Quenching of Singlet Oxygen and Sensitized Delayed Phthalocyanine Fluorescence

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Quenching of singlet-oxygen-sensitized 703 nm delayed fluorescence (SOSDF) of tetra-*tert*-butylphthalocyanine (Pc) by β-carotene, α-tocopherol, 1,4-diazabicyclo[2.2.2]octane, 2,6-di-*tert*-butyl-4-methylphenol, and lauric acid, compounds whose singlet oxygen quenching rates vary by 6 orders of magnitude, was found to be caused entirely by singlet oxygen quenching. The apparent rate constants for quenching of SOSDF are twice those for quenching of singlet oxygen 1279 nm phosphorescence under all conditions, as required by the fact that two molecules of $^1O_2$ are needed. Quenching of the visible SOSDF provides a highly sensitive method for measurement of rate constants for $^1O_2$ quenching, which will be usable with commonly available apparatus or in systems where the 1270 nm luminescence is difficult to detect.

Introduction

We have shown previously that $^1O_2(^1\Delta_g)$ can produce strong delayed fluorescence (SOSDF) from the singlet state of metal-free tetraalkylphthalocyanines (Pc) at the normal Pc fluorescence wavelength of 703 nm.[1−5] Singlet Pc molecules are formed as a result of a process involving two $^1O_2$ molecules.[1−5] Pc excitation is a consequence either of energy transfer to Pc from singlet oxygen dimols formed by collisions of $^1O_2$ molecules or of $^1O_2$ reaction with an exciplex formed from reaction of PC and $^1O_2$.[1−5] A recent paper by Gorman et al.[6] suggested a mechanism in which uphill energy transfer to Pc from $^1O_2$ leads to ^{3}Pc formation, and delayed fluorescence appears as a result of collisions of $^1O_2$ with ^{3}Pc.

$$\text{Sens} \xrightarrow[h\nu]{} \text{Sens}^* \longrightarrow {}^1\text{O}_2 \underset{\text{Pc}}{\overset{\longrightarrow}{}} \text{Pc}^* \xrightarrow[\text{(Pc fluorescence)}]{} h\nu' \qquad {}^3\text{O}_2$$

Independent of mechanistic details, red luminescence is far more easily observed than the 1270 nm phosphorescence of $^1O_2$ monomols because of the great sensitivity of photomultipliers. In addition, the 1270 nm luminescence is highly forbidden and rarely exceeds a quantum yield of 10^{-4}−10^{-5}.[7] Since the intensity of this delayed fluorescence can exceed that of 1270 nm phosphorescence by several orders of magnitude at moderate laser powers and Pc concentrations above 10^{-7} M,[4,5,8] it provides an attractive method for detection and quantification of $^1O_2$. In this paper, we show that this luminescence can be used to study $^1O_2$ quenching by organic compounds.

The compounds selected are well-documented singlet oxygen quenchers. β-Carotene is one of the most effective $^1O_2$ quenchers; it acts by energy transfer from $^1O_2$ to the low-lying triplet level of β-carotene.[9,10] In addition to their activity as inhibitors of radical chain oxidation,[11,12] highly substituted phenols and α-tocopherol quench $^1O_2$ through a charge-transfer complex mechanism.[13−15] The bicyclic tertiary diamine, 1,4-diazabicyclo[2.2.2]octane (DABCO), also quenches $^1O_2$ through this mechanism and has been reported to enhance dimol light emission under certain conditions.[16,17] Lauric acid was chosen as a quencher of very low efficiency which deactivates singlet oxygen by energy transfer to vibrational sublevels of CH and OH groups.[18]

Experimental Section

Materials. Lauric acid, D,L-α-tocopherol (97%), *all-trans*-β-carotene (95%), 2,6-di-*tert*-butyl-4-methylphenol (ionol, 99+%), and 1,4-diazabicyclo[2.2.2]octane (DABCO) from Aldrich Chemical and benzene-d_6 (99.6% d) from Cambridge Isotope Laboratories were used as received. C_{70} was prepared and purified as previously reported.[19] Tetra-*tert*-butylphthalocyanine was synthesized and purified by the procedure of Mikhalenko et al.[20]

