Singlet-Oxygen-Sensitized Delayed Fluorescence: Direct Detection of Triplet Phthalocyanine as an Intermediate

Sean T. Murphy, Kunio Kondo, and Christopher S. Foote*

Contribution from the Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095-1569
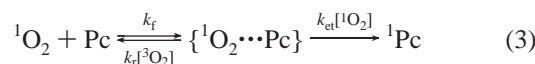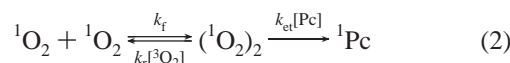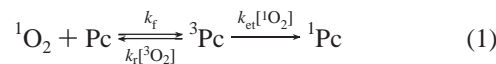
Received December 18, 1997. Revised Manuscript Received November 4, 1998

Abstract: We have detected an intermediate in the process of singlet-oxygen-sensitized delayed fluorescence (SOSDF) using tetra-*tert*-butylphthalocyanine (Pc) as the fluorescer and C_{60} as the sensitizer. The observed intermediate is dependent on the concentrations of Pc, $^1O_2$, and $^3O_2$, as is SOSDF. By modeling the kinetics of the intermediate according to previously proposed mechanisms for SOSDF, we are able to rule out the singlet oxygen dimol as the intermediate. The intermediate kinetics are in agreement with either an exciplex or a triplet Pc mechanism. Since the intermediate has a spectrum identical to that of the triplet Pc, the triplet is the most likely intermediate.

Introduction

We and others[1−18] have reported the production of singlet-oxygen-sensitized delayed fluorescence (SOSDF) from phthalocyanines and other fluorescent pigments. In the case of phthalocyanines, it has been shown that SOSDF requires two molecules of singlet oxygen and one of the phthalocyanine, as demonstrated by the lifetime and quenching behavior of the luminescence.[7−10,15−17,19,20] To date, studies of the SOSDF process have monitored either singlet oxygen phosphorescence and/or the resulting Pc fluorescence, but not the intermediate. We now report direct detection of the SOSDF intermediate by transient absorption spectroscopy.

The identity of the intermediate in SOSDF has been controversial, and four principal mechanisms for SOSDF have been advanced. In the first, singlet oxygen is in equilibrium with the triplet state of the fluorescer (eq 1). This mechanism has been suggested in systems where the fluorescer is violanthrone,[4] rubrene,[5] and octahexadecylphthalocyanine (OHPC).[16,21] The second mechanism, first proposed by Khan and Kasha,[3] involves a singlet-oxygen dimol as an intermediate (eq 2), but such a species has not yet been directly observed and is believed to have a very short lifetime.[17,22−25] In the third mechanism, first suggested by Stauff and Fuhr,[11] an exciplex between Pc and $^1O_2$ is the intermediate (eq 3).

$$^1O_2 + Pc \underset{k_r[^3O_2]}{\overset{k_f}{\rightleftharpoons}} {}^3Pc \xrightarrow{k_{et}[^1O_2]} {}^1Pc \qquad (1)$$

$$^1O_2 + {}^1O_2 \underset{k_r[^3O_2]}{\overset{k_f}{\rightleftharpoons}} (^1O_2)_2 \xrightarrow{k_{et}[Pc]} {}^1Pc \qquad (2)$$

$$^1O_2 + Pc \underset{k_r[^3O_2]}{\overset{k_f}{\rightleftharpoons}} \{^1O_2 \cdots Pc\} \xrightarrow{k_{et}[^1O_2]} {}^1Pc \qquad (3)$$

A fourth mechanism, resulting from ^3Pc triplet−triplet annihilation, was ruled out by Gorman et al.[16] because of the inverse dependence of SOSDF on $[^3O_2]$. In the three schemes shown, quenching steps involving ground-state oxygen have been added to accommodate Gorman's observed inhibition of SOSDF by oxygen,[16] which we have confirmed. Gorman interpreted the oxygen inhibition as evidence for the triplet and against the dimol because oxygen is known to quench the triplet but not the dimol. However, since the dimol is not well understood, it is possible that it too could be quenched by oxygen.

