Singlet Oxygen Dimol-Sensitized Luminescence from Thermally Generated Singlet Oxygen

Yulan Fu, Alexander A. Krasnovsky, Jr.,† and Christopher S. Foote*

Contribution from the Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024-1569

Received May 24, 1993. Revised Manuscript Received July 27, 1993®

Abstract: Delayed fluorescence (700 nm) of tetra-*tert*-butylphthalocyanine (Pc) can be sensitized by singlet oxygen generated by thermolysis of 1,4-dimethylnaphthalene endoperoxide. The initial intensity is proportional to the square of the initial concentration of the endoperoxide, and the apparent rate constants of its decay are twice those for singlet oxygen monomol emission. The apparent activation energies for the reaction of the endoperoxide from Arrhenius plots of the first-order rate constants for luminescence decay at 1270 and 700 nm were $\Delta H^{\ddagger} = 21.1 \pm 1.1$ kcal/mol, $\Delta S^{\ddagger} = -7 \pm 3$ eu and $\Delta H^{\ddagger} = 21.2 \pm 1.1$ kcal/mol, $\Delta S^{\ddagger} = -6 \pm 3$ eu, respectively, in reasonable agreement with the literature (Turro, N. J.; Chow, M. F.; Rigaudy, J. *J. Am. Chem. Soc.* **1981**, *103*, 7218–7224). However, values of $\Delta H^{\ddagger}$ calculated from the luminescence intensities were 22.7 ± 4.4 and 50.3 ± 1.4 kcal/mol, respectively; the apparent activation enthalpy at 700 nm is roughly twice that at 1270 nm. These results are in accord with a mechanism in which singlet oxygen is in reversible equilibrium with the dimol, which transfers energy to produce the phthalocyanine excited singlet state, which fluoresces.

Introduction

Emission from singlet O_2 ($^1\Delta_g$) "monomols" at 1270 nm is well-known and can be detected in photosensitized and thermal systems by modern detectors.[2-5] In addition, collisions between two $^1O_2$ molecules in the gas phase generate singlet oxygen dimols, $(^1O_2)_2$, with principal emission at 634 and 703 nm.[6] Luminescence of organic chromophores sensitized by singlet oxygen has been reported for many years;[3,6-17] several different mechanisms have been proposed.

Khan and Kasha suggested a purely physical mechanism involving energy transfer from singlet oxygen dimols to the fluorescer (Fl), producing the singlet (^{1}Fl), which fluoresces (Scheme I).[7] In this scheme, k_{et} is the rate constant of energy transfer from dimols to the fluorescer and $h\nu_f$ is acceptor fluorescence. This mechanism should permit excitation of fluorescers with energies ≤44 kcal/mol, twice the energy of singlet oxygen. Wilson[9] and Stauff[14,15] also supported this mechanism. The problem with this scheme is that no evidence for a bound state of the dimol has been presented, and it is questionable whether it could have a lifetime long enough to transfer energy.

Scheme I

$$2\ {}^1O_2 \rightleftharpoons ({}^1O_2)_2$$

$$({}^1O_2)_2 + \mathrm{Fl} \xrightarrow{k_{et}} 2\ {}^3O_2 + {}^1\mathrm{Fl}$$

$${}^1\mathrm{Fl} \rightarrow \mathrm{Fl} + h\nu_f$$

Ogryzlo and Pearson suggested a mechanism for the energy transfer involving energy transfer from singlet oxygen ($^1O_2$) to violanthrone (Fl), producing the triplet (^{3}Fl), which then reacts with a second molecule of $^1O_2$ to give ^{1}Fl.[8] This reaction is shown in Scheme II. Since very few organic molecules have triplet energies below 22 kcal/mol, required for exothermic energy transfer, the first step of this mechanism cannot be general. Nevertheless, the second and third steps have been observed upon photoexcitation of photosensitizers in polymer matrices[10] and in solution.[16,17]

Scheme II

$${}^1O_2 + \mathrm{Fl} \xrightarrow{k_{et}} {}^3O_2 + {}^3\mathrm{Fl}$$

$${}^1O_2 + {}^3\mathrm{Fl} \rightarrow {}^3O_2 + {}^1\mathrm{Fl}$$

$${}^1\mathrm{Fl} \rightarrow \mathrm{Fl} + h\nu_f$$

A third mechanism is conceivable, in which a complex or exciplex of singlet oxygen with Fl is formed (k_c); reaction of this complex with a second mole of singlet oxygen forms ^{1}Fl. This mechanism has been suggested by Stauff and Fuhr,[14] and is related to a mechanism suggested by Deneke and Krinsky[18] for dimol luminescence enhancement by the singlet oxygen quencher DABCO. However, there is no evidence for the formation of long-lived complexes of this sort.