$^1O_2$ Luminescence Measurements. Solutions containing C_{70} (about 2×10^{-5} M), Pc ($(3-7) \times 10^{-7}$ M) and the quencher were excited at 532 nm by the third harmonic of a QuantaRay DCR-2 Nd:YAG laser with pulse energy of about 2 mJ in a 10 mm rectangular quartz cell. Only C_{70} has appreciable absorption at 532 nm. The laser pulse was filtered with a 532 nm pass−1060 nm reflecting mirror (Newport Corp.) and a KG-3 (Schott Glass) infrared absorbing filter. The 1270 or 700 nm emission was monitored at right angles to the laser beam and filtered with 1270 (Oriel, 10 nm band-pass) or 700 nm (Oriel, 10 nm band-pass) interference filters, respectively. Luminescence was measured with a cryogenic germanium photodetector (North Coast Corp., Model EO-817P, −250 V bias). The analog signal from the detector was sent to a digital storage oscilloscope (LeCroy 9410 Dual 150 MHz). The luminescence decays were normally averaged over 20−50 laser shots and then transferred to a Macintosh IIci computer with Labview software. The data were analyzed using the Igor program. The 700 nm luminescence could also be detected with common photomultipliers (data not shown), but these detectors tend to overload at the very high signal levels produced in the experiments described here.

Results

In agreement with prior reports,[4] illumination of air-saturated solutions containing C_{70} and Pc by 532 nm laser flashes led to luminescence at 1270 and 700 nm (Figure 1). Decays of this luminescence are exponential. The lifetime of the 1270 nm luminescence was 670 μs in C_6D_6, while that at 700 nm was shorter by a factor of 2. The absorbance of C_{70} at 532 nm was 0.11−0.12, and that of Pc was more than 2 orders of magnitude

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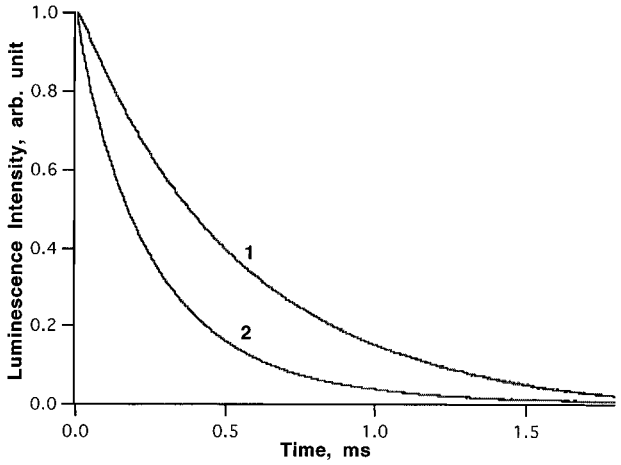

Figure 1. Decay kinetics of 1270 nm luminescence of singlet oxygen monomols (1) and 703 nm Pc delayed fluorescence (2) after laser flash in deuterated benzene.

TABLE 1: Ratios of Zero-Time Intensities of 700 and 1270 nm Emission (I_{700}/I_{1270}^2) at Different Quencher Concentrations

quencher	relative I_{700}/I_{1270}^2 (conc, μM, except as noted)[a]				
β-carotene	1 (0)	0.9 (0.12)	0.8 (0.37)	0.9 (0.62)	1.1 (1.2)
DABCO	1 (0)	0.9 (1.5)	0.8 (3.0)	1.1 (6.1)	1.2 (9.1)
α-tocopherol	1 (0)	1.0 (30)	1.1 (76)	1.0 (164)	1.0 (245)
2,6-di-*tert*-butyl-4-methylphenol[b]	1 (0)	1.0 (3.9)	1.2 (12.0)	1.1 (16)	1.3 (20)
lauric acid[b]	1 (0)	1.2 (29)	0.9 (57)	0.9 (140)	

[a] Normalized at zero quencher concentration. [b] In mM.