(1) Krasnovsky, A. A., Jr. *Photochem. Photobiol.* **1979**, *29*, 29−36.

(2) Khan, A. U.; Kasha, M. *J. Am. Chem. Soc.* **1970**, *92*, 3293−3300.

(3) Khan, A. U.; Kasha, M. *J. Am. Chem. Soc.* **1966**, *88*, 1574−1576.

(4) Orgryzlo, E. A.; Pearson, A. E. *J. Phys. Chem.* **1968**, *72*, 2913−2916.

(5) Wilson, T. *J. Am. Chem. Soc.* **1969**, *91*, 2387−2388.

(6) Kenner, R. D.; Khan, A. U. *J. Chem. Phys.* **1977**, *67*, 1605−1613.

(7) Krasnovsky, A. A., Jr.; Neverov, K. V. *Biofizika (Sov. Biophys.)* **1988**, *23*, 884−885.

(8) Krasnovsky, A. A., Jr.; Neverov, K. V. *Chem. Phys. Lett.* **1990**, *167*, 591−597.

(9) Krasnovsky, A. A., Jr.; Foote, C. S. *J. Am. Chem. Soc.* **1993**, *113*, 6013−6016.

(10) Krasnovsky, A. A., Jr.; Fu, Y.; Bashtanov, M. E.; Murphy, S.; Foote, C. S. *Optics Spectrosc.* **1997**, *83*, 571−574.

(11) Stauff, J.; Fuhr, H. *Ber. Bunsen-Ges. Phys. Chem.* **1969**, *73*, 245−251.

(12) Stauff, J.; Fuhr, H. *Z. Naturforsch.* **1971**, *26B*, 260−263.

(13) Brukhanov, V. V.; Ketzle, G. A.; Laurinas, V. C.; Levshin, L, V. *Opt. Spektrosk.* **1986**, *60*, 205−207.

(14) Nickel, B.; Rodriguez Prieto, M. F. *Ber. Bunsen-Ges. Phys. Chem.* **1988**, *92*, 1493−1503.

(15) Neverov, K. V.; Krasnovsky, A. A., Jr. *Opt. Spektrosk.* **1991**, *71*, 691−696.

(16) Gorman, A. A.; Hamblett, I.; Hill, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 10751−10752.

(17) Chou, P. T.; Chen, Y. C.; Wei, C. Y.; Chen, S. J.; Lu, H. L.; Wei, T. H. *J. Phys. Chem. A* **1997**, *101*, 8581−8586.

(18) Chou, P. T.; Chen, Y. C.; Wei, C. Y.; Lee, M. Z. *J. Am. Chem. Soc.* **1998**, *120*, 4883−4884.

(19) Fu, Y.; Krasnovsky, A. A., Jr.; Foote, C. S. *J. Am. Chem. Soc.* **1993**, *115*, 10282−10285.

(20) Fu, Y.; Krasnovsky, A. A., Jr.; Foote, C. S. *J. Phys. Chem.* **1997**, *101*, 2552−2554.
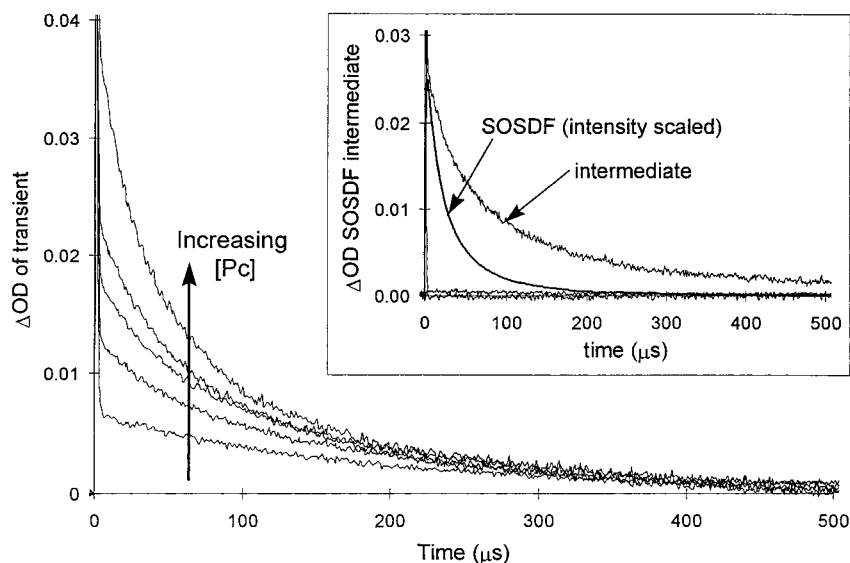
(21) Baigel, D. M.; Gorman, A. A.; Hamblett, I.; Hill, T. J. *J. Photochem. Photobiol. B* **1998**, *43*, 229−231.