† On leave from Department of Biology, Moscow State University, Moscow, Russia.

* Abstract published in *Advance ACS Abstracts,* October 1, 1993.

(1) Turro, N. J.; Chow, M. F.; Rigaudy, J. *J. Am. Chem. Soc.* **1981**, *103*, 7218–7224.
(2) Ogilby, P. R.; Foote, C. S. *J. Am. Chem. Soc.* **1982**, *104*, 2069–2070.
(3) Krasnovsky, A. A., Jr. *Photochem. Photobiol.* **1979**, *29*, 29–36.
(4) Khan, A. U.; Kasha, M. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 6047–6049.
(5) Wilson, T.; Khan, A. U.; Mehrotra, M. M. *Photochem. Photobiol.* **1986**, *43*, 661–662.
(6) Khan, A. U.; Kasha, M. *J. Am. Chem. Soc.* **1970**, *92*, 3293–3300.
(7) Khan, A. U.; Kasha, M. *J. Am. Chem. Soc.* **1966**, *88*, 1574–1576.
(8) Ogryzlo, E. A.; Pearson, A. E. *J. Chem. Phys.* **1968**, *72*, 2913–2916.
(9) Wilson, T. *J. Am. Chem. Soc.* **1969**, *91*, 2387–2388.
(10) Kenner, R. D.; Khan, A. U. *J. Chem. Phys.* **1977**, *67*, 1605–1613.
(11) Krasnovsky, A. A., Jr.; Neverov, K. V. *Biofizika* **1988**, *23*, 884–886.
(12) Krasnovsky, A. A., Jr.; Neverov, K. V. *Chem. Phys. Lett.* **1990**, *167*, 591–596.
(13) Krasnovsky, A. A., Jr.; Foote, C. S. *J. Am. Chem. Soc.* **1993**, *115*, 6013–6016.
(14) Stauff, J.; Fuhr, H. *Ber. Bunsen-Ges. Phys. Chem.* **1969**, *73*, 245–251.
(15) Stauff, J.; Fuhr, H. *Z. Naturforsch.* **1971**, *26B*, 260–263.
(16) Brukhanov, V. V.; Ketzle, G. A.; Laurinas, V. C.; Levshin, L. V. *Opt. Spektrosk.* **1986**, *60*, 205–207.
(17) Nickel, B.; Prieto, F. R. *Ber. Bunsen-Ges. Phys. Chem.* **1988**, *92*, 1493–1503.
(18) Deneke, C. F.; Krinsky, N. I. *Photochem. Photobiol.* **1977**, *25*, 299–304.

0002-7863/93/1515-10282$04.00/0

Scheme III

$$^1O_2 + Fl \xrightarrow{k_c} O_2\cdots Fl$$

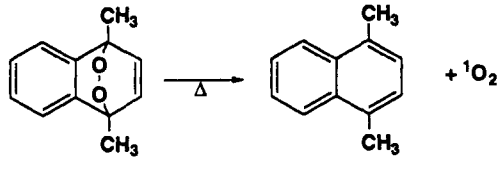
$$O_2\cdots Fl \xrightarrow{^1O_2} 2\,^3O_2 + {}^1Fl$$

$$^1Fl \rightarrow Fl + h\nu_f$$

Excitation of Fl could also occur via an unstable peroxide such as a dioxetane, formed by reaction of singlet oxygen with various compounds, including Fl. A systematic study of such luminescence has been reported.[19]

