $H_2Nc(OBu)_8$ but with PPDME to photosensitize the formation of $O_2(^1\Delta_g)$ resulted in spectral changes analogous to those seen with $PdNc(OBu)_8$, *i.e.*, disappearance of the Q-absorption bands at 866 and 763 nm and appearance of a new band near 700 nm. These spectral changes were partially reversed upon storage (22 °C) of the solution in the dark for 2 days.

Discussion

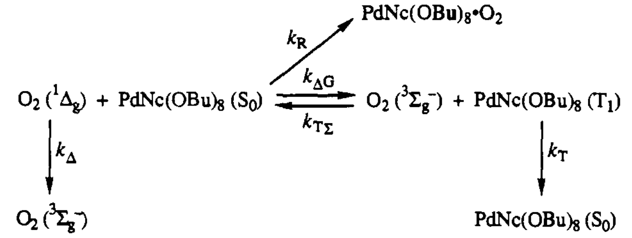
As noted above, the primary motivation for initiating the study of $PdNc(OBu)_8$ was to investigate the possibility of using platinum metal complexes of octaalkoxynaphthalocyanine as luminescence probes for $O_2(^1\Delta_g)$. Phosphorescence in fluid solutions at room temperature is a property exhibited by a variety of platinum metal complexes, including porphyrins and phthalocyanines, but their T_1 states are generally greater in energy than the $^1\Delta_g$ state of O_2.[5] $PdPc(OBu)_8$, which is the phthalocyanine analogue of $PdNc(OBu)_8$, is one of these compounds.[6b] On the basis of the facts that $Nc(OBu)_8$ compounds have S_1 energies approximately 4.4 kcal/mol lower than the corresponding $Pc(OBu)_8$ compounds and the T_1 energy of $PdPc(OBu)_8$ is 26.0 kcal/mol, we expected the T_1 state of $PdNc(OBu)_8$ to be somewhat less energetic than the $^1\Delta_g$ state of O_2, assuming that the Pd complexes have similar S_1–T_1 gaps. The energy of $PdNc(OBu)_8(T_1)$ is 21.4 kcal/mol, which is 0.9 kcal/mol less than that of $O_2(^1\Delta_g)$. The radiative rate constant obtained for $PdNc(OBu)_8(T_1)$, $k_r = 65 \pm 10$ s^{-1}, is the same order of magnitude as the values found for Pd(II) porphyrins and phthalocyanine at 77 K (80–260 s^{-1}).[5] Since the values for the corresponding Pt(II) complexes are at least 10 times higher than for Pd(II),[5] it may be possible to increase k_r by replacing Pd(II) with Pt(II) in the octabutoxynaphthalocyanine ring. This substitution may result in a corresponding decrease in the triplet-state lifetime, however, so that the phosphorescence quantum efficiency will not be affected so much.

Our results clearly show that benzene solutions of $PdNc(OBu)_8$ and O_2 are photochromic. The photochemical conversion of $PdNc(OBu)_8$ into another highly colored species requires O_2 and probably involves $O_2(^1\Delta_g)$ as the reactive intermediate. This transformation of $PdNc(OBu)_8$ is reversible both thermally and photochemically. In these respects the behavior of $PdNc(OBu)_8$ resembles that of polycyclic aromatic compounds which photooxygenate into transannular endoperoxides and undergo photocycloreversion reactions,[8] so that it is reasonable to expect the photoproduct of $PdNc(OBu)_8$ to be an endoperoxide. The NMR evidence is consistent with the sites of oxygenation being the carbon atoms bearing the butoxy substituents on one of the naphthyl rings of the $PdNc(OBu)_8$ molecule. The fact that the visible absorption spectra associated with the transformation have isosbestic points supports the NMR evidence for a 1:1 stoichiometry between $PdNc(OBu)_8$ and O_2, *i.e.*, only one of the four naphthyl rings is modified in the process.

Various porphyrins and metalloporphyrins decompose in solution when exposed to light and O_2.[14] The photooxygenation of *meso*-tetraphenylporphyrins, for example, occurs by the addition of $O_2(^1\Delta_g)$ followed by ring cleavage, yielding biliones as products.[14a] Some metal complexes of porphyrins and phthalocyanines reversibly form adducts with O_2, but in these cases O_2 is coordinated to the metal atom rather than being bonded to the ligand itself.[15] Thus, $PdNc(OBu)_8$ and presumably $H_2Nc(OBu)_8$, also, may be the first examples of tetrapyrrolic compounds that form stable adducts with O_2 bonded to the ring system.

Kinetic analysis of the photooxygenation of $PdNc(OBu)_8$ requires that reversible energy transfer between the O_2 and $PdNc(OBu)_8$ molecules be included due to the proximity of the $O_2(^1\Delta_g)$ and $PdNc(OBu)_8(T_1)$ energy levels.[6] The kinetic model for this system is shown in Scheme I, where $PdNc(OBu)_8{\cdot}O_2$ represents the photooxygenated product. This is the same model

Scheme I



---

(14) (a) Cavaleiro, J. A. S.; Neves, M. G. P. S.; Hewlins, M. J. E.; Jackson, A. H. *J. Chem. Soc., Perkin Trans. 1* **1990**, 1937–1943. (b) Spikes, J. D. *Photochem. Photobiol.* **1992**, *55*, 797–808.

