Singlet Oxygen Chemistry in Water. 2. Photoexcited Sensitizer Quenching by O₂ at the Water–Porous Glass Interface

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Insight into the O₂ quenching mechanism of a photosensitizer (static or dynamic) would be useful for the design of heterogeneous systems to control the mode of generation of ¹O₂ in water. Here, we describe the use of a photosensitizer, meso-tetra(N-methyl-4-pyridyl)porphine (I), which was adsorbed onto porous Vycor glass (PVG). A maximum loading of 1.1 × 10⁻⁴ mol I per g PVG was achieved. Less than 1% of the PVG surface was covered with photosensitizer I, and the penetration of I reaches a depth of 0.32 mm along all faces of the glass. Time-resolved measurements showed that the lifetime of triplet ¹*-ads was 57 µs in water. Triplet O₂ quenched the transient absorption of triplet ¹*-ads; for samples containing 0.9 × 10⁻⁶–0.9 × 10⁻⁵ mol I adsorbed per g PVG, the Stern–Volmer constant, K_S, ranged from 23 700 to 32 100 M⁻¹. The adduct formation constant, K_A, ranged from 1310 to 510 M⁻¹. The amplitude of the absorption at 470 nm decreased slightly (by about 0.1) with increased O₂ concentrations. Thus, the quenching behavior of triplet ¹*-ads by O₂ was proposed to be strongly dependent on dynamic quenching. Only ∼10% of the quenching was attributed to the static quenching mechanism. The quenching of triplet ¹*-ads was similar to that observed for photosensitizers in homogeneous solution which are often quenched dynamically by O₂.

1. Introduction

Heterogeneous materials have been studied for many years, and chemists discovered that some could be used as supports for the generation of singlet oxygen [¹O₂(¹Δg)]. Recently, we reported that meso-tetra(N-methyl-4-pyridyl)porphine (I) adsorbed onto porous Vycor glass (PVG), in which a pH decrease of the surrounding solution indicated the displacement of protons from the surface silanol groups via cation exchange (Scheme 1). Singlet oxygen was generated cleanly in aqueous solution upon irradiation of this heterogeneous sensitizer, I-ads. Despite the effectiveness of this and other heterogeneous systems to generate ¹O₂, surprisingly little is known about the mechanism of sensitizer quenching by O₂ at water–solid interfaces. For example, how does the oxygen encounter the excited PVG heterogeneous sensitizer? What mechanism (static or dynamic) converts ground-state O₂ into ¹O₂, which then diffuses into the bulk solution?

Some detail of the O₂ quenching process may be gleaned from previous studies of gas–solid systems. These studies often indicate the static quenching of O₂–where a ground-state O₂ adduct is formed at the surface–rather than a dynamic encounter of O₂ with the surface. At the gas–solid interface, Gafney showed that photoexcited Ru(bpy)₃²⁺-adsorbed to PVG statically quenches O₂.³ Avnir showed that photoexcited Ru(bpy)₃²⁺-adsorbed to porous silica and porous glass statically quench O₂ at low temperatures, but dynamically quench O₂ at high temperatures, and Thomas showed that aromatic compounds adsorbed ont nonporous glass statically quench O₂.¹⁻⁶ Pore size of silica-adsorbed photosensitizers can be tailored to statically or dynamically quench O₂ in gas–solid systems.⁷⁻⁸

Few studies have examined sensitizer quenching by O₂ at organic solvent–solid interfaces or water–solid interfaces.¹⁰ Despite reports on ¹O₂ production (Φₐ) and ¹O₂ lifetimes (τₐ) in homogeneous aqueous media, Nafion membranes,¹¹ micellar media,¹² water-soluble supramolecular hosts,¹³ or aqueous reactions using TiO₂,¹⁴ studies of the quenching mechanism of heterogeneous photosensitizers by O₂ at the water–solid interface are uncommon and are in need of elaboration.