Krasnovsky *et al.* reported the first visible luminescence derived from singlet oxygen produced by protoporphyrin photosensitization in solution.[3,11-13,20] Along with the usual monomol emission at 1270 nm, visible luminescence with intensity proportional to the square of the excitation power can be produced by added fluorescent compounds. Certain compounds such as naphthalocyanine and other phthalocyanines are particularly efficient at producing this luminescence; one of the most effective additives is tetra-*tert*-butylphthalocyanine (Pc).[11,12,20] The luminescence was characterized as Pc fluorescence and was suggested to be formed by energy transfer from singlet oxygen dimols. Recently, time-resolved measurements of phthalocyanine luminescence sensitized by singlet oxygen dimols using the fullerenes C_{60} and C_{70} as sensitizers were reported; the kinetics were consistent with the mechanism shown in Scheme I, but not with those in Schemes II or III.[13]

Energy-transfer processes that could complicate the proposed mechanism are conceivable under photochemical conditions. We therefore tested the scheme in a simpler system, in which $^1O_2$ was produced by thermolysis of 1,4-dimethylnaphthalene endoperoxide.[1] The results are fully consistent with Scheme I.



Experimental Section

Materials. Benzene-d_6, 99.6% (Cambridge Isotope Laboratories), was used as received. Tetra-*tert*-butylphthalocyanine (Pc) was synthesized and purified at the Moscow Institute of Organic Intermediates and Dyes by the procedure reported by Mikhalenko *et al.*[21] 1,4-Dimethylnaphthalene endoperoxide[1] was synthesized and purified by Mary C. Roslaniec.

Instruments. The 1270-nm luminescence was measured with the apparatus described in a previous paper, using a 1100-nm silicon cuton filter instead of the monochromator.[22] The 700-nm luminescence was detected with a 700-nm interference filter (Oriel, 12-nm bandwidth) and a Thorn EMI 9203B photomultiplier cooled by a Thorn EMI FACT 50 MK III cooler. The output was measured by a Keithley 177 Microvolt DMM microvoltmeter. Generally, 1.4 mL of Pc solution or solvent was placed in a thermostated (±0.2 °C) cuvette and preheated for 5 min, and then 0.1 mL of peroxide solution at room temperature was added to the cuvette. The luminescence measurement started 10–20 s after the solutions were mixed and vigorously stirred. The "initial intensity" of the luminescence was calculated by extrapolating the exponential decay obtained from curve fitting (Igor, Macintosh IIci) to time 0. Pc was added except in the case of temperature dependence of the 1270-nm luminescence from which the activation energy of the endoperoxide decomposition was calculated. The visible spectrum was taken in a 1-cm cell after each luminescence measurement where Pc was added. At low endoperoxide concentration (<5 × 10^{-4} M), the visible spectra of the Pc solutions were identical to those of the reaction mixture after endoperoxide decomposition (initially at the same Pc concentration). The absorbance at 700 nm (A_{700}) was slightly lower after reaction at high endoperoxide concentration. In all cases where Pc was added, A_{700} was equal or close to 0.40, corresponding to an initial Pc concentration of 1.95 × 10^{-6} M.

The errors shown (see figures) are calculated from the plots using Student's *t* distribution. Systematic errors from the instruments and curve-fitting procedures, which are difficult to estimate, are not included.

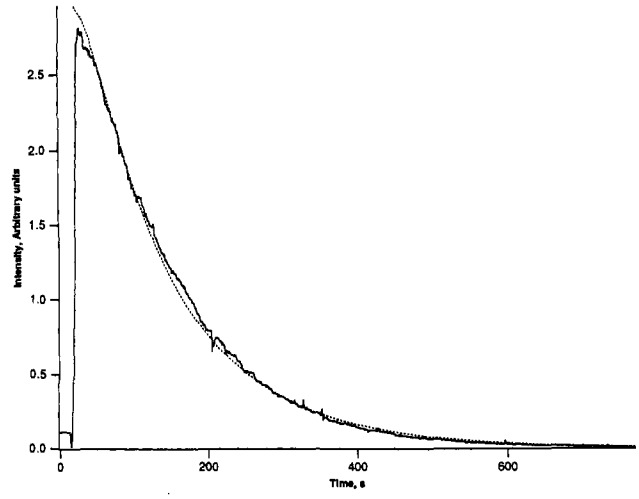


Figure 1. Luminescence at 700 nm (dashed curve) plotted with the square of that at 1270 nm (solid). The 700-nm luminescence decay curve was normalized to the same scale as the 1270-nm curve (1.35 × 10^{-3} M endoperoxide, 1.95 × 10^{-6} M Pc, 65.0 ± 0.2 °C).

