Professor Heesing, a colleague of the late Professor Dyong, for a sample of **8b**.

Registry No. **2a**, 34147-09-6; **2b**, 80471-15-4; **3a**, 80462-77-7; **3b**, 80462-78-8; **4a**, 80462-79-9; **4b**, 80462-80-2; **5a**, 80462-81-3; **5b**, 80462-82-4; **6**, 80462-83-5; **7a**, 80462-84-6; **7b**, 80462-85-7; **7c**, 80462-86-8; **8b**, 78013-88-4; D-mannosan, 14168-65-1.

Photooxidation of Water by *p*-Benzoquinone

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There is strong interest in understanding photosynthesis, and in aqueous photosynthetic-like systems utilizing light for chemical purposes.[1-3] Naturally occurring quinones play an essential role in electron transport in bacterial reaction centers,[4,5] photosystem II of green plants,[6] and mitochondria.[7] Therefore it seems important to understand the aqueous photoredox behavior of the simplest quinone, *p*-benzoquinone (BQ). Using the technique of transient spontaneous Raman spectroscopy, we report here two- and apparently one-photon photooxidation of water by BQ without catalysis.

Our apparatus and methods have been recently described.[8,9] A 266-nm pulse (10 Hz) photolyzes the flowing sample, and a Raman spectrum is generated by a time-delayed 416-nm pulse. The pulses have $\simeq$10-ns widths, and sensitivity is enhanced by extensive averaging with gated, multichannel optical detection. BQ (freshly sublimed) solutions were studied within a few minutes of preparation.

Aqueous BQ (pH $\simeq$6.0) has its $S_0 \rightarrow S_1$ ($n-\pi^*$) transition maximum ($\epsilon \simeq 20$ M^{-1} cm^{-1}) near 430 nm.[10] An energetic 416-nm pulse by itself has the potential to both make transient species and generate their Raman spectra. Figure 1 shows spectra as a function of 416-nm pulse energy *without* prior 266-nm excitation. At least three different species appear to be present. Peaks labeled S_0 are assigned to S_0 BQ as they scale approximately linearly with pulse energy and agree with S_0 vibrational frequencies.[11] Peaks labeled T_1, and $Q^-\cdot + QH\cdot$, vary together as a higher (approximately second) power of energy. These peaks represent transient species created by absorption of one photon, with a second photon required for Raman scattering. These species appear within the pulse width and cannot be bimolecular BQ reaction products.

$Q^-\cdot$ refers to the semiquinone radical anion, which can be made independently by MnO_2 oxidation of aqueous hydroquinone at neutral pH.[12] The $Q^-\cdot$ spectrum thus generated[13] (Figure 2a) agrees with a $Q^-\cdot$ spectrum recently obtained via pulsed radiolysis.[14] $QH\cdot$ is protonated $Q^-\cdot$. Previous studies have shown that $Q^-\cdot$ (pK_a = 4.1) protonates in acidic solution.[15] Figure 2b shows a $QH\cdot$ 416-nm spectrum observed at long delay time Δt after photolysis of acidic hydroquinone.[13] In agreement with these assignments, we observe a smooth transformation of $Q^-\cdot$ into $QH\cdot$ at long Δt as a function of pH.

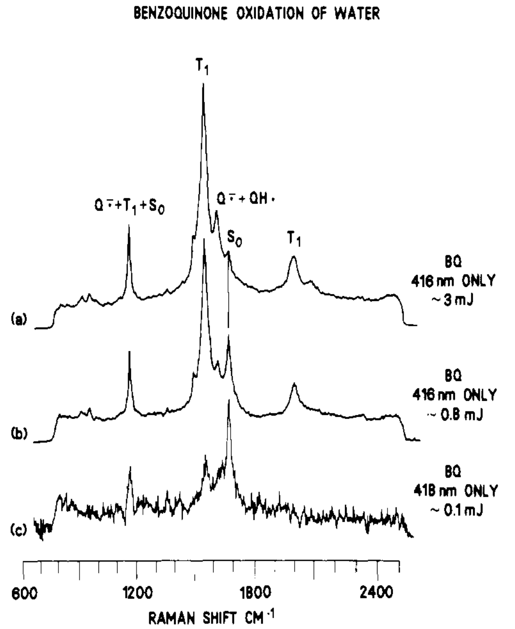

Figure 1. 416-nm Raman spectra, as function of pulse energy, of an aqueous solution of BQ (3×10^{-2} M, pH $\simeq$6). Transient species produced and probed by the same laser pulse are the lowest $n\pi^*$ triplet of BQ (T_1) and apparently semiquinone radicals $Q^-\cdot + QH\cdot$. The ground-state vibrations are labeled S_0. Trace a, taken at 3-mJ, 416-nm power, is an average of 600 laser pulses; trace b, taken at 0.8-mJ laser power, is an average of 3000 laser pulses (vertical axis is expanded by 2×); trace c, taken at 0.1-mJ laser power, is an average of 12 000 laser pulses (vertical axis is expanded by 8×).