(15) (a) James, B. R. In *The Porphyrins*, Volume V (Physical Chemistry, Part C); Dolphin, D., Ed.; Academic Press: New York, 1978; Chapter 6, pp 205–302. (b) Stillman, M. J.; Nyokong, T. In *Phthalocyanines: Properties and Applications*; Leznoff, C. C., Lever, A. B. P., Eds.; VCH: New York, 1989; Chapter 3, pp 133–289.

used previously[6] for excited-state processes involving O_2 and naphthalocyanines and octakis(butyloxy)phthalocyanines except for the additional photooxygenation reaction characterized by the bimolecular rate constant k_R. This scheme applies whether $O_2(^1\Delta_g)$ formation is either self-sensitized or photosensitized. The value of the intrinsic rate of decay of $O_2(^1\Delta_g)$ via physical deactivation by solvent molecules, k_Δ, in benzene is 3.1×10^4 s^{-1}. The concentrations of O_2 and PdNc(OBu)$_8$ were typically 9.1×10^{-3} M (O_2-saturated benzene)[16] and 5×10^{-6} M, respectively. From the laser flash photolysis experiments we know the following values: $k_T = 1.1 \times 10^6$ s^{-1}, $k_{T\Sigma} = 2.9 \times 10^8$ M^{-1} s^{-1}, and $(k_R + k_{\Delta G}) = 8.8 \times 10^9$ M^{-1} s^{-1}. On the basis of these parameters, it is evident that the decay of PdNc(OBu)$_8$(T$_1$) by intersystem crossing to the ground state occurs at a rate that is comparable to energy-transfer quenching by $O_2(^3\Sigma_g^-)$, so that the energy is drained before equilibration between the excited states is achieved. The upper limit on the quantum efficiency of photooxygenation of 0.01 indicates that k_R is very inefficient compared to k_Δ and k_T at draining the equilibrium and that the quenching of $O_2(^1\Delta_g)$ by PdNc(OBu)$_8$ occurs mainly by energy transfer instead of chemical reaction to give PdNc(OBu)$_8$·O_2.[17]

Photocycloreversion of the endoperoxides of polycyclic aromatic compounds occurs from an S_n ($n \geq 2$) $\pi\pi^*$ singlet state to give the S_0 state of the parent compound and $O_2(^1\Delta_g)$ in a 1:1 ratio.[8,18] Population of the $S_1(\pi^*\sigma^*)$ state by either internal conversion or direct excitation leads to products derived from cleavage of the peroxide bridge because this state is localized on the peroxide chromophore.[8,18] Similar products arise from thermally induced rupture of the O–O bond.[8,18] The energy of the $S_1(\pi^*\sigma^*)$ state is estimated to be in the vicinity of 66 kcal/mol (435 nm).[8,18] These reactions result in the irreversible degradation of the parent compound and compete with cycloreversion, so that they are undesirable side reactions in applications that rely on photochromism.[8e]

The absorption and fluorescence spectra of PdNc(OBu)$_8$·O_2 (Figure 5) point to an S_1 energy of *ca.* 32 kcal/mol (880–885 nm), so that the S_1 state is $\pi\pi^*$ rather than $\pi^*\sigma^*$ in character. The fact that photoexcitation of PdNc(OBu)$_8$·O_2 with 355- or 532-nm light regenerates PdNc(OBu)$_8$ much more efficiently than 683-nm light indicates that upper level S_n states are more active than the lower one(s), but this compound appears to be the first example of an endoperoxide that is subject to photocycloconversion with visible light.

The metal-free derivative of PdNc(OBu)$_8$, H$_2$Nc(OBu)$_8$, also seemed to form a metastable adduct with O_2, but this reaction only became apparent when a photosensitizer was used to generate $O_2(^1\Delta_g)$. The apparent inability of H$_2$Nc(OBu)$_8$ to self-sensitize the reaction may reflect a relatively poor capacity for generating $O_2(^1\Delta_g)$ compared to PdNc(OBu)$_8$.

Conclusion

Two properties exhibited by PdNc(OBu)$_8$ distinguish it from known compounds. First of all, PdNc(OBu)$_8$ possesses an emissive electronic state, the triplet, which can be populated by collisional energy transfer from $O_2(^1\Delta_g)$. This behavior suggests that the platinum group metal complexes of octaalkoxynaphthalocyanines may prove to be useful as luminescence probes for the detection of singlet molecular oxygen. Secondly, PdNc(OBu)$_8$ may be the first known example of a tetrapyrrole which adds molecular oxygen reversibly to a site other than the metal atom. The reaction is photoinitiated and probably involves $O_2(^1\Delta_g)$. The product of the addition reaction, which is probably an endoperoxide, decomposes both thermally and photochemically to regenerate the parent compound. Visible light is as effective as near ultraviolet light in promoting decomposition of the oxygen adduct. This sensitivity to visible light distinguishes the PdNc(OBu)$_8$–O_2 photochromic system from those based on polycyclic aromatic compounds.

Acknowledgment. The contributions of Ellie Palmer (Bowling Green State University) and Jim Faulk (Case Western Reserve University) to this work are gratefully acknowledged. Support for this project was provided in part by NIH Grant GM 24235 and by the Center for Photochemical Sciences at Bowling Green State University.

---

[16] Murov, S. *Handbook of Photochemistry*; Dekker: New York, 1973; p 89.

[17] The values of $k_{\Delta G}$ and $k_{T\Sigma}$ quoted yield a triplet energy for PdNc(OBu)$_8$ which is 0.9 kcal/mol lower than the spectroscopic value (21.4 kcal/mol). This difference is as expected from the spin statistics.[6]

[18] For a recent discussion of mechanisms of photochemical cycloreversion of the endoperoxides of aromatic compounds, see the following reference and literature cited therein: Katscher, U.; Schmidt, R.; Brauer, H.-D. *Chem. Phys. Lett.* **1993**, *205*, 75–79.