Results

As reported,[5] thermolysis of the endoperoxide in C_6D_6 gave $^1O_2(^1\Delta_g)$ luminescence at 1270 nm. The luminescence decayed exponentially as the peroxide reacted by a first-order reaction. In agreement with the photochemical work,[13,23] tetra-*tert*-butylphthalocyanine quenched $^1O_2$ monomol emission. Weak dimol luminescence near 700 nm was strongly enhanced by the addition of Pc. The 700-nm luminescence decay is also exponential (1.66 × 10^{-4} to 5.31 × 10^{-3} M endoperoxide and 50–75 °C). At the same temperature and endoperoxide concentration, decay of the 700-nm luminescence is almost exactly the square of that at 1270 nm (Figure 1).

Figure 2 shows that, at various temperatures, the rate constants of the 700-nm luminescence decay (phthalocyanine added) are always twice those of the $^1O_2$ monomol emission (no phthalocyanine).

The initial intensity of the 700-nm luminescence is proportional to the square of the initial concentration of the endoperoxide, while that of the 1270-nm luminescence is directly proportional (Figure 3). Here, the 1270- and 700-nm luminescence were both measured in the presence of phthalocyanine.

Figure 4 shows that, at a number of different temperatures, the initial intensity of the luminescence at 700 nm (Pc added) is proportional to the square of that at 1270 nm (no Pc).

The activation energies for the reaction of the endoperoxide calculated from Arrhenius plots of the first-order rate constants of luminescence decay at 1270 and 700 nm (Figure 5) were $\Delta H^* = 21.1 \pm 1.1$ kcal/mol, $\Delta S^* = -7 \pm 3$ eu (no phthalocyanine) and $\Delta H^* = 21.2 \pm 1.1$ kcal/mol, $\Delta S^* = -6 \pm 3$ eu (phthalocyanine added) in C_6D_6, respectively (1.35 × 10^{-3} M endoperoxide, 55.0 ± 0.2 to 75.0 ± 0.2 °C). In contrast, Arrhenius plots of the initial luminescence *intensities* (Figure 6) gave $\Delta H^* = 22.7 \pm$

(19) Krasnovsky, A. A., Jr.; Litvin, F. F. *Photochem. Photobiol.* **1974**, *20*, 133–149.
(20) Neverov, K. V.; Krasnovsky, A. A., Jr. *Opt. Spektrosk.* **1991**, *71*, 691–696.
(21) Mikhalenko, S. A.; Barkanova, O. L.; Lebedev, L. O.; Lukjanetz, E. A. *Zh. Obshch. Khim.* **1971**, *41*, 2735–2739.
(22) Niu, Q. J.; Foote, C. S. *Inorg. Chem.* **1992**, *31*, 3472–3476.
(23) Krasnovsky, A. A., Jr.; Rodgers, M. A. J.; Galpern, M. G.; Rihter, B.; Kenney, M. E.; Lukjaners, E. A. *Photochem. Photobiol.* **1992**, *55*, 691–696.

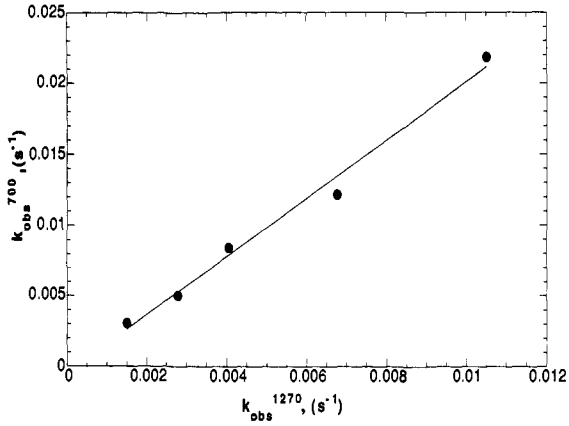


Figure 2. Rate constants of decay of luminescence at 700 nm (1.95×10^{-6} M Pc) vs those at 1270 nm (1.35×10^{-3} M endoperoxide, 55.0 ± 0.2 to 75.0 ± 0.2 °C); the slope is 2.05 ± 0.42.