We report here a photophysical analysis of how O₂ quenches ³¹* at the water–PVG interface. We also examined the effects of surface loading and percent coverage of the photosensitizer and the depth that I can penetrate into the PVG material. An assessment of the quenching of the photosensitizer (static or dynamic) could help in the design of heterogeneous systems that attempt to control the exact mode of generation of ¹O₂ in water.

2. Experimental Section

2.1. Materials and Sample Preparation. Deionized H₂O was obtained from a U.S. Filter Corp. deionization system. meso-Tetra(N-methyl-4-pyridyl)porphine tetratosylate was purchased commercially and used as received. The PVG was used as a host material and was purchased from Advanced Glass and Ceramics (Corning 7930). The PVG has a void space of ∼28% of the volume, average pore sizes of 40 Å, a hydrophilic absorbing surface area of 250 m²/g, a density of 1.38 g/mL, and transparency in the near-UV (50% T at 351 nm), visible, and parts of the near-IR.¹⁵ Pieces of PVG (1.5 cm × 1.5 cm; thickness: 1.15–1.53 mm) were heated in a muffle furnace at 500 °C and stored in a desiccator under vacuum at 30 mmHg.
SCHEME 1: Adsorption of Photosensitizer 1 onto the PVG Surface and Production of Singlet Oxygen

The photosensitizer-coated PVG was prepared by soaking 1.4 g of PVG into a 20 mL 3.7 × 10⁻⁵ M aqueous solution of I for 15–64 h. The amount of I adsorbed onto PVG was calculated from the difference in absorbance of the solution before introduction of PVG and the absorbance of the same solution after the removal of PVG. For the transient absorption studies, PVG was cut such that each piece fits diagonally into a 1 cm path-length quartz cuvette. Each PVG/I sample was placed into a quartz cuvette, which contained deionized water, and was sparged with N₂ gas for 20 min. Any bubbles that stuck onto the PVG surface were removed by sonication for a few seconds. Some PVG samples (1.5 cm × 1.5 cm; thickness: 1.53 mm) were cut into 0.3 cm × 1.5 cm pieces and photographed with a microscope.

2.2. Instruments. Photographic images were taken with a Nikon TE200 microscope equipped with an Orca 100 monochrome charge-coupled device (CCD) camera and a Hamamatsu camera controller (C4742-95). The light source used was a 100 W mercury arc lamp. The objective used was a Plan Apo 60×/0.6 DIC. Images were recorded and analyzed with Cam- Media software. Absorption spectra were collected with a Hitachi UV–vis U-2001, a Hewlett-Packard 8453 diode array, or a Varian Cary 4 spectrophotometer. In some experiments with the Carey 14 instrument, the Q-bands of I at 525, 552, 585, and 640 nm were followed because the intense Soret band at 422 nm gave absorbances of 2.5 or greater, which saturated with the Carey 14 instrument, the Q-bands of I at 525, 552, 585, and 640 nm were followed because the intense Soret band at 422 nm gave absorbances of 2.5 or greater, which saturated.

2.3. Transient Absorption Spectroscopy. The PVG samples used in these experiments contained 0.9 × 10⁻⁸–1.1 × 10⁻⁶ mol I/g PVG. Room-temperature time-resolved measurements were conducted as previously described. The PVG samples were excited at 417 nm but oriented so that reflected laser light was directed at a 45° angle away from the detector on the transient absorption apparatus. Each kinetic trace is an average of 64 laser pulses. The triplet of 1-ads was monitored at 470 nm, in which a 435 nm long pass filter was placed in front of the detector monochromator to block scattered laser light. The data points in the transient absorption experiments were collected every 10 nm from 450 to 550 nm. An MKS Instruments multigas controller (MKS 647C) was used to control the flow of O₂ and N₂ through two MKS Instruments flow controllers. The flow controllers were set for a flow rate of 100 standard cubic centimeters per minute (scm). Gas correction factors (GCFs) programmed into the MGC were utilized to correct for specific heat, density, and molecular structure of O₂ and N₂. The samples were purged with different ratios of an O₂:N₂ stream of gas for 5 min before each kinetic trace was taken. The oxygen concentration of a solution bubbled with the O₂:N₂ gas stream were determined by using Henry’s law.