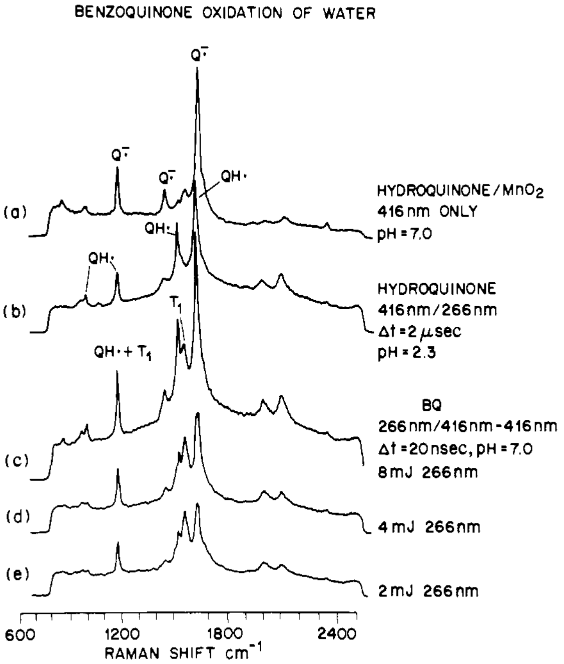

Figure 2. (a) Raman spectrum of 1×10^{-2} M neutral pH aqueous solution of hydroquinone passed over powdered MnO_2 (416-nm laser only); all peaks are assigned to $Q^-\cdot$; (b) Raman spectrum of aqueous hydroquinone (1×10^{-2} M; pH 2.3) 2 μs after 266-nm photolysis; all peaks assigned to $QH\cdot$; (c)–(e) Raman spectra of 5×10^{-3} M aqueous BQ solution taken 20 ns following 266-nm excitation, as a function of 266-nm pulse energy. The contribution of the 416-nm laser to transient production has been approximately subtracted so that peaks are due mainly to 266-nm excitation. Trace b was taken at 8-mJ, 266-nm power; trace c, 4 mJ; trace d, 2 mJ.

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T_1 peaks separate from $QH\cdot$ and $Q^{-}\cdot$ peaks in experiments using both 266- and 416-nm pulses. Figure 2c–e shows spectra as a function of 266-nm power. Comparison with Figure 1a shows $QH\cdot$ and $Q^{-}\cdot$ to be strongly enhanced by 266-nm photolysis. The $Q^{-}\cdot$ and $QH\cdot$ peaks grow approximately as the square of the 266-nm energy, suggesting a two-photon process for their formation. T_1 peaks grow approximately as the first power of energy, thus showing that S_0 is not appreciably depleted at these 266-nm fluxes. T_1 peaks can also be differentiated from $Q^{-}\cdot$ and $QH\cdot$ peaks via time dependence: T_1 peaks decay with a (200 ± 50)-ns lifetime, while $Q^{-}\cdot$ and $QH\cdot$ show little decay for $t \leq 1$ μs.

We assign T_1 to be the lowest n–π* triplet state, known to occur in high yield following singlet excitation in various environments.[16-19] T_1 has not been previously detected in water. The short T_1 lifetime is consistent with previous observations of fast unimolecular $T_1 \rightarrow S_0$ intersystem crossing.[16,17] Quinone triplets are typically strongly oxidizing and may abstract hydrogen atoms or electrons in alcohol and hydrocarbon solvents.[20-25] We observe that addition of 1% methanol decreases the T_1 lifetime to ≤30 ns, with a concomitant increase in $QH\cdot$ signal.[13]

Detection of $Q^{-}\cdot$, $QH\cdot$, and T_1 is enhanced by resonance Raman effects, in each case apparently stronger than that of S_0. Both $Q^{-}\cdot$ and $QH\cdot$ show $\epsilon \sim 5000\ M^{-1}\ cm^{-1}$ at 416 nm.[26] The 395- and 448-nm Raman spectra of these species both show weaker intensities. Apparently the T_1 triplet–triplet spectrum closely overlaps the $Q^{-}\cdot$ and $QH\cdot$ absorption spectra; the kinetic usefulness of the transient Raman technique is shown by its ability to clearly distinguish among these species.