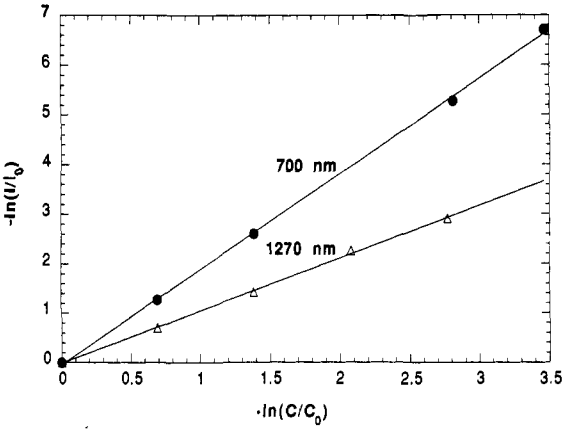


Figure 3. Log–log plot of the initial intensity at 1270 and 700 nm vs the initial concentration of endoperoxide (1.95×10^{-6} M Pc, 65.0 ± 0.2 °C). The slopes of the plots are 1.06 ± 0.18 and 1.93 ± 0.09 at 1270 and 700 nm, respectively. I_0 is the initial intensity at concentration C_0.

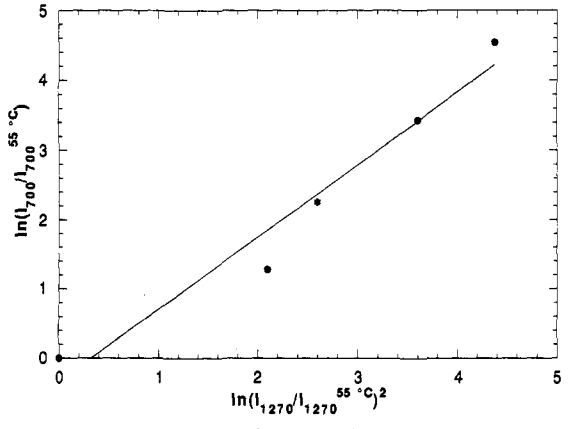


Figure 4. Log–log plot of the initial intensities at 700 nm (1.95×10^{-6} M Pc) at temperatures varying from 55.0 ± 0.2 to 75.0 ± 0.2 °C (normalized to those at 55 °C) vs the squares of those at 1270 nm (no Pc). The slope is 1.04 ± 0.40.

4.4 and 50.3 ± 1.4 kcal/mol for 1270 and 700 nm, respectively. Thus, the activation enthalpy at 700 nm is roughly twice that at 1270 nm.

Discussion

Figures 1 and 2 show that, at the same temperature, the rate constant of the luminescence decay at 700 nm is twice that at 1270 nm. In contrast to the time-resolved results reported previously, this decay is caused by reaction of the peroxide, not

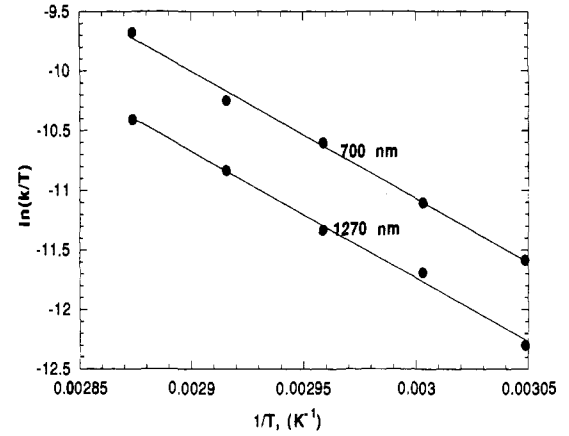


Figure 5. Arrhenius plots of the first-order rate constants. The slopes and intercepts are 10 600 ± 600, 20.0 ± 3.4 and 10 700 ± 600, 20.9 ± 3.4 for the 1270-nm (no Pc) and 700-nm emissions (1.95×10^{-6} M Pc), respectively.