2.4. Computational Methods. Density function theoretical (DFT) calculations were conducted by the exchange-correlation of B3LYP along with Pople basis set 6-31G(d) with the use of the Gaussian 03 program package. The solvent accessible surface was computed by the method of Lee and Richards.

3. Results and Discussion

3.1. Time-Dependent Adsorption of Photosensitizer onto PVG. A clean piece of PVG placed into an aqueous solution containing I led to the adsorption of I onto PVG. Figure 1 shows the time-dependent adsorption of I onto PVG over a 15 h period. The adsorption process was followed by monitoring the largest of the four Q-bands of 1-ads at λ = 525 nm. A plateau is reached when there is 8.8 × 10⁻⁷ mol I adsorbed onto 1 g PVG. Loadings of 1.1 × 10⁻⁶ mol I onto PVG can be achieved, but only after a 48–72 h period. Once the 1-ads samples contained the desired surface coverage, they were rinsed with distilled water prior to use.

3.2. Uniform Photosensitizer Distribution. Absorption spectra were recorded at different points on the PVG film to analyze the dispersal of adsorbed I. The Q-band absorptions (475–700 nm) are found to be identical to within 0.01 absorbance unit, suggesting that the distribution of I is uniform; thus, the surface coverage of I adsorbed onto PVG could then be estimated. Two methods were used to determine the surface coverage of I adsorbed onto PVG. Both are in qualitative agreement with each other: (1) The amount of uncoated PVG was determined by subtracting 1.0 g of PVG from (8.83 × 10⁻⁷ mol I/g PVG × 679.61 g/mol I), which is 0.9994 g. Dividing 8.83 × 10⁻⁷ mol I/g PVG into (0.9994 g uncoated PVG × 250 m²/g PVG) yielded 3.5 × 10⁻⁹ mol I/m², indicating that the amount of I adsorbed is not uniform. Figure 1 shows the transient absorption spectra at different points on the PVG sample that was sitting in a solution containing I. The PVG sample was removed at the indicated times. The plateau region at 14 h corresponds to 8.83 × 10⁻⁷ mol I adsorbed onto 1 g PVG.
0.35% of the PVG surface is covered by I, (2) Surface coverage was determined by a calculation, in which porphyrin I is taken as a rectangular shape (22.2 Å × 22.2 Å × 7.3 Å) multiplied by (8.83 × 10⁻⁷ mol l/g PVG × 6.02 × 10²³ molecules/mol × 10⁻²¹ mm²Å⁻³), which equals 1.91 mm³/g PVG. The rectangular shape of I was estimated on the basis of the B3LYP/6-31G(d) optimized structure and the corresponding solvent accessible contour map (Figure 2), in which the pyridinium rings are nearly orthogonal to the plane of the porphyrin (67°). The corresponding weight of I-adsorbed PVG (1.91 mm³ × 1.38 g PVG/mL) equals 2.64 g PVG. Therefore, the surface coverage of I onto PVG was calculated by taking [8.83 × 10⁻⁷ mol l/g PVG × 250 m²/g PVG] or 1.4 × 10⁻⁹ mol l/m², yielding 0.13% PVG surface coverage by I. Both calculations [(1) and (2), vide supra] indicated that <1% of the PVG surface is covered with the photosensitizer I. For comparison, the surface coverage of Ru(bpy)³⁺ on PVG is <1%,³ on porous silica is ∼6%, and on porous glass is ∼10%.⁴