(22) Arnold, S. J.; Kubo, M.; Ogryzlo, E. A. *Adv. Chem. Ser.* **1968**, *77*, 133.

(23) Chou, P. T.; Wei, G. T.; Lin, C. H.; Wei, C. Y.; Chang, C. H. *J. Am. Chem. Soc.* **1996**, *118*, 3031−3032.

(24) Chou, P. T.; Chen, Y. C.; Wei, C. Y.; Chen, S. J.; Lu, H. L.; Lee, M. Z. *Chem. Phys. Lett.* **1997**, *280*, 134−140.

(25) Scurlock, R. D.; Ogilby, P. R. *J. Phys. Chem.* **1996**, *100*, 17226−17231.

Figure 1. Main plot: observed intermediate decay at [Pc] = 2.3, 4.1, 5.4, 6.8, and 11 μM. Inset plot: intermediate decay compared to SOSDF decay ([Pc] = 8.2 μM); the traces at the baseline are irradiated solutions of either Pc or C_{60} alone.

At the beginning of our investigations, none of the mechanisms shown in eqs 1−3 were particularly appealing. Although the triplet mechanism accounted for the inverse dependence of SOSDF on $^3O_2$, the triplet energy of Pc was estimated to be 7 kcal/mol greater than that of singlet oxygen[26] and we felt that this ruled out this intermediate in the strong emission from SOSDF. The dimol was unattractive (although we originally supported it because we believed other mechanisms were even more unattractive). The estimated lifetime in solution is probably on the order of tens of picoseconds,[17,22−25] although its energy corresponds very well with the singlet energies of the most strongly emitting dyes in SOSDF.[27] An exciplex could be both long-lived and quenched primarily by $^3O_2$, but we had no evidence that such a complex existed.[28] In this work, we attempted to observe the intermediate because its kinetics should allow distinction of the dimol mechanism from the others by the dependence on [Pc] (see below). In addition, comparison of the absorption spectrum of ^3Pc to that of the intermediate should distinguish the triplet from the exciplex.

Several papers have been published since this manuscript was submitted and require some comment. Gorman and co-workers[21] published the energy of a triplet Pc (22.8 ± 0.2 kcal/mol), which they measured by examining the kinetics of the transient absorption of the Pc irradiated in an oxygenated benzene solution. They concluded that the low energy of the triplet Pc provides strong evidence in support of the triplet as intermediate in SOSDF and against the dimol mechanism. We regard their work and ours as mutually supportive. A paper by Chou et al.[18] has recently appeared supporting the dimol-sensitized mechanism on the basis of a lack of oxygen inhibition of luminescence using Nile Blue as a fluorescer. The luminescence observed in

Chou's paper appears to be many orders of magnitude weaker than that described in this and other recent papers, and its relationship to the luminescence studied here is unclear.

Materials and Methods

Benzene-d_6 (99.6%, Cambridge Isotope Laboratories) was used as received. Tetra-*tert*-butylphthalocyanine was synthesized and purified at the Moscow Institute of Organic Intermediates and Dyes by the procedure reported by Mikhalenko et al.[29] Samples were irradiated in a 1 cm quartz cell with a pulsed Nd:YAG laser as previously described.[9] Absorbance changes were detected by a monitoring system consisting of a Xe lamp (75W), a monochromator (Jarrell Ash 82−410 or Schoeffel GM-252), and a photomultiplier tube (Hamamatsu R928) connected to a digital storage oscilloscope (LeCroy 9410). Digitized data were averaged over 50 laser shots and then transferred to an Macintosh personal computer with LabVIEW2 software and processed with IGOR pro software.