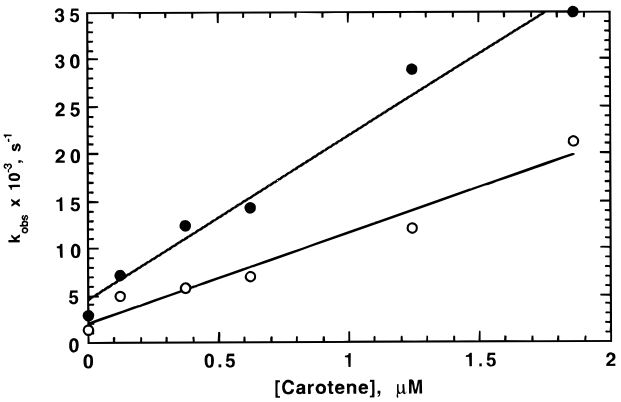

Figure 2. Luminescence decay rates at 1270 (○) and 700 nm (●) vs concentrations of *all-trans*-β-carotene in C_6D_6. Pc concentration was 3.4×10^{-7} M.

lower. Therefore, in this system, singlet oxygen formation was photosensitized only by C_{70} while the 700 nm luminescence came only from Pc.

In the presence of the singlet oxygen quenchers, the zero-time intensities of both 1270 and 700 nm light emission and their ratio did not depend upon concentration of the quenchers within the precision of our measurements (Table 1). This implies that the quenchers do not influence $^1O_2$ photogeneration by the fullerene. However, the decay rates at both 1270 and 700 nm increased with quencher concentration. The decay rate constants (k_{obs}) depended linearly upon quencher concentration and gave excellent Stern−Volmer plots. (Figures 2−4 show results for three of the plots; very similar results were obtained for the others.) The rate constants (k_q) for $^1O_2$ quenching calculated from the slopes of these lines were similar to those reported previously for these compounds.[10,13−18] The quenching rate constants for 700 nm luminescence were larger than those

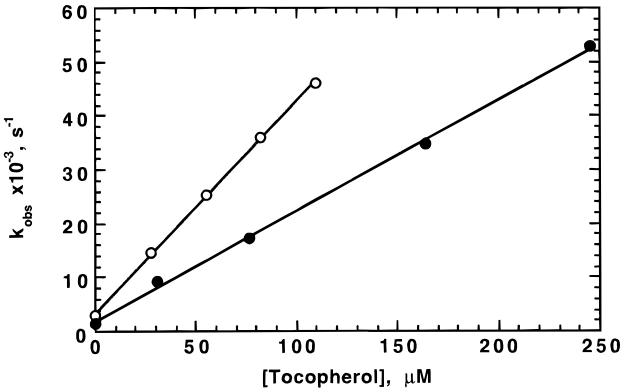

Figure 3. Plots of the luminescence decay rates at 1270 (●) and 700 nm (○) vs concentrations of α-tocopherol in C_6D_6. Pc concentration was 2.9×10^{-7} M.

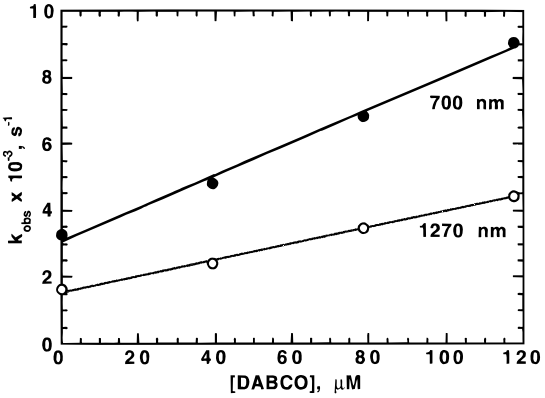

Figure 4. Plots of the luminescence decay rates at 1270 (○) and 700 nm (●) vs concentrations of DABCO in C_6D_6. [Pc] = 4.5×10^{-7} M.