3.3. Photosensitizer Penetration Depth. The depth that I can penetrate into PVG was examined using a microscope equipped with a CCD camera. Figure 3 shows a 1.5 mm thick (sensitizer coated) PVG sample, cut so that the depth of I penetrated into PVG could be viewed. The microscope image shows the penetration of I reaches a maximum depth of 0.32 mm along all faces of the sample, which corresponds to the plateau region of 8.8 × 10⁻⁷ mol l/g PVG (Figure 1). Although O₂ and other gases are permeable and can pass through the connected pores of PVG,⁵ I neither penetrates to the center of the PVG film nor is I localized on the outer surface of PVG. A 10-fold mole increase of I resulted in only a 4-fold local increase in sensitizer distribution into PVG [cf. 0.9 × 10⁻⁶ mol l I (penetration depth 0.32 mm) and 0.9 × 10⁻⁷ mol l I adsorbed onto 1 g PVG (penetration depth 0.09 mm)]. Oxygen is expected to reach the excited sites of I-ads, controlled by Knudsen diffusion, in which O₂ collides numerous times within the pore walls, eventually proceeding through the PVG channels. For comparison, Ru(bpy)³⁺ penetrates 0.5 ± 0.1 mm into PVG.³ Streptocyanine dyes also possessed diffusivity into silica gels, influenced by the gel porosities.²⁶

3.4. Spectral Properties. Previously, we reported that the spectral features of I-ads are nearly identical to I in fluid water solution.² Here, we report the spectral features measured at different concentrations of I adsorbed onto PVG. Figure 4 shows absorption spectra of I in water and I adsorbed onto PVG. While the effect of higher coverage dose of I produces neither red shifts nor blue shifts in the Q-bands, the adsorption of I on PVG leads to an unexpected effect on the absorption intensity. Higher coverages of I adsorbed onto PVG led to a decrease of the Q-band absorption intensity, (cf. 0.9 × 10⁻⁶, 0.9 × 10⁻⁷, and 0.9 × 10⁻⁸ mol l/g PVG). At higher surface coverage, the absorption spectrum of I-ads becomes somewhat similar to that of I in aqueous solution (cf. spectra in blue and black, Figure 4). Deducing a possible orientational effect of the porphyrin on the PVG surface is challenging based upon these normalized absorption spectra. Polarization effects are known for porphyrins result in symmetric changes of all the S₀ → S₁ transitions. However, atomic-level
Figure 5. Nanosecond transient absorption spectra observed at 500 ns after pulsed-light excitation (417 nm, 1.6 mJ/pulse) of 1 in water solution (inset) and 1 adsorbed onto PVG in an N2-purged H2O solution. The absorbance at ~470 nm was assigned to $3^1\text{-ads}$. Similar transient features were observed for $3^1\text{-ads}$ in fluid water (Figure 5, inset) and also by Reddi et al. for $3^1\text{-ads}$ in phosphate buffered solution and in aqueous 2% sodium dodecyl sulfate solution. First-order decay kinetics were observed for the transient absorption of $3^1\text{-ads}$, which decayed cleanly to baseline. The lifetime of $3^1\text{-ads}$ ($\tau_0 = 57 \pm 1 \mu s$) is similar to $3^1\text{-ads}$ in liquid solution ($\tau_0 = 49 \pm 1 \mu s$). Our absorption measurements in the UV–vis region before and after transient absorption experiments revealed no significant change. Next we describe how O2 quenches the transient absorption of $3^1\text{-ads}$ and $3^1\text{-ads}$ in water solution.

Figure S1 shows the lifetime and the amplitude quenching of the $3^1\text{-ads}$ transient absorption by O2 (Supporting Information). Photoexcited 1 quenching by O2 at the PVG/water interface encouraged a Stern–Volmer analysis for insight into quenching mechanism. Two mechanisms were considered: (1) the dynamic encounter of O2 with an excited site on the surface, and (2) a ground-state O2 adduct formed at the surface with migration of adsorbed O2 to an excited site (Scheme 2).