Photophysical Measurements. Solutions were prepared in benzene-d_6 and were air-saturated (i.e., $[^3O_2] = 2$ mM) unless otherwise noted. All measurements were made in a 1 cm cell at ambient temperature. The sensitizer, C_{60}, was added to give an OD at 532 nm between 0.7 and 0.8. The solution was irradiated at 532 nm with a pulse rate of 10 s^{-1}, and the decay of the intermediate was measured at 465 nm. For the Pc dependence studies, solutions were prepared with Pc concentrations of 2.3, 4.1, 5.4, 6.8, and 11 μM. The SOSDF was measured by blocking the probe beam and monitoring at 710 nm. The Pc triplet absorption spectrum was measured in Ar saturated benzene by irradiating at 355 nm.

Results

As previously reported,[9] SOSDF was observed on irradiation of a solution of tetra-*tert*-butylphthalocyanine (Pc) and C_{60} in benzene-d_6. Irradiation at 532 nm gave emission at 710 nm as shown in Figure 1 (inset). In agreement with previous observations, the SOSDF had the same spectrum as Pc fluorescence.[7,8,15] We have also confirmed that the rate of SOSDF production for phthalocyanines, as measured by the initial intensity, is first order in [Pc],[9] second order in $[^1O_2]$,[9,19] and inversely proportional to the ground-state oxygen concentration.[16]

The absorption spectrum of the irradiated sample was monitored from 400 to 590 nm (the effective window, because

(26) McVie, J.; Sinclair, R. S.; Truscott, T. G. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1870−1879.

(27) The previous support of one of the authors (C.S.F.) for the dimol mechanism (ref 9) was due to the following: (a) the dimol emission wavelength corresponds very well with the absorption maxima of the most strongly emitting dyes and (b) the published triplet energy of Pc (ref 26) was too high for efficient energy transfer from singlet oxygen and because naphthalocyanines, which do have triplet energies in the right range, absorb well to the red of the phthalocyanines. The second argument has become invalidated because of the unexpectedly low energy of the triplet Pc as well as our latest results on the kinetic behavior of the SOSDF intermediate.

(28) We originally felt that the exciplex mechanism was unlikely because the luminescence should saturate when the quenching of singlet oxygen by the Pc was complete, which it does not.

(29) Mikhalenko, S. A.; Barkanova, O. L.; Lebedev, L. O.; Lukjanetz, E. A. *Zh. Obshch. Khim.* **1971**, *41*, 2735−2739.
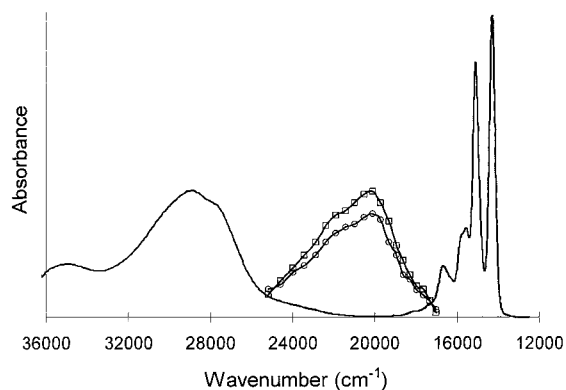
Figure 2. Absorption spectra of ground-state Pc (solid line), the SOSDF intermediate (circles), and triplet state Pc (squares). The extinction coefficients of the intermediate and triplet are unknown and were scaled to reveal the similarities in spectral shape.
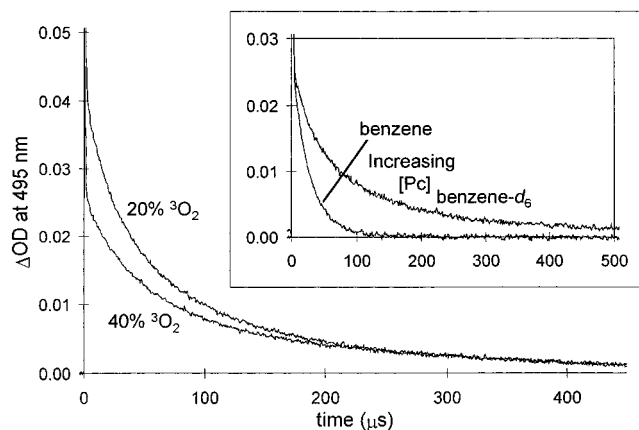
Figure 3. Main plot: comparison of intermediate decay with 2 and 4 mM dissolved oxygen concentration ([Pc] = 8.5 μM). Inset plot: comparison of intermediate decay in deuterated and nondeuterated benzene ([Pc] = 10 μM).

