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ATMOSPHERIC GAS PHASE GENERATION OF SINGLET OXYGEN BY HOMOGENEOUS PHOTOSENSITIZATION

Walter C. Eisenberg * and Mutha DeSilva

Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois 60616

Summary. Singlet oxygen was generated in the gas phase at atmospheric pressure using homogeneous photosensitization and organic substances. The emission of O_2 $(^1\Delta_g)$ at 1.27 μm was observed.

The generation of singlet oxygen in the gas phase at atmospheric pressure has been actively studied over the past decade.[1a-e] Generation methods have been reported that utilize heterogeneous photosensitization,[1a,b] the direct absorption of radiation by ground-state molecular oxygen,[1c] direct laser excitation,[1d] and the reaction of ozone with organic substances.[1e]

The formation of singlet oxygen in the gas phase by homogeneous photosensitization has been reported.[2a-k] Snelling[2a] detected the 1.27 μm emission of $O_2(^1\Delta_g)$ after irradiating benzene oxygen mixtures at near-atmospheric pressures. Kummler and Bortner[2b] made a similar observation in irradiated benzaldehyde oxygen mixtures. Kearns et al.[2c] and Wasserman et al.[2d] identified singlet oxygen in irradiated oxygen sensitizer mixtures at reduced pressures by its characteristic epr spectrum. The emission at 1.27 μm was also used by Pitts et al.[2e] for evidence of the near-atmospheric production of $O_2(^1\Delta_g)$ by energy transfer using benzene and naphthalene as sensitizers. In experiments with benzaldehyde, singlet oxygen was detected by monitoring the hydroperoxide product of tetramethylethylene by long path IR spectroscopy.[2f] Davidson and Abrahamson [2g,h] demonstrated the photosensitized generation of $O_2(^1\Sigma_g{}^+)$ by monitoring the emission at 762 nm in experiments with the sensitizers: SO_2, benzene, naphthalene, fluoronaphthalene, phenanthrene, and benzaldehyde. Frankiewicz and Berry,[2i] and Bayes and Jones[2j] reported the production of singlet oxygen by energy transfer from electronically excited NO_2 in emission and photoionization studies, respectively. With one exception, all of these studies were conducted at reduced pressure. Estes and Rawls[2k] presented some incomplete evidence that singlet oxygen was produced when air containing NO_2 was irradiated.

We now report the gas-phase observation of the 1.27 μm emission of singlet delta oxygen that was formed using homogeneous photosensitization and organic substances at atmospheric pressure. The flow generator consisted of a Rayonet™ apparatus modified to internally support a 1.0 cm inverted quartz U-shaped tube, 75 cm x 32 cm. A series of flow controllers and valves connected by 1/4 in.

Teflon^{TM}tubing was used to produce a flowing gas stream composed of 98% nitrogen and 2% oxygen by volume and containing the sensitizer. Volatile sensitizer was added to the gas phase by passing nitrogen through a glass bubbler containing the sensitizer. The sensitizer concentration was controlled by dilution with nitrogen.[3] A liquid nitrogen cooled germanium photodiode detector was used to detect $O_2(^1\Delta_g)$ in the gas phase at the end of the quartz tube.

When a gas mixture composed of 98% nitrogen and 2% oxygen and containing benzene was irradiated at 254 nm, $O_2(^1\Delta_g)$ was formed as evidenced by the observation of the 1.27 μm emission[4,5](Table 1). Control experiments performed in nitrogen or in the absence of light gave signals near background levels. The 1.27 μm emission also decreased to near background levels when the singlet oxygen quencher, triethylamine,[6] or the chemical trapping agent, tetramethylethylene,[7] were added prior to the optical detector at gas-phase concentrations greater than 100 ppm. Trace quantities of $O_2(^1\Delta_g)$ were observed in the absence of benzene. In this experiment singlet oxygen was formed by the direct absorption of radiation by ground-state molecular oxygen.[1c] However, the quantity of singlet oxygen generated in the presence of sensitizer was always greater than the quantity formed without sensitizer.

