Detection of the Naphthalene-Photosensitized Generation of Singlet (${}^1\Delta_g$) Oxygen by Paramagnetic Resonance Spectroscopy[1]

Sir:

Much of the renewed interest in sensitized photooxygenation reactions was prompted by recent experimental observations which indicate that electronically excited singlet oxygen molecules (${}^1\Sigma$ or ${}^1\Delta$) are involved as reaction intermediates.[2] A crucial assumption in the "singlet oxygen theory" of sensitized photooxygenations is that singlet oxygen molecules are efficiently generated in these reactions by transfer of electronic energy from excited sensitizer to ground triplet-state oxygen molecules.[3] Although the data supporting the involvement of singlet oxygen in sensitizer photooxygenation reactions are quite compelling, evidence for the key energy transfer step is nonetheless circumstantial. Most arguments are based upon comparison of oxygenation products or product distributions obtained in sensitized photooxygenation with those obtained using oxygen which has been excited in a microwave discharge or generated by decomposition of hydrogen peroxide, or they are based upon kinetic studies.[2-4] In this communication we present evidence based on paramagnetic resonance spectroscopy (epr) which conclusively proves that singlet oxygen molecules are generated in a photosensitized process involving an aromatic hydrocarbon sensitizer.

The system which we studied consisted of a cylindrical quartz cell (23-mm i.d.) containing oxygen at pressures ranging from ~0.1 to 0.3 mm and saturated with naphthalene as the sensitizer (vapor pressure ~0.5 mm at room temperature). This cell was placed in a large stack cylindrical cavity of a Varian V-4500 X-band epr spectrometer equipped with a Mark II Fieldial, and illuminated by focusing the output of a 1000-W AH-6 mercury lamp on one end of the cell which extended slightly outside of the cavity.

Naphthalene was specifically chosen as the sensitizer in these experiments because it is relatively stable toward photooxidation. Benzene might have been used except that it is known to undergo a photochemical reaction with oxygen to produce long-chain aldehydes.[5] The filtering system (5 cm of water, ~2 cm of quartz) and the spectral distribution from the lamp ensured that no light of wavelength shorter than about 2200 Å was admitted into the cell.

The epr spectrum of ${}^1\Delta$ oxygen in the $J = \Lambda = 2$ state is characterized by a nearly symmetrical quartet of lines centered at $|g_J| \sim {}^2/_3$. The spectrum was first observed in the products of a microwave discharge of O_2 by Falick, Mahan, and Myers, who assigned the individual lines to the appropriate $|\Delta M_J| = 1$ transitions.[6] When we irradiated our cell in the epr spectrometer with light under the conditions described above, resonances were observed at exactly the positions expected for ${}^1\Delta$ oxygen molecules. These results are shown in Figure 1b. For comparison, the ${}^1\Delta$ oxygen spectrum obtained using a microwave discharge unit to generate ${}^1\Delta$ oxygen is shown in Figure 1a. The coincidence (within 0.05% of predicted position) of the four lines observed during irradiation with those observed in the microwave discharge and comparison of their relative intensities establishes beyond doubt that the photogenerated resonances reported here are due to ${}^1\Delta$ oxygen. We further established that, under identical experimental conditions, it was impossible to observe the signals from ${}^1\Delta$ in the absence of light (Figure 1c), and that no ${}^1\Delta$ signals were observed when we irradiated O_2 in the absence of naphthalene. This set of observations unequivocally establishes that ${}^1\Delta$ molecules are generated in a photosensitized process which depends upon excitation of the naphthalene molecules and thus provides a firm foundation for a crucial element of the "singlet oxygen theory" of sensitized photooxygenation reactions. Our results confirm the recent work of Snelling[7] who observed photoinduced luminescence at 12,700 Å from irradiated benzene–oxygen mixtures which he assigned as emission from ${}^1\Delta$ oxygen.

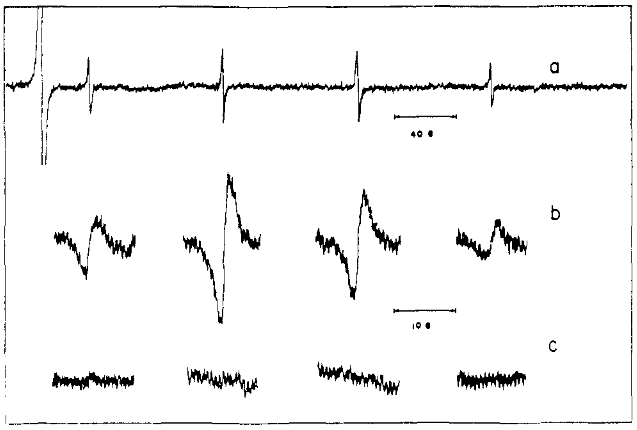

Figure 1. Paramagnetic resonance spectra of ${}^1\Delta$ oxygen. Magnetic field increases from left to right. (a) ${}^1\Delta$ oxygen generated by a microwave discharge unit ($P_{O_2} = 0.2$ mm). The quartet due to ${}^1\Delta$ is centered at $|g| \sim {}^2/_3$. The intense line to the left is due to ${}^3\Sigma$ oxygen. (b) ${}^1\Delta$ oxygen generated by energy transfer from photoexcited naphthalene vapor. Each resonance is the result of 144 passes with a CAT through a 25-G region of field predicted to contain a ${}^1\Delta$ signal. Note that the photogenerated signals are presented on an expanded gauss scale in comparison with the spectrum above and that the phase of the signal is inverted by the CAT. Some broadening of each line is the result of drift in the microwave cavity frequency during the 1.5-hr run. (c) Paramagnetic resonance signals observed under same conditions as 1b, except without irradiation of the cell.

