Measurement of Concentration of Singlet Molecular Oxygen in the Gas Phase by Electron Paramagnetic Resonance

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The concentration of the lowest excited state of molecular oxygen, $O_2(^1\Delta_g)$, generated by gas-phase photosensitization with octafluoronaphthalene has been determined by electron paramagnetic resonance spectroscopy. The ground-state oxygen molecule, $O_2(^3\Sigma_g{}^-)$, was used as a quantitative standard. At low pressures, $\approx$0.12 Torr, about 30% of $O_2(^3\Sigma_g{}^-)$ was converted to $O_2(^1\Delta_g)$ under steady-state conditions.

The lowest electronically excited singlet state of oxygen molecule, $O_2(^1\Delta_g)$, has been a subject of study for many years, with particular interest being taken in many photochemical and biological problems.[1–5] $O_2(^1\Delta_g)$ is an active intermediate in the photooxygenation reactions. It is important to measure the concentration of $O_2(^1\Delta_g)$ for most applications requiring $O_2(^1\Delta_g)$ as a reactive intermediate.[6] There are several methods for detecting $O_2(^1\Delta_g)$ in the gas phase and in condensed phases. The IR emission ($a^1\Delta_g \rightarrow X^3\Sigma_g{}^-$ transition) spectroscopy is the most widely used technique to detect $O_2(^1\Delta_g)$.[7] However, since the ground-state oxygen molecule, $O_2(^3\Sigma_g{}^-)$, is recommended as a quantitative standard, the most reliable technique for determining $O_2(^1\Delta_g)$ concentration has been electron paramagnetic resonance (EPR) spectroscopy.[8–11]

In the present study, we have observed the EPR spectra of $O_2(^1\Delta_g)$ in the gas phase. Oxygen in the $^1\Delta_g$ state can be detected using the EPR technique, because $O_2(^1\Delta_g)$ is paramagnetic owing to its orbital angular momentum. The first-order energy for the interaction of the magnetic moment associated with the total angular momentum J and an external magnetic field $\boldsymbol{B}$ can be described by the following equation:[8,12,13]

$$E = \frac{(\Lambda + 2\Sigma)(\Lambda + \Sigma)}{J(J+1)}\mu_B B M_J = g_J \mu_B B M_J \qquad (1)$$

Here, Λ and Σ are the orbital and spin angular momentum along the molecular axis (Hund's case a), respectively.

In the present study, we have observed the $\Delta M_J = \pm 1$ transitions for the lowest rotational state of $O_2(^1\Delta_g)$, $J = 2$. For this state, $J = \Lambda = 2$ and $g_J = 2/3$. The EPR absorption is expected at $\approx$0.95 T with a microwave frequency of $\approx$9 GHz. These $\Delta M_J = \pm 1$ transitions are expected to split into a quartet of lines by the off-diagonal Zeeman interaction with the higher rotational state.[8]

Octafluoronaphthalene obtained from Aldrich was used without further purification. The EPR spectra were measured at room temperature by a JEOL JES-ME3XG X-band spectrometer equipped with a homemade 100 kHz power amplifier and a Varian V-4535 large sample access cylindrical cavity. For the EPR measurements, conventional 100 kHz magnetic field modulation was used. The static magnetic filed was calibrated with an Echo Electronics EFM-2000 proton NMR gauss meter. O_2–octafluoronaphthalene mixtures were passed through a 23-mm-i.d. quartz tube located in the cavity. The excitations were carried out using a Canrad–Hanovia 1 kW Xe–Hg arc lamp through 5 cm of distilled water and a Toshiba UV-D33S glass filter. The gas pressure was monitored by an MKS Baratron capacitance manometer.

$O_2(^1\Delta_g)$ molecules were generated from $O_2(^3\Sigma_g{}^-)$ by energy transfer from the excited triplet states of the sensitizer molecules. Octafluoronaphthalene was chosen as the sensitizer because it is relatively stable toward photooxidation. The observed EPR spectra are shown in Figure 1.

As is clearly seen in Figure 1b, the characteristic nearly symmetrical four-line EPR spectrum was observed during excitation. The EPR signals of $O_2(^3\Sigma_g{}^-)$ decreased immediately with rise of $O_2(^1\Delta_g)$ signals on excitation. After shutting off the exciting light, the $O_2(^3\Sigma_g{}^-)$ signals rose and the $O_2(^1\Delta_g)$ signals disappeared. The EPR spectrum of $O_2(^1\Delta_g)$ was observed for the first time with a microwave discharge in O_2 by Falick et al.[8] They estimated that under their conditions the size of the $O_2(^1\Delta_g)$ signal indicated a concentration of 10% of the

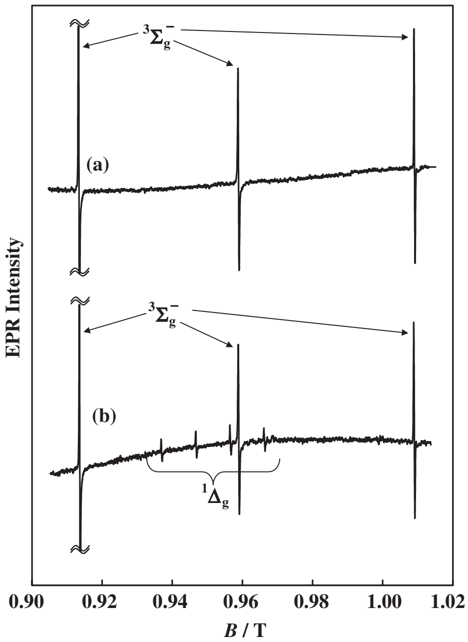

Figure 1. EPR spectra of $O_2(^1\Delta_g)$ and $O_2(^3\Sigma_g{}^-)$ observed at 0.20 Torr with the microwave frequency of 8.873 GHz. (a) EPR spectrum of $O_2(^3\Sigma_g{}^-)$ before excitation. (b) EPR spectrum of $O_2(^1\Delta_g)$ and $O_2(^3\Sigma_g{}^-)$ under excitation. Each spectrum is the result of a single scan.

ground state $O_2(^3\Sigma_g^-)$. However, no spectra were shown in their article.

