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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 × 10−9 mol I g−1 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 g−1 PVG, the Stern–Volmer constant, K0, ranged from 23 700 to 32 100 M−1. The adduct formation constant, Kf, 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).1–6 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).2 Singlet oxygen was generated cleanly in aqueous solution upon irradiation of this heterogeneous sensitizer, 1−ads.3

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,4 and Thomas showed that aromatic compounds adsorbed onto nonporous glass statically quench O2.5,6 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 interfaces9 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 1* 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.
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 1 for 15–64 h. The amount of 1 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.²¹²² For the transient absorption studies, PVG was cut such that each piece fits diagonally into a 1 cm path-length quartz cuvette. Each PVG/1 sample was placed into the 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 mono-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 was a Plan Apo 60×OIL DIC. Images were recorded and analyzed with CamMedia software. Absorption spectra were collected with a Hitachi UV–vis U-2001, a Hewlett-Packard 8453 diode array, or a Varian Cary 14 spectrophotometer. In some experiments with the Carey 14 instrument, the Q-bands of 1 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 the UV–vis detector. A Quantel Brilliant B Nd:YAG laser (417 nm, 1.6 mJ/pulse) was used in the transient absorption studies. 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.²¹²²

3. Results and Discussion

3.1. Time-Dependent Adsorption of Photosensitizer onto PVG. A clean piece of PVG placed into an aqueous solution containing 1 led to the adsorption of 1 onto PVG. Figure 1 shows the time-dependent adsorption of 1 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 1 adsorbed onto 1 g PVG. Loadings of 1.1 × 10⁻⁶ mol 1 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 1. The Q-band absorptions (475–700 nm) are found to be identical to within 0.01 absorbance unit, suggesting that the distribution of 1 is uniform; thus, the surface coverage of 1 adsorbed onto PVG could then be estimated. Two methods were used to determine the surface coverage of 1 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 1/g PVG × 679.61 g/mol 1), which is 0.9994 g. Dividing 8.83 × 10⁻⁷ mol 1/g PVG into (0.9994 g uncoated PVG × 250 m²/g PVG) yielded 3.5 × 10⁻⁹ mol 1/m², indicating that...
PVG was calculated by taking \[8.83 \times 10^{-6} \text{ g} \] PVG. Therefore, the surface coverage of 10 mm along all faces of the sample, which corresponds to the penetration of PVG could be viewed. The microscope image shows the penetration of (sensitizer coated) PVG sample, cut so that the depth of penetrated into PVG was examined using a microscope equipped with a CCD camera. Figure 3 shows a 1.5 mm thick (sensitizer coated) PVG sample. The horizontal line in the middle of the PVG sample corresponds to where two glass layers meet due to the commercial fabrication process.

0.35% of the PVG surface is covered by 1. (2) Surface coverage was determined by a calculation, in which porphyrin 1 is taken as a rectangular shape (22.2 Å × 22.2 Å × 7.3 Å) multiplied by \((8.83 \times 10^{-7} \text{ mol} \times 6.02 \times 10^{23} \text{ molecules/mol} \times 10^{-21} \text{ mm}^2/\text{Å}^3)\), which equals 1.91 mm\(^3\)/g PVG. The rectangular shape of 1 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 1-adsorbed PVG (1.91 mm\(^3\) × 1.38 g PVG/mL) equals 2.64 g PVG. Therefore, the surface coverage of 1 onto PVG was calculated by taking \([8.83 \times 10^{-7} \text{ mol} \times 2.64 \text{ g PVG} \times 250 \text{ m}^2/\text{g PVG}]\) or \(1.4 \times 10^{-9} \text{ mol L/m}^2\), yielding 0.13% PVG surface coverage by 1. Both calculations [(1) and (2), vide supra] indicated that <1% of the PVG surface is covered with the photosensitizer 1. 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 1 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 1 penetrated into PVG could be viewed. The microscope image shows the penetration of 1 reaches a maximum depth of 0.32 mm along all faces of the sample, which corresponds to the plateau region of \(8.8 \times 10^{-7} \text{ mol L/g PVG}\) (Figure 1). Although O\(_2\) and other gases are permeable and can pass through the connected pores of PVG,\(^25\) I neither penetrates to the center of the PVG film nor is 1 localized on the outer surface of PVG. A 10-fold mole increase of 1 resulted in only a 4-fold local increase in sensitizer distribution into PVG [cf. \(0.9 \times 10^{-6} \text{ mol L}1\text{-adsorbed onto PVG}\), the Q-band maximum is at 525 nm. Oxygen is expected to reach the excited sites of 1-ads, controlled by Knudsen diffusion, in which O\(_2\) collides numerous times within the pore walls, eventually proceeding through the PVG channels. For comparison, Ru(bpy)\(^2+\) 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 1-ads are nearly identical to 1 in fluid water solution.\(^2\) Here, we report the spectral features measured at different concentrations of 1 adsorbed onto PVG.