High gas flow rates, light intensity, carrier gas composition, and sensitizer concentration were found to be critical parameters in the generation of singlet oxygen by homogeneous photosensitization. The gas-phase $O_2(^1\Delta_g)$ concentration increased significantly with increasing light intensity, sensitizer concentration, and nitrogen composition of the carrier gas. Increasing the gas flow rate produced only a minimal effect. A maximum 1.27 μm emission of 62.5 mv was observed with the following conditions: maximum light intensity; fourteen 254 nm lamps; 27,900 ppm benzene; gas composition, 98% N_2 and 2% O_2; and gas flow rate, 16 L/min. This signal corresponds to a gas-phase $O_2(^1\Delta_g)$ concentration of 2.00 ppm. In air the $O_2(^1\Delta_g)$ concentration was 0.650 ppm under similar conditions.

These results are consistent with a mechanism in which singlet oxygen is formed by energy transfer from excited sensitizer molecules. This process is summarized below and initially involves excitation of the ground state of an organic sensitizer ($^1S_0$) to its first excited singlet state($^1S_1$). Intersystem crossing results in the formation of excited triplet sensitizer($^3S_1$). Energy transfer from excited sensitizer results in the formation of $O_2(^1\Delta_g)$. Singlet oxygen is most likely formed by energy transfer from the excited triplet state of benzene, although energy transfer from the excited singlet state has not been ruled out. When observing the 1.27 μm emission, Kearns et al. showed that sensitization proceeded via energy transfer from the excited triplet state of benzene.[2c] Our experiments also do not permit distinguishing whether the $^1\Delta_g$ state of singlet oxygen is formed directly or via the $^1\Sigma_g^+$ state. Work is in progress to clarify these points.

Table 1 also lists some other organic compounds that sensitized the formation of singlet oxygen at 254 nm. The 1.27 μm emission of $O_2(^1\Delta_g)$ was observed at lower intensities when the experiments were repeated using a 350 nm. light source. The observation that singlet oxygen is formed by organic

$$^1S_0 + h\nu \longrightarrow {}^1S_1$$

$$^1S_1 \longrightarrow {}^3S_1 \quad \text{(intersystem crossing)}$$

$$^3S_1 + O_2({}^3\Sigma_g^-) \longrightarrow {}^1S_0 + O_2({}^1\Delta_g \text{ or } {}^1\Sigma_g^+)$$

TABLE 1. ATMOSPHERIC GAS PHASE GENERATION OF SINGLET OXYGEN BY HOMOGENEOUS PHOTOSENSITIZATION[a]

Sensitizer	Sensitizer Concentration (ppm)	$O_2({}^1\Delta_g)$ 1.27 μm Emission (mv)	$O_2({}^1\Delta_g)$ Gas Phase Concentration[b] (ppm)
no(background)	--	0.5 (0.25)	0.016 (0.012)
benzene	3312	13.5 (1.70)	0.418 (0.054)
naphthalene	24	12.0 (1.22)	0.381 (0.040)
anthracene	14	12.9 (2.80)	0.409 (0.079)
toluene	3458	5.0 (2.00)	0.159 (0.063)
xylene	950	2.5 (1.30)	0.079 (0.041)
cumene	963	2.0 (0.71)	0.064 (0.022)
fluorobenzene	3200	81.5 (16.3)	2.58 (0.517)
benzaldehyde	3000	1.0 (0.54)	0.032 (0.017)

a. gas flow rate, 16 L/min, carrier gas composition, 98% $N_2/2\%O_2$.

b. The values were obtained using light of the wavelength 254 nm. and (for values in parentheses) 350 nm.

compounds absorbing at wavelengths greater than 290 nm. adds support to the suggestion by Pitts and co-workers,[8] our laboratory,[1a,1c-e] and others[9] that a variety of singlet oxygen generation processes operate in polluted atmospheres and may produce a significant concentration of this oxidant. We plan to extend these studies to other compounds having large extinction coefficients in the near ultraviolet such as aromatics, aldehydes, and ketones. These experiments have demonstrated that observation of the 1.27 μm emission of singlet oxygen is a rapid and accurate method for evaluating sensitizers.

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5. The 1.27 μm emission of singlet delta oxygen was monitored using a liquid nitrogen cooled germanium photodiode equipped with a 1.27 ± 0.02 μm band-pass filter. The IR region from 0.70 to 1.70 μm was scanned by replacing the band-pass filter with a Bausch and Lomb Model 3 IR monochrometer. A narrow band was observed at 1.27 μm corresponding to the $^1\Delta_g (v = 0) \dashrightarrow {}^3\Sigma_g^- (v = 0)$ transition of $^1O_2$, and a less intense band was observed at 1.58 μm corresponding to the $^1\Delta_g (v = 0) \dashrightarrow {}^3\Sigma_g^- (v = 1)$ transition.

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