$Q^{-}\cdot$ and $QH\cdot$ observed at 10^{-8} s are unequilibrated oxidation products corresponding to the net transfer of an electron and a hydrogen atom from water. Our data do not preclude the possible existence of an intermediate species on shorter time scales. With both 266- and 416-nm pulses, the dominant process involves two 266-nm photons. As the S_1 lifetime is extremely short and the T_1 quantum yield is high, the probable route involves absorption of a second photon by T_1. Spectral simulations indicate that the initial $[QH\cdot]/[Q^{-}\cdot]$ ratio is $\simeq 2$; this conclusion assumes that the two 416-nm Raman cross sections are equal. This assumption is plausible (but not proven) as the two ϵ_{416} are approximately equal, and the chromophores are similar.

With only 416-nm pulses, the Figure 1 power dependence demonstrates that the small peak tentatively assigned to semiquinone results from a single 416-nm photon process. We cannot distinguish $Q^{-}\cdot$ from $QH\cdot$ as both species have strong lines at this position. Single photon oxidation of water is supported by previous studies detecting permanent photoproducts following low flux irradiation.[10,27,28] Our Raman assignment must remain tentative until the overlapping T_1 spectrum can be independently generated. Photooxidation of water apparently occurs during relaxation to vibrationally equilibrated T_1, as this peak appears within laser pulse and does not "grow in" as T_1 subsequently decays in water.

Oxidation of water as in

$$BQ^*(T_1) + H_2O \rightarrow BQ^{-}\cdot + OH + H^+ \tag{1}$$

requires that unrelaxed $BQ^*(T_1)$ overcome the estimated 2.65-V (vs. NHE) half-cell potential of $OH + H^+ + e^- \rightarrow H_2O$.[29] The reduction potential E_0 of relaxed T_1 can be estimated[30] as $E_0(T_1) = E_0[BQ(S_0)/BQ^{-}\cdot] + E_T \simeq 2.4$ V where we use $E_0[BQ(S_0)/BQ^{-}\cdot] = 0.099$ V.[31] *Relaxed* T_1 BQ, while being one of the most potent oxidizing agents known, is apparently not quite able to oxidize water. It is interesting that duroquinone, with $E_0(T_1) = 2.17$ V,[25] does not oxidize water even during relaxation to T_1.[24]

Redox potentials do not predict the rate of oxidation. In this regard the electronic structure of T_1 is especially interesting. This state involves promotion of an O atom n electron to a delocalized π* orbital. The positive "hole" thus created is not equally divided between the two oxygens, but resides essentially on one oxygen, as in the valence bond model, despite C_{2v} formal symmetry.[17,32] Such a fully localized electrophilic site appears favorable for oxidation processes.

Acknowledgment. We thank E. Chandross, B. Miller, and H. Roth for useful discussions.

Registry No. BQ, 106-51-4; $Q^{-}\cdot$, 3225-29-4; $QH\cdot$, 3225-30-7; hydroquinone, 123-31-9; water, 7732-18-5.

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Generation of $O_2(^1\Delta_g)$ by Direct Absorption of Radiation by Ground-State Oxygen

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We recently reported evidence for the gas-phase generation of singlet Δ oxygen at atmospheric pressure using heterogeneous photosensitization.[1,2] Using a similar apparatus we have now obtained optical evidence for the production of $O_2(^1\Delta_g)$ by direct absorption of radiation by ground-state oxygen at atmospheric pressure.

The transition from ground-state oxygen to the electronically excited singlet state (Reactions 1 and 2) is a forbidden process.[3]

$$O_2(^3\Sigma_g^-) + h\nu\ (7619\ \text{Å}) \rightarrow O_2(^1\Sigma_g^+) \tag{1}$$

$$O_2(^3\Sigma_g^-) + h\nu\ (12\,690\ \text{Å}) \rightarrow O_2(^1\Delta_g) \tag{2}$$

$$O_2(^1\Sigma_g^+) + M \rightarrow O_2(^1\Delta_g) + M \tag{3}$$

Evidence exists, however, for the formation of $O_2(^1\Delta_g)$ as well as $O_2(^1\Sigma_g^+)$, in the atmosphere by the direct absorption of sunlight.[4] In addition, the possibility that formation of singlet oxygen in this manner could play a role in the complex chemistry of photo-

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