of Pc absorption). A transient with λ_{max} = 495 nm was observed with a lifetime of several hundred microseconds. The spectrum of the transient (circles) and the ground-state absorption (solid line) are shown in Figure 2. The intermediate concentration was found to depend on [Pc], and the decay profiles at various [Pc] are shown in Figure 1. No transient is observed when either Pc or C_{60} is irradiated alone in air-saturated benzene-d_6 (Figure 1, inset).

Like the SOSDF, the intermediate is also dependent on the concentrations of singlet oxygen and of ground-state oxygen. To test the singlet oxygen dependence, the transient decay was measured in benzene and benzene-d_6, in which the lifetimes of singlet oxygen are 27 and 550 μs, respectively.[30] As shown in Figure 3 (inset), the transient decayed more quickly in benzene but the initial intensity remained the same. To test the dependence on ground-state oxygen, the [O_2] was doubled from 2 to 4 mM, and the initial intensity decreased while the decay rate was not significantly changed (Figure 3, main plot).

For comparison with the intermediate spectrum, the absorption spectrum of the triplet Pc was measured by direct irradiation of Pc at 355 nm in Ar-saturated benzene, which eliminates quenching by ground-state oxygen. The spectrum of the triplet Pc (Figure 2, squares) has the same shape as the spectrum of the transient involved in SOSDF (Figure 2, circles). To confirm the identity of the intermediate as the triplet, the isosbestic points

were examined for the two species. The triplet- and ground-state spectra show isosbestic points at 389 and 587 nm. The intermediate- and ground-state spectra also show an isosbestic point at 587 nm; the point at 389 nm could not be confirmed because the weak signal is obscured.

Discussion

The intermediate concentration is strongly dependent on [Pc], as shown in Figure 1. The nature of the dependence will be discussed below. The effect of singlet oxygen lifetime on the intermediate is seen clearly by the shortened lifetime in benzene compared to that in benzene-d_6 (see Figure 3, inset). The dependence on ground-state oxygen of the equilibrium between the intermediate and singlet oxygen is also clearly seen when the dissolved oxygen concentration is increased (Figure 3, main plot). The increase in ground-state oxygen reduces the concentration of the intermediate (see eqs 1−3), and hence, the initial ΔOD is decreased. We conclude from these dependencies that the observed transient is indeed the intermediate in the SOSDF process.

Because the triplet and exciplex intermediates are both formed from one molecule of singlet oxygen and one of Pc, the kinetics are indistinguishable. However, the dimol intermediate, formed from two singlet oxygen molecules, should have a dramatically different dependence on Pc concentration. In all three mechanisms (eqs 1−3), a fast equilibrium should exist between singlet oxygen and the intermediate; the reverse reaction must involve $^3O_2$ to conform to the observed oxygen dependence. In the triplet and exciplex mechanisms, Pc is involved in the intermediate formation step. Therefore, the maximum concentration of the intermediate should increase with increasing [Pc]. In the dimol mechanism, the maximum concentration should be nearly constant since [Pc] is only involved in the second step. The observed increase in the maximum ΔOD with increasing [Pc] (Figure 1) is consistent with the exciplex and triplet mechanisms but not with the dimol mechanism.