Stern–Volmer data collected at nine O2 concentrations (from 0 to 0.4 mM) are shown in Table 1 and Figure 6, in which the symbol $\tau$ refers to the lifetime of the excited porphyrin, $k_q$ is the rate constant for O2 quenching, $K_D$ is the Stern–Volmer constant, $K_S$ is the association constant for complex formation between the sensitizer and O2, and the subscript “0” indicates data in the absence of O2. The left axis of Figure 6 shows the plot of $\tau_0/\tau$ vs [O2] to be linear over the O2 concentration examined and corresponded to the Stern–Volmer equation: $\tau_0/\tau = 1 + K_D[O_2] = 1 + K_D[O_2]$. For $0.9 \times 10^{-7}$ mol 1 adsorbed onto 1 g PVG, $K_D = 26 500 \text{ M}^{-1}$ and the quenching rate constant $k_q = 4.6 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$, indicating that 50% of $3^1\text{-ads}$ was quenched at an [O2] of 0.04 mM. For the samples containing $0.9 \times 10^{-6} - 0.9 \times 10^{-8}$ mol 1 adsorbed onto 1 g PVG, the $K_D$ values ranged from 32 000 to 23 700 M$^{-1}$.

Interestingly, the bimolecular quenching constant $k_q$ for 1-ads ($k_q = 5 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$) is about one-quarter-the value measured for 1 in fluid water ($k_q = 1.8 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$). The experiments for 1 in fluid water solution produced a $K_D$ value of 89 600 M$^{-1}$. Thus, the time scale for O2 diffusion may be slower in the water–PVG heterogeneous system compared to fluid solution. By analogy, Thomas et al. used the Einstein equation $\langle x^2 \rangle = 6Dt$ to suggest that nitromethane quenching of excited anthracene is $10^3 - 10^6$ times slower in a zeolite compared to fluid solution (cf. $10^{-8} - 10^{-11} \text{ cm}^2 \text{s}^{-1}$). In our system, the smaller $K_D$ values in the heterogeneous samples may result from reduced directions for access of O2 to $3^1\text{-ads}$ compared to O2 to $3^1\text{-ads}$ in fluid solution.

The amplitude of the time-resolved absorbance at 470 nm was examined (Figure S1, Supporting Information). Because a
ground-state adduct equilibrium of 1-ads and O₂ would be expected to have a different absorption spectrum from 1-ads, an absorption decrease can point to a static quenching mechanism. Figure 6 (right-hand Y-axis) shows the plot of \( \alpha_0/\alpha \) vs [O₂] was linear over the O₂ concentration examined and followed the equation \( \alpha_0/\alpha = 1 + K[O_2] \). For 1-ads, the adduct formation constant \( K_3 \) ranged from 510 to 1310 M⁻¹. The amplitude of the absorption at 470 nm decreased slightly (by about 0.1) with increasing O₂ concentrations. Therefore, we estimate that ~10% of the quenching occurred via the static quenching mechanism (colored blue in Scheme 2). The above Stern–Volmer analysis suggests that quenching of 31*-ads by O₂ is primarily dynamic, the route colored black in Scheme 2. In the absence of aggregation, photosensitizers in homogeneous fluid solution are often quenched dynamically by O₂.

4. Conclusion

In isotropic heterogeneous media static and dynamic quenching modes can operate. In the present case, we have evidence that O₂ quenches triplet 1* at the water–PVG interface primarily by a dynamic quenching mechanism. The contribution from static quenching remains low even with loadings of 1 onto PVG that varied by 100-fold. The O₂ quenching constants \( k_q \) for 31*-ads were only ~3–4 times smaller than for 1* itself, suggesting the heterogeneous system is capable of generating singlet oxygen for its use as a reagent in the surrounding aqueous solution.

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Supporting Information Available: Time-resolved absorbance of 31*-ads in the presence of increasing concentrations of oxygen. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes


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