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From an estimate of the steady-state concentration of $^1\Delta$ oxygen generated during the irradiation and a measurement of the effective lamp output we find that the quantum yield for the formation of $^1\Delta$ is of the order 0.5 ± 0.3, assuming a $^1\Delta$ lifetime of $\sim$1 sec in the cell.[6] While we consider this number uncertain, it indicates that a significant fraction of the excitation energy is utilized to generate $^1\Delta$. Furthermore, if the value of $\sim$0.5 could be established, sensitization by the naphthalene triplet would be indicated. This result tends, therefore, to support the theoretical work of Kawaoka, Khan, and Kearns,[8] who predicted that the oxygen quenching of triplet-state molecules proceeds primarily by energy transfer to oxygen. To verify this point, however, a careful study of the pressure dependence of the $^1\Delta$ resonance intensity will be required. Preliminary measurements indicate that over a range of oxygen pressures from 0.1 to 0.3 mm the steady-state concentration of $^1\Delta$ is still increasing with increasing O_2 pressure. A detailed study of this point is in progress and will be presented elsewhere.

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Electron Paramagnetic Resonance of $^1\Delta$ Oxygen Produced by Gas-Phase Photosensitization with Naphthalene Derivatives

Sir:

We have observed the formation of $^1\Delta$-O_2 on uv irradiation of vapor-phase mixtures of oxygen with naphthalene and some of its derivatives. Under steady-state conditions as much as 70% of the total oxygen can be converted to the excited form so that the systems could serve as convenient sources of $^1\Delta$ for gas-phase reactions. The excited oxygen was detected by its characteristic epr spectrum, a procedure which had been previously used in demonstrating its formation on decomposition of a triphenyl phosphite–ozone complex.[1] These photosensitization experiments may be regarded as giving strong support to Foote's hypothesis that many photooxidations involve excited oxygen as the reactive intermediate, this upper state being produced from ground-state oxygen by energy transfer from the photosensitizer.[2] To our knowledge, the first direct physical evidence for this transfer has been the very recent report of Snelling who observed the near-infrared emission of $^1\Delta$ oxygen produced by benzene photosensitization.[3] Our experiments, and the similar ones by Kearns, *et al.*, described in the accompanying communication,[4] give additional evidence using other sensitizers and another method of detection which allows direct measurements of concentrations. Also, our results lead to quite high $^1\Delta$ concentrations, some two orders of magnitude larger than the benzene system.[3]

The experiments were performed by including a few crystals or drops of the naphthalene derivative in a quartz tube of $\sim$24 mm o.d. containing from 0.1 to 1.0 mm of oxygen. Irradiation was accomplished with unfiltered medium or high-pressure mercury or xenon lamps of 150–500 W through a Supersil window. The characteristic four-line epr spectrum of $^1\Delta$-O_2, due to the orbital magnetic moment of the π^* electrons, was readily observed during irradiation between 9–10 kG at X-band. The origin of the spectrum was established by comparison with that observed with a microwave discharge in O_2 as first reported by Falick, *et al.*,[5] and with that observed in the phosphite–ozone decomposition.[1] The concentrations of the $^1\Delta$ and $^3\Sigma$ were established by comparing the intensities of the epr absorptions with those of discharged oxygen where the $^1\Delta$ concentration is 7–10%.[1,5]

Naphthalene (I), 1- (II) and 2-fluoronaphthalene (III), and octafluoronaphthalene (IV) were used as sensitizers. With I–III, steady-state $^1\Delta$ concentrations of 3–6% were readily obtained. Sensitizer, O_2, and light must all be present if $^1\Delta$ is to be observed. With I, and somewhat less readily with II and III, irradiation was also associated with the largely irreversible disappearance of the $^3\Sigma$ oxygen within a period of tens of minutes. While ground state I is supposedly inert to reaction with $^1\Delta$-O_2, the conditions of our experiment are such that collisions are likely between excited I and excited oxygen, so that reaction may well occur. With IV the irreversible removal of O_2 was slower, and we have concentrated on IV–O_2 mixtures for a more detailed study.

The absolute concentration $^1\Delta$-O_2 was independent of the original O_2 pressure in the range of 0.2–1.0 mm for a given set of irradiation conditions. The independence implies that effectively all excited IV transferred energy to O_2 before deactivation. Consistent with this conclusion is the observation that even with the more powerful lamps the concentration of the $^1\Delta$ was linearly proportional to the intensity of light irradiating the sample. At the lower O_2 pressures, with the higher proportions of $^1\Delta$, we could easily see the immediate decrease in $^3\Sigma$ associated with rise of $^1\Delta$ on initial illumination. Blocking the light produced a corresponding rise in $^3\Sigma$ and disappearance of $^1\Delta$. In most experiments, the $^3\Sigma$ and $^1\Delta$ changes balanced one another, although in some the loss of $^3\Sigma$ on illumination was greater than the amount of $^1\Delta$ produced. The oxygen balance in the majority of experiments indicates that a substantial amount of O_2 is not present in some metastable form other than $^1\Delta$. These results do not imply that the $^1\Delta$ must be formed immediately on sensitization. The $^1\Sigma$ might be formed first but would

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