The intermediate decay rate vs [Pc] should also be distinguishable for the two types of mechanisms. For the triplet or exciplex, the intermediate is removed by energy transfer from a second molecule of singlet oxygen to form ^{1}Pc. Since this step is not affected by varying [Pc], the decay rate should remain constant. In contrast, the dimol intermediate is depleted by reaction with Pc, and increasing [Pc] should increase its decay rate. Again, the constant decay rate observed in the experimental data (Figure 1) agrees with the triplet and exciplex mechanisms but not with the dimol.
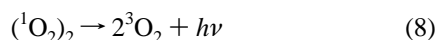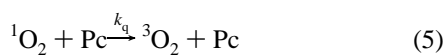
To support the above arguments, the intermediate decay profiles for the triplet and dimol mechanisms were calculated by numerically solving the differential rate equations with *Mathematica*.[31] The simulations take into account three reaction pathways involving singlet oxygen: nonradiative decay (eq 4), quenching by Pc (eq 5), and SOSDF (eq 1 or 2). The formation of $^1O_2$ is fast on the time scale of the other processes, and the generation of ^{3}Pc by excitation and subsequent intersystem crossing is neglected because of the low absorbance of Pc at 532 nm. Any direct energy transfer from $^3C_{60}$ to Pc rather than to $^3O_2$ leads to the same state at ca. 1 μs, since ^{3}Pc and $^1O_2$ are in equilibrium. The processes of ^{3}Pc nonradiative decay (eq 6), ^{3}Pc triplet−triplet annihilation (eq 7), and dimol emission (eq 8) were not included because the contributions are insignificant.

(30) Ogilby, P. R.; Foote, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 3423−3440.

(31) *Mathematica*, Version 3.0; Wolfram Research, Inc.: Champaign, IL, 1996.
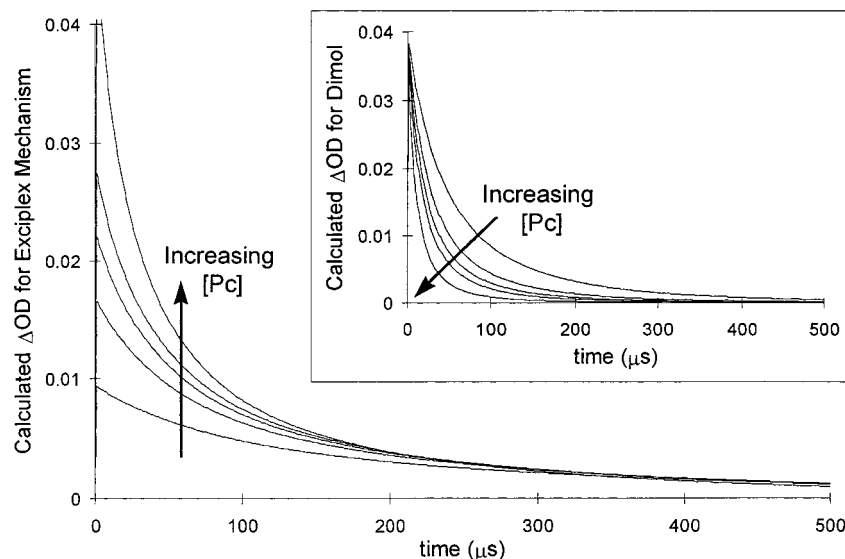
Figure 4. Calculated decay profiles for a triplet intermediate (main plot) and for a dimol intermediate (inset plot) with [Pc] = 2.3, 4.1, 5.4, 6.8, and 11 μM (see text for details of the calculation).

$$^1O_2 \xrightarrow{k_{nr}} {}^3O_2 \qquad (4)$$

$$^1O_2 + Pc \xrightarrow{k_q} {}^3O_2 + Pc \qquad (5)$$

$$^3Pc \rightarrow Pc \qquad (6)$$

$$^3Pc + {}^3Pc \rightarrow {}^1Pc + Pc \qquad (7)$$

$$(^1O_2)_2 \rightarrow 2{}^3O_2 + h\nu \qquad (8)$$

The values for the rate constants were either taken from the literature or estimated; accurate values are not needed to see the difference in behavior between the two mechanisms. The rate constants for the processes shown in eqs 4 and 5 have been previously measured[9] as $k_{nr} = 1280$ s^{-1} and $k_q = 1.6 \times 10^8$ s^{-1} M^{-1} in benzene-d_6. The rate constants involved in the equilibrium were estimated to be $k_f = 1 \times 10^{10}$ s^{-1} M^{-1} (one-half the diffusion-limited rate constant) and $k_r = 1 \times 10^9$ s^{-1} M^{-1} (one-half diffusion-limited for two triplet species). The value for k_f is not far from the value measured by Gorman et al. for OHPC.[21] The final exothermic energy transfer rate constant, k_{et}, was estimated to be 2×10^{10} s^{-1} M^{-1} (diffusion-limited). The concentration of ground-state oxygen is 2 mM for air-saturated benzene.[32]