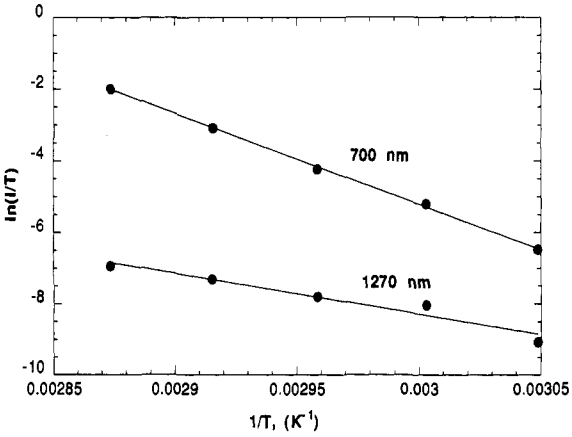


Figure 6. Arrhenius plots of the initial intensities of luminescence at 1270 nm (no Pc) and 700 nm (1.95×10^{-6} M Pc). The slopes are 11 400 ± 2200 and 25 300 ± 700 at 1270 and 700 nm, respectively. The intercepts are arbitrary.

by the decay of singlet oxygen. This result is consistent with any of the mechanisms in Schemes I–III, since the 1270-nm luminescence is proportional to $[^1O_2]$, which is in turn proportional to endoperoxide concentration; in contrast, the intensity of the 700-nm luminescence is proportional to dimol concentration, which is proportional to $[^1O_2]^2$.

In Figure 3, the initial intensities at 1270 and 700 nm are shown to be proportional to the endoperoxide concentration and its square, respectively, which also supports these mechanisms, since $[^1O_2]$ is proportional to the endoperoxide concentration. Also as predicted by this mechanism, Figure 4 shows that the initial intensity at 700 nm over a range of temperatures is proportional to the square of that at 1270 nm at the same temperature.

The difference in activation energies from the decay rates (Figure 5) and that from the intensities (Figure 6), while at first surprising, is in accord with expectations. The decay rates of the luminescence at 700 nm are just twice those at 1270 nm (Figure 2); thus, the Arrhenius plots have the same slopes, but are offset by a constant value of ln 2. (The measured value is 0.9 ± 0.2, within the experimental error of ln 2 = 0.69.) In contrast, the *intensities* at 700 nm are proportional to the dimol concentration (see Scheme I). Since the 700-nm intensities are proportional to the square of the singlet oxygen concentration, which is in turn proportional to the rate of peroxide decomposition, the slope of the log(intensity/T) vs $1/T$ plot at 700 nm and the resulting activation energy should be twice that at 1270 nm. The results shown in Figure 6 show that this is indeed the case. The activation

enthalpy for decomposition of the endoperoxide calculated using the decomposition rates and the initial intensities should give the same value at 1270 nm; the two values are within experimental error and in reasonable agreement with the literature value ($\Delta H^{\ddagger}$ = 24.2 ± 0.2 kcal/mol, $\Delta S^{\ddagger}$ = 2 ± 1 eu in dioxane) determined by following loss of the endoperoxide.[1]

The results show that singlet oxygen dimol-sensitized luminescence of phthalocyanine can be detected in a system where $^1O_2$ is produced chemically. The decay rates of the luminescence, the initial intensities, and the activation behavior all show that the 700-nm luminescence depends on the square of $^1O_2$ concentration. Unlike the time-resolved results, which are consistent only with Scheme I,[13] these results do not distinguish between Schemes I–III. However, they are consistent with arguments developed in the previous paper[13] supporting Scheme I.

This type of sensitized luminescence may account for the wide distribution of red luminescence often attributed to singlet oxygen dimol emission in biological and other systems. Further work to test the mechanism proposed is in progress.

Acknowledgment. We thank Mary C. Roslaniec for the synthesis of 1,4-dimethylnaphthalene endoperoxide. This research was supported by the NIH, GM-20080.