In the late 1960s and early 1970s, EPR studies of $O_2(^1\Delta_g)$ generated by photosensitization were performed.[9–12,14] However, to our knowledge, EPR studies have not been performed for more than 30 years, Wasserman et al. observed the EPR spectra of $O_2(^1\Delta_g)$ produced by photosensitization with naphthalene derivatives in the gas phase.[10] They estimated percentages of $O_2(^3\Sigma_g^-)$ converted to $O_2(^1\Delta_g)$ for many sensitizers. However, they did not show any spectra in their article. To our knowledge, the work by Kearns and his co-workers is the only literature to show the EPR spectra of $O_2(^1\Delta_g)$ generated by photosensitization.[9] In their work, however, the observed EPR signal of $O_2(^3\Sigma_g^-)$ is much stronger than those of $O_2(^1\Delta_g)$ and it is difficult to estimate the $O_2(^1\Delta_g)$ concentration.

In the present work, we have estimated the concentration of $O_2(^1\Delta_g)$ by using $O_2(^3\Sigma_g^-)$ as a quantitative standard. The EPR spectra were observed at 0.12 Torr, as shown in Figure 2. To measure the $O_2(^1\Delta_g)$ concentration, the $J = 2$, $M_J = 0 \leftarrow -1$ transition was used. The concentration ratio of $O_2(^1\Delta_g)$ to $O_2(^3\Sigma_g^-)$ was determined from the double integrals of the first-derivative EPR signals for the $O_2(^1\Delta_g)$ and $O_2(^3\Sigma_g^-)$ lines at 956.6 and 958.8 mT, respectively, as follows.

$$\frac{[O_2(^1\Delta_g)]}{[O_2(^3\Sigma_g)]} = \frac{k(^1\Delta_g)\iint S(^1\Delta_g)dBdB}{k(^3\Sigma_g^-)\iint S(^3\Sigma_g^-)dBdB} \qquad (2)$$

Here, S is the EPR signal and the factor $k(^1\Delta_g)/k(^3\Sigma_g^-)$ represents the ratio of $O_2(^3\Sigma_g^-)$ and $O_2(^1\Delta_g)$ line strength. The constant $k(^3\Sigma_g^-)$ is easily obtained while $k(^1\Delta_g)$ is difficult to be obtained.

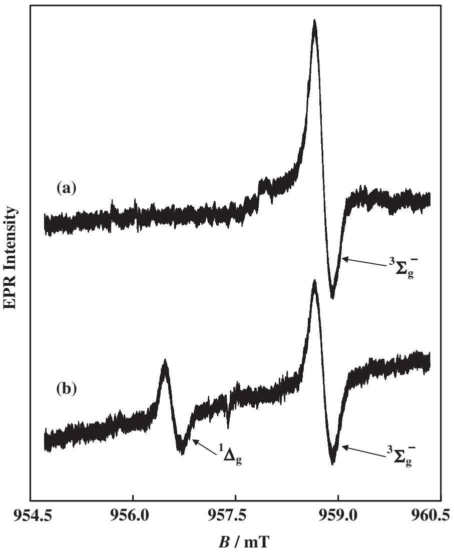

Figure 2. EPR spectra of $O_2(^1\Delta_g)$ and $O_2(^3\Sigma_g^-)$ observed at 0.12 Torr with the microwave frequency of 8.873 GHz. (a) EPR spectrum of $O_2(^3\Sigma_g^-)$ before excitation. (b) EPR spectrum of $O_2(^1\Delta_g)$ and $O_2(^3\Sigma_g^-)$ under excitation. Each spectrum is the result of a single scan.

At the lower O_2 pressures, the excitation decreases the $O_2(^3\Sigma_g^-)$ intensity and shutting off the exciting light produces the initial $O_2(^3\Sigma_g^-)$ intensity. These results show that the loss of $O_2(^3\Sigma_g^-)$ on excitation is negligible compared to the amount of produced $O_2(^1\Delta_g)$. We can safely assume that the amount of O_2 in some metastable state other than $^1\Delta_g$ is negligible. The second lowest excited state $O_2(^1\Sigma_g^+)$ might be produced but it deactivates rapidly to $O_2(^1\Delta_g)$. Therefore, we estimated the concentration ratio directly without using the line strength factor. We can see from Figure 2 that 30% of the $O_2(^3\Sigma_g^-)$was converted to $O_2(^1\Delta_g)$ under our conditions. The line strength factor $k(^1\Delta_g)/k(^3\Sigma_g^-)$ can be estimated to be about 1.0 from Figure 2.

In conclusion, we have demonstrated that the EPR spectroscopy is a reliable technique for determining the $O_2(^1\Delta_g)$ concentration in the gas phase. Under our experimental conditions, the steady-state $O_2(^1\Delta_g)$ concentration of 30% was obtained by the photosensitization with octafluoronaphthalene. Further detailed investigations including $O_2(^1\Delta_g)$ lifetime measurements are currently in progress.

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