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

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

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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Received July 20, 1981

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]

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

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

$$O_2(^1\Sigma_g^+) + M \rightarrow O_2(^1\Delta_g) + M \qquad (3)$$

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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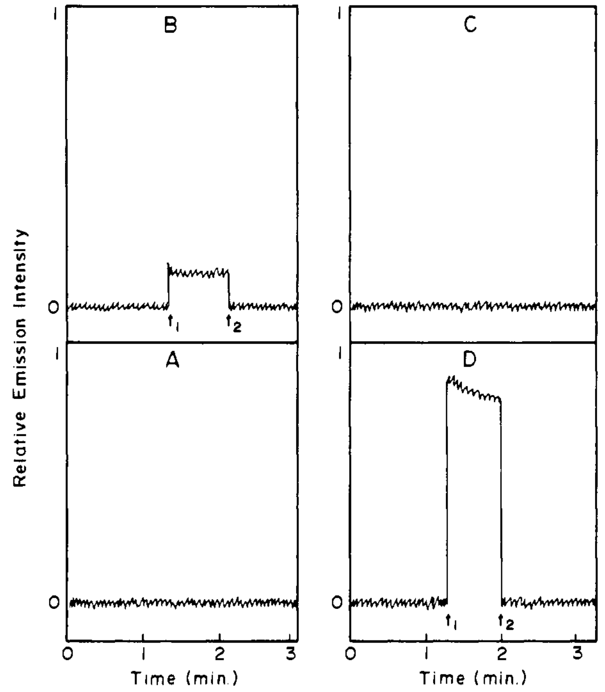

Figure 1. Emission of $O_2(^1\Delta_g \rightarrow {}^3\Sigma_g^-)$ at 1.27 μm produced by direct excitation in the gas phase at atmosphere pressure. (A) Blank, air flowing, and no illumination; (B) air flowing, time t_1, illumination, time t_2, no illumination; (C) nitrogen flowing and illumination; (D) Rose Bengal sensitized emission, air flowing, time t_1, illumination, time t_2, no illumination.

chemical smog has been considered by several groups.[5-11]

Leighton[5] had earlier considered the possibility that singlet oxygen might be produced in polluted atmospheres by direct absorption of solar radiation but concluded that no significant concentrations of $O_2(^1\Sigma_g^+)$ would be produced in this manner. By taking account of the increased probability of reactions 1 and 2 when the forbiddeness is relaxed via collisions, Bayes[6,7] concluded that the rate of absorption of solar radiation would become significant enough to contribute to the chemistry of photochemical smog. On the other hand, Kummler and Bortner[8] have calculated the direct absorption rate, including the collisionally assisted contribution, but conclude that self-absorption by atmospheric oxygen will reduce the transmission and give a negligible absorption rate.

Some time ago, Khan, Pitts, and Smith[9] again raised the possibility that singlet oxygen might play a role in atmospheric photochemistry, and subsequently Pitts et al.[10] suggested direct absorption of sunlight by molecular oxygen as one possible generation mode. Coomber and Pitts[11] later observed the formation of the singlet oxygen product, 2,3-dimethyl-3-hydroperoxy-1-butene, when tetramethylethylene and oxygen were irradiated in the absence of a sensitizer. Several mechanisms were considered to explain this result, including the possibility that $O_2(^1\Delta_g)$ was formed from $O_2(^1\Sigma_g^+)$, which in turn was produced by direct absorption of radiation by ground-state oxygen.

The gas phase formation of singlet Δ oxygen by direct absorption of radiation at atmospheric pressure has been observed in our laboratories by using an apparatus in which intense illumination and high gas flow rates appear to be the critical parameters. The generation system consists of a Pyrex tube cooled with a water jacket and irradiated with four 1000-W General Electric Model DPT projection lamps. The entire assembly is enclosed in a metal light shield and cooled with a cage blower. The exit of the generation zone is equipped with an inlet for the introduction of acceptors and quenchers followed by a light baffle, a reaction zone, and product traps. When the optical detector is in place, the gas exiting from the light baffle passes into the detector sample tube. The detection system consists of a light chopper, interference filter, and a liquid nitrogen-cooled germanium photodiode.[12a] The signal is led through a lock-in amplifier and then to a strip chart recorder.

Evidence for the formation of $O_2(^1\Delta_g)$ by the direct absorption of radiation by ground-state oxygen was obtained through the spectroscopic observation of the 1.27 μm emission of the excited state (Figure 1).[12a-c,13] This characteristic emission was detected in all experiments in which air or a nitrogen/oxygen mixture (95/5, v/v) was irradiated as it passed through the generation tube. No 1.27 μm emission was detected, however, when irradiation was used, and nitrogen instead of air was passed through the generation tube. When the generation tube was coated with Rose Bengal and air or N_2/O_2 (95/5, v/v) was passed through the generation tube with irradiation, the 1.27 μm emission was approximately 6–8 times larger than in experiments without sensitizer[14] (Figure 1). While additional work on reaction parameters is required before optimal conditions are established, the conditions used in these experiments appear to be near optimal.

There are two possible mechanisms for the formation of $O_2(^1\Delta_g)$ under these conditions. One is that shown in reaction 2. The other is the indirect route involving reactions 1 and 3. The latter is the path considered earlier by Coomber and Pitts.[11] Our experiments do not permit us to distinguish between these two routes, but the route via $O_2(^1\Sigma_g^+)$ (Reactions 1 and 3) would seem to be more probable.

The experiments described here as well as in our previous work involving heterogeneous photosensitization[1,2] demonstrate that singlet Δ oxygen can be formed in the gas phase at atmospheric pressure. It has previously been shown that singlet oxygen can be produced at near atmospheric pressure by using homogeneous photosensitization.[8,15a-d] In preliminary experiments we have also recently shown that the formation of singlet Δ oxygen may be accomplished at atmospheric pressure by using atmospheric pollutants such as polycyclic aromatic hydrocarbons as sensitizers. These results add support to the suggestion made by Pitts and co-workers[9,10] and others[6,7,16] that singlet oxygen may play a significant role in the chemistry of air pollution.

Acknowledgment. We would like to thank the National Institutes of Environmental Health Sciences for providing support for this work through Public Health Grant 1-R01-ES01 524-01A1-PHTB.

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