TABLE 2: Rate Constants of Luminescence Quenching at 1270 and 700 nm in C_6D_6

quenchers	apparent rate constants (M^{-1} s^{-1})	
	1270 nm	700 nm
lauric acid	$(9.5 \pm 0.9) \times 10^3$	$(1.8 \pm 0.2) \times 10^4$
2,6-di-*tert*-butyl-4-methylphenol	$(1.3 \pm 0.1) \times 10^6$	$(2.6 \pm 0.3) \times 10^6$
α-tocopherol	$(2.1 \pm 0.2) \times 10^8$	$(3.9 \pm 0.4) \times 10^8$
trans-β-carotene	$(1.5 \pm 0.2) \times 10^{10}$	$(3.1 \pm 0.3) \times 10^{10}$
DABCO	$(2.4 \pm 0.2) \times 10^7$	$(4.9 \pm 0.5) \times 10^7$

at 1270 nm by a factor of 2 in all cases (Table 2). DABCO did not differ from other tested compounds and showed no anomalous behavior in the inhibition of the Pc delayed fluorescence. Some earlier reports suggested anomalous behavior of DABCO in producing excess "dimol" luminescence in the 700 nm region.[16,17]

Discussion

Our data indicate that quenching of Pc delayed fluorescence by the studied compounds derives entirely from singlet oxygen quenching. The kinetics of singlet oxygen monomol decay and delayed Pc fluorescence both follow the Stern−Volmer equation. The exponential decay of 1270 nm luminescence in the presence of a quencher can be described as follows:

$$k_{mobs} = (k_{mobs})_0 + k_q[Q] \quad (1)$$

where k_{mobs} is the rate of decay of singlet oxygen monomol luminescence after the laser flash, $(k_{mobs})_0$ is the rate in the absence of quencher, k_q is the rate constant for bimolecular quenching of singlet oxygen, and [Q] is the concentration of the quencher.

As shown in the figures, the decay rates of 700 nm luminescence (k_{700}) are larger by a factor of 2 than those of 1270 nm luminescence. Hence

$$k_{700} = 2k_{\text{mobs}} = 2\{(k_{\text{mobs}})_0 + k_q[Q]\} = 2(k_{\text{mobs}})_0 + 2k_q[Q] \quad (2)$$

Equation 2 shows that the rate constant calculated from the slope of the plot corresponding to quenching of 700 nm luminescence should be equal to $2k_q$, as observed. This analysis demonstrates that quenching of singlet-oxygen-sensitized Pc delayed fluorescence can be used for accurate measurements of the rate constants of $^1O_2$ interaction with organic molecules. Quenching rate constants calculated from the 703 nm experiments should be divided by a factor of 2 to obtain $^1O_2$ quenching rate constants. Under the conditions, no quenching of the fluorescence from the singlet excited state of the Pc is observed, nor is any expected at the concentrations of quenchers used.

These results also confirm our previous reports[1−5,8] that the $^1O_2$-sensitized luminescence is rigorously proportional to the square of the $^1O_2$ concentration over an enormous range of lifetimes. Subsequent reports will discuss the quantum yield and mechanism of production of this delayed fluorescence, which can be much more intense than the low quantum yield 1268 monomol emission of singlet oxygen.[8,21]

Unlike the 1268 nm luminescence of singlet oxygen, which requires a cooled Ge diode or other specialized detector and has time resolution limited to somewhat less than 1 μs, the 700 nm luminescence can be detected with conventional photomultipliers with their considerably better time resolution and sensitivity, raising the possibility of using this luminescence for detection of singlet oxygen in cases where the monomol luminescence is too weak to detect or has too short a lifetime for the Ge detector. The Ge detector was used in the experiments reported here because photomultipliers overload at the maximum light levels used in these experiments.

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