The rate equations for the triplet (^3Pc) mechanism are shown in eqs 9 and 10, and those for the dimol (DM) mechanism in eqs 11 and 12.

$$\frac{d[^1O_2]_{3Pc}}{dt} = -k_f[^1O_2][Pc] + k_r[^3O_2][^3Pc] \qquad (9)$$

$$\frac{d[^3Pc]}{dt} = k_f[^1O_2][Pc] - (k_r[^3O_2] + k_{et}[^1O_2])[^3Pc] \qquad (10)$$

$$\frac{d[^1O_2]_{DM}}{dt} = -k_f[^1O_2]^2 + k_r[^3O_2][DM] \qquad (11)$$

$$\frac{d[DM]}{dt} = k_f[^1O_2]^2 - (k_r[^3O_2] + k_{et}[Pc])[DM] \qquad (12)$$

When these differential equations are solved numerically, they provide values of concentrations vs time for both singlet oxygen and the proposed intermediate. The initial concentration of singlet oxygen was set to 4×10^{-5} M, and the intermediate concentration was set to zero. The former value was chosen to reproduce the experimental initial absorbance of the intermediate and is close to the value we calculate from actinometry (data not shown). The calculated intermediate concentration was multiplied by the intermediate extinction coefficients (chosen to fit the data at a single point) to provide ΔOD values of 25 000 cm^{-1} M^{-1} for the triplet and 5000 cm^{-1} M^{-1} for the dimol intermediate.

The results for both simulations at the experimental Pc concentrations are shown in Figure 4. As predicted above, when [Pc] is increased the maximum ΔOD of the triplet intermediate increases while its decay rate remains constant. On the other hand, the maximum ΔOD of the dimol remains constant while the dimol decay rate becomes faster with increasing [Pc]. In agreement with the above analysis, the simulations reproduce the experimental behavior of the intermediate (Figure 1) very well for the triplet or exciplex mechanisms but rule out the dimol mechanism.

Since the triplet and exciplex mechanisms cannot be distinguished from the kinetics, we sought to identify the intermediate by its spectral characteristics. As is seen from Figure 2, the triplet absorption spectrum is identical to the intermediate spectrum. Furthermore, an isosbestic point at 587 nm was observed for both species. This is strong evidence that the triplet Pc is the intermediate. However, we were initially reluctant to make this assignment because the triplet energy of the parent phthalocyanine has been reported to be 28.7 kcal/mol.[26] With such a large triplet energy, the equilibrium concentration of ^3Pc would be so low as to be undetectable in our experiment. The report from Gorman et al.[21] that the triplet energy for a Pc is actually near 22.8 kcal/mol eliminates our concern, and we are therefore in agreement that the intermediate in SOSDF is the triplet phthalocyanine.

Conclusion

This work and previous evidence shows that the dimol mechanism cannot be responsible for the singlet-oxygen-sensitized delayed fluorescence from phthalocyanines. Of the

(32) Battino, R.; Rettich, T. R.; Tominaga, T. *J. Phys. Chem. Ref. Data* **1983**, *12*, 163−178.

two kinetically equivalent mechanisms involving a triplet or an exciplex intermediate, the triplet mechanism is more likely because the intermediate has a spectrum identical with that of the triplet. The recent report by Gorman et al.[21] supports this conclusion because the low triplet energy measured for Pc allows significant concentrations of ^{3}Pc to be formed. We are continuing our investigations into SOSDF from Pc and plan to report direct measurements of the efficiency of this process, which may have important applications in the detection of singlet oxygen in biological systems.

JA974293G