Figure 4 shows absorption spectra of 1 in water (blue line) and 1-ads at different loadings: \(0.9 \times 10^{-8}\) (green line), \(0.9 \times 10^{-7}\) (red line), and \(0.9 \times 10^{-6}\) (black line) mol of 1 adsorbed onto PVG. The spectra were normalized at 532 nm. Except for the green line (\(0.9 \times 10^{-3}\) mol 1 adsorbed onto PVG), the Q-band maximum is at 525 nm.
revealed no significant change. Next we describe how O$_2$ collection every 10 nm from 450 to 550 nm.

detail is unavailable for PVG and how it may relate to the conformation of adsorbed 1. Interestingly, recent studies have shown a reduced hydrating ability of ~2.2 H-bonds per water molecule confined in PVG pores compared bulk water with ~3.6 H-bonds per water molecule, pointing to the importance for confinement effects.27,28

3.5. Time-Resolved Photophysical Studies. Figure 5 shows a nanosecond transient absorption spectrum generated from pulsed 417 nm light excitation of 0.9 × 10$^{-7}$ mol l$^{-1}$ adsorbed onto 1 g PVG in an N$_2$-purged H$_2$O solution. The absorption band at ~470 nm was assigned to 31*-ads. Similar transient features were observed for 31* in fluid water (Figure 5, inset) and also by Reddi et al. for 31* in phosphate buffered solution and in aqueous 2% sodium dodecyl sulfate solution.29 First-order decay kinetics were observed for the transient absorption of 31*-ads, which decayed cleanly to baseline. The lifetime of 31*-ads ($\tau_0 \approx 57 \pm 1 \mu s$) is similar to 31* in fluid aqueous solution ($\tau_0 \approx 49 \pm 1 \mu s$). Our absorption measurements in the UV-vis region before and after transient absorption experiments revealed no significant change. Next we describe how O$_2$ quenches the transient absorption of 31*-ads and 31* in water solution.

Figure S1 shows the lifetime and the amplitude quenching of the 31*-ads transient absorption by O$_2$ (Supporting Information). Photoexcited 1 quenching by O$_2$ at the PVG/water interface encouraged a Stern–Volmer analysis for insight into quenching mechanism. Two mechanisms were considered: (1) the dynamic encounter of O$_2$ with an excited site on the surface, and (2) a ground-state O$_2$ adduct formed at the surface with migration of adsorbed O$_2$ to an excited site (Scheme 2).

Stern–Volmer data collected at nine O$_2$ 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 O$_2$ quenching, $K_D$ is the Stern–Volmer constant, $K_S$ is the association constant for complex formation between the sensitizer and O$_2$, and the subscript “0” indicates data in the absence of O$_2$. The left axis of Figure 6 shows the plot of $\tau_0$/$\tau$ vs $[O_2]$ to be linear over the O$_2$ concentration examined and corresponded to the Stern–Volmer equation: $\tau_0/\tau = 1 + k_q[q]/K_D = 1 + K_S/[O_2]$. For 0.9 × 10$^{-7}$ mol l$^{-1}$ adsorbed onto 1 g PVG, $K_D = 26 500$ M$^{-1}$ and the quenching rate constant $k_q = 4.6 \times 10^9$ M$^{-1}$ s$^{-1}$, indicating that 50% of 31*-ads was quenched at an $[O_2]$ of 0.04 mM. For the samples containing 0.9 × 10$^{-6}$–0.9 × 10$^{-5}$ mol l$^{-1}$ 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 ($k_q \approx 5 \times 10^8$ M$^{-1}$ s$^{-1}$) is about one-quarter the value measured for 1 in fluid water ($k_q = 1.8 \times 10^9$ M$^{-1}$ 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 O$_2$ diffusion may be slower in the water–PVG heterogeneous system compared to fluid solution. By analogy, Thomas et al. used the Einstein equation $\langle x^2 \rangle = 6D\tau$ to suggest that nitromethane quenching of excited anthracene is $10^3$–$10^6$ times slower in a zeolite compared to fluid solution (cf. $10^{-8}$–$10^{-11}$ cm$^2$ s$^{-1}$).30 In our system, the smaller $K_D$ values in the heterogeneous samples may result from reduced directions for access of O$_2$ to 31*-ads compared to O$_2$ to 31* in fluid solution.

The amplitude of the time-resolved absorbance at 470 nm was examined (Figure S1, Supporting Information). Because a
ground-state adduct equilibration 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 $\alpha / \alpha_0$ vs $[O_2]$ was linear over the O₂ concentration examined and followed the equation $\alpha / \alpha_0 = 1 + K_{O_2}$. 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. Thus, we estimate that ~10% of the quenching occurred via the static quenching mechanism (colored blue in Scheme 2). The above Stern–Volmer analysis suggested 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 O₂. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes