Singlet Delta Oxygen Production from a Gas–Solid Reaction**

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Dedicated to Dr. Robert Corley

The long and interesting history of singlet delta ($^1\Delta_g$) oxygen, including its discovery, study, understanding, and applications, has been described in several publications.[1–4] The singlet delta state is the lowest lying excited electronic state of oxygen and it differs from the triplet ground state, $^3\Sigma_g^-$, in spin multiplicity. The generation of $^1\Delta_g$ O_2 from ground state $^3\Sigma_g^-$ O_2, using direct electronic excitation, is spin forbidden and inherently inefficient.[5] Therefore, either complex chemical reactions that produce intermediates capable of spontaneously eliminating electronically excited O_2, or compounds that can decompose directly to produce excited state oxygen have been studied for $^1\Delta_g$ O_2 production. Typical examples include: hydrogen peroxide with aqueous hypochlorite,[6] basic hydrogen peroxide (BHP) with molecular halogens or phenols,[7] the superoxide anion with water,[4,8] ozone with organic substrates such as triaryl phosphates,[9] alkaline peroxo acids,[7,10] organic peroxides,[11] and transition-metal–oxygen complexes.[12] Although some of these reactions efficiently generate $^1\Delta_g$ O_2, they are all carried out in liquid-phase systems that cause quenching of the excited oxygen. The required rapid extraction of the gaseous singlet delta oxygen is very difficult. Furthermore, molecules capable of spontaneous elimination of electronically excited oxygen are thermodynamically unstable and, therefore, can present serious handling problems. Similar arguments may also apply to some of the precursors, such as the basic hydrogen peroxide in the BHP/Cl_2 system.[13] In view of the significance of an efficient and safe $^1\Delta_g$ O_2 generator for the chemical oxygen iodine laser (COIL)[14] and other chemical and biochemical applications,[1,4] the development of new methods that can overcome these problems is of great importance.

Herein, we describe chemical reactions that spontaneously and efficiently produce singlet delta oxygen from solid alkali metal or alkaline-earth metal peroxides and dry hydrogen(deuterium) halide gases at room temperature. The reactions do not require external energy sources, such as heat, light, or electricity (discharge), and they avoid liquid-phase quenching and dangerous reagents.

The apparatus for generating and monitoring O_2 $^1\Delta_g$ from solid peroxides and gaseous hydrogen(deuterium) halides is depicted in Figure 1. The reaction/observation cell consisted

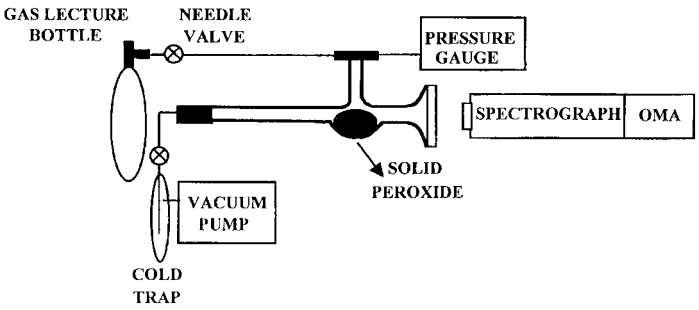

Figure 1. Apparatus for generating singlet delta oxygen and observing its emission.

of a 5 mm (i.d.) Pyrex glass tube that was attached to a 5 mm O-ring seal joint and a perpendicular sidearm. Opposite from the sidearm, the diameter of the tube was increased to provide a repository for the solid peroxide samples. A sodium chloride or an S-1 UV quartz window was clamped to the O-ring joint, and the whole assembly was placed 3 cm in front of an optical multichannel analyzer (OMA) spectrograph combination with the optical window facing the entrance slit. No collection optics were used.

In a typical experiment, 400 mg of a solid alkai metal or alkaline-earth metal peroxide was added to the cell within the dry nitrogen atmosphere of a glove box. The cell was installed into the test apparatus, evacuated, and dry hydrogen(deuterium) halide gas was added through the sidearm up to a maximum total pressure of 760 Torr. The OMA was kept at 160 K and an uninterrupted sequence of ten emission spectra (120 s collection time each) was recorded. Background subtraction was performed on all data. Several combinations of solid peroxide and gaseous hydrogen halide were tested: sodium peroxide/hydrogen(deuterium) chloride, sodium peroxide/hydrogen(deuterium) bromide, sodium peroxide/hydrogen iodide, barium peroxide/hydrogen chloride, barium peroxide/hydrogen bromide, and lithium peroxide/hydrogen chloride.

The O_2 $^1\Delta_g$ generation was monitored by the emission from its A→X ($^1\Delta_g \rightarrow {}^3\Sigma_g^-$) spin-forbidden transition at 1.27 microns using a 0.3 m Czerny–Turner spectrograph with a 600 groove per mm grating blazed at 1 micron and a near-IR sensitive OMA. The emission was identical in wavelength and contour to those produced by either a microwave discharge of an oxygen–helium mixture[15] or a BHP–chlorine sparger[16] (see Figure 2 a and b, respectively).

All the above listed combinations of peroxide and gaseous hydrogen halide produced readily observable O_2 $^1\Delta_g$ emissions, except when hydrogen iodide was used. Figure 2 c shows the results obtained from sodium peroxide and 580 Torr of hydrogen chloride. The data represent an OMA exposure time of 120 s. Singlet delta oxygen emission from the Na_2O_2/HCl reaction was recorded for ten consecutive 120 s exposures

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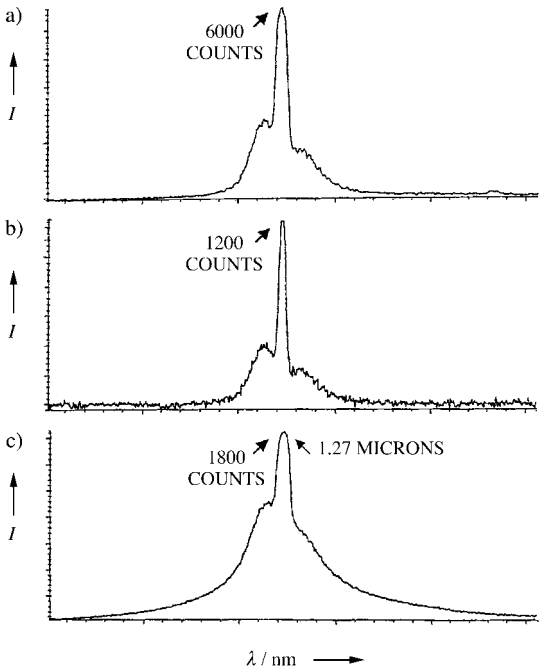

Figure 2. Emission spectra of singlet delta oxygen from a helium–oxygen microwave discharge (a; exposure time 1 s), a basic hydrogen peroxide/chlorine sparger (b; exposure time 1 s), and the Na_2O_2/HCl reaction system (c; exposure time 120 s).

under three different reaction pressure conditions. The pressure of the reaction cell was either maintained constant by repeated addition of HCl, allowed to fall as HCl was consumed, or increased by continuous addition of HCl. In the latter case, the emission increased logarithmically with pressure. Constant or decreasing cell pressures resulted in exponentially decreasing emission signals over a 20-minute period. At a constant cell pressure of 450 Torr, the observed decay of the excited state emission over a 20-minute observation period was four orders of magnitude slower than that predicted from the known quenching rates of HCl and water vapor.[18,19] These results demonstrate that the loss of emission due to quenching is largely offset by the continuous production of $O_2\ ^1\Delta_g$.

The stoichiometry of the sodium peroxide/HCl reaction was experimentally established by quantitatively analyzing the material balance on a vacuum line. The results are in excellent agreement with Equation (1).

$$Na_2O_2 + 2\,HCl \rightarrow H_2O + 2\,NaCl + 1/2\,O_2\ (^1\Delta_g) \quad (1)$$

Equation (1) is also consistent with the condensation of some water vapor on the cell walls, the conversion of the yellow peroxide starting material to a white solid (NaCl), and a decrease in pressure as the emission data were recorded.

In Figure 2, the $O_2\ ^1\Delta_g$ emission signals from the microwave discharge, the BHP sparger, and the Na_2O_2/HCl system are compared. The discharge was operated with a flow rate of 1×10^{-5} mol of O_2 per second plus helium, and the sparger could produce a maximum of 1.2×10^{-4} mol of O_2 per second, assuming 100% chlorine utilization. A single sample of 5×10^{-3} mol of sodium peroxide was recharged ten times with 500 to 700 Torr of HCl and produced $O_2\ ^1\Delta_g$ emission for a total of 200 minutes. Although a quantitative comparison of these three $O_2\ ^1\Delta_g$ production methods is difficult due to the differences in exposure times, observation geometries, and signal durations, the gas–solid reaction must be considered a highly efficient source of excited oxygen based upon the duration and strength of the emission signal in nearly one atmosphere of a quenching gas.

An additional experiment was conducted with the sodium peroxide/hydrogen chloride pair to check for potential emission at 634 nm from the energy-pooling reaction [Eq. (2)].At sufficiently high $O_2\ ^1\Delta_g$ concentrations, this

$$2\,O_2\ (^1\Delta_g) \rightarrow 2\,O_2\ (^3\textstyle\sum_g^-) + h\nu\ (634\,nm) \quad (2)$$

energy-pooling process is known to produce a visible red glow.[20] In our study, a separate OMA system sensitive in this region was used, but no evidence for this transition was found, possibly due to the dilution imparted by the high HCl pressure.

The other gas–solid reaction systems were tested in a larger cell that consisted of a 10 mm O-ring seal joint connected to a 7 inch length of 1/2 inch (o.d.) Pyrex tubing with 1/4 inch (o.d.) sidearms for gas inlet and evacuation. Larger amounts of sample were spread over a longer reaction zone, thus increasing the gas–solid contact time over that allowed by the cell of Figure 1. The listed reagent pairs were tested in a qualitative fashion. Typically, a one gram sample of solid peroxide was slowly pressurized with the hydrogen(deuterium) halide gas to 300 to 400 Torr. The gas was allowed to flow into the cell during the measurement so that the net pressure rose during the recording of the emission data. The emission from the sodium peroxide/hydrogen bromide system was especially strong and OMA saturation was experienced at exposure times of 120 s. The results from these tests are summarized in Table 1. The emission signal intensities varied somewhat from experiment to experiment. This was partially due to small changes in the positioning of the sample cell after cleaning and reloading with fresh solid peroxide. The reactions with the deuterated halides are of special interest since deuterated compounds are significantly weaker quenchers than their hydrogen-containing counterparts.[21] Other simple systems were also tested. For example, potassium superoxide, KO_2, was allowed to react with hydrogen chloride, and a weak emission signal due to $O_2\ ^1\Delta_g$ was observed.

Table 1. Solid peroxides and gaseous hydrogen halides yielding singlet delta oxygen.

Peroxide	Hydrogen halide	Qualitative emission strength
Na_2O_2	HCl	strong
Na_2O_2	DCl	strong
Na_2O_2	HBr	very strong
Na_2O_2	DBr	very strong
BaO_2	HCl	medium
BaO_2	HBr	medium
Li_2O_2	HCl	strong

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However, these systems are inferior to those involving the alkali metal and alkaline-earth metal peroxides.

In summary, the results of this study demonstrate the feasibility of efficiently generating singlet delta oxygen from gas–solid reactants without the problems associated with liquid-phase quenching. Furthermore, the required starting materials are commercially available, moderately priced, and safe to handle.

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[15] A 70 watt microwave discharge (2.45 GHz) of an oxygen–helium mixture at a total pressure of 5 Torr was used to record the O_2 $^1\Delta_g$ emission spectrum. At the typical flow conditions of the measurement 1×10^{-5} moles of oxygen were delivered per second. A glass wool plug was placed in the discharge tube to aid in the recombination of oxygen atoms. If the discharge, gas flow, and vacuum pumping were simultaneously stopped, the emission signal decayed within one second.
[16] The BHP–chlorine sparger contained 100 mL of an aqueous mixture that was 1.1 M in NaOH and 7.5 M in H_2O_2. It was prepared by slowly adding the NaOH to cold 85% H_2O_2 over a 30-minute period while keeping the temperature of the mixture below 273 K. The sparger was immersed into a 258-K recirculating bath, and chlorine gas was introduced at a flow rate of 160 sccm. The sparger was connected to the inlet of a gas cell that was located in front of the spectrograph. The outlet of the cell was connected to a cold trap (−77 K) and a vacuum pump that maintained the pressure in the cell at 4 Torr. The addition of 6 Torr of either helium or nitrogen to the sparger effluent at the gas cell entrance resulted in comparable quenching of the O_2 $^1\Delta_g$ signal. Since the known quenching coefficients for He and N_2 with O_2 $^1\Delta_g$ differ by two orders of magnitude,[17] the increased quenching had to be due to a longer residence time in the liquid resulting from the increased backpressure of the added gas.
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Controlled Release of a Dendritically Encapsulated Template Molecule**

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Over the past few years there has been intense interest in the unique properties exhibited by molecules with branched superstructures (namely, dendrimers).[1] In particular, there has been a focus on the effect of dendritic encapsulation on a variety of physical and chemical properties—for example, the optical, redox, and catalytic behavior of core units have all been modified by dendritic functionalization.[2]

Chemists have increasingly begun to focus on the assembly of dendritic structures in which the core unit is held in place by noncovalent interactions rather than by covalent bonds.[3] Zimmerman et al. published reports of dendritically functionalized rosettes, assembled through hydrogen-bond formation,[4] as well as other hydrogen-bonded assemblies.[5] Hydrogen bonds have also been used by other research groups for dendritic assembly.[6] Kenda and Diederich reported well-defined "dendrophane" assemblies based on hydrophobic interactions,[7] whilst Percec et al. have used similar forces to assemble distinctive architectures from dendritic building blocks.[8] A wide range of dendrimers assembled around metal ions have also been reported.[9] Gibson and co-workers have used interactions between secondary amines and dibenzo[24]crown-8 to assemble dendrimers with rotaxane-like mechanical branching.[10] Recently, we used COOH···NH_2 hydrogen bonds at the focal point of individual dendritic branches to assemble them around hydrophilic dyes, thus modulating the solubility profiles and optical properties.[11]

Herein we report a novel series of dendritic branches based on L-lysine, in which the focal point has been functionalized with benzo[18]crown-6. We have characterized the strength and stoichiometry of binding with potassium and benzylammonium cations, and report the effect of dendritic branching on the host–guest binding process. In addition, we have assembled dendritic branches around a bis-ammonium cation, thus encapsulating it within a supramolecular dendritic shell. We were able to achieve controlled release of the encapsulated template molecule by the addition of potassium ions. In this way, we have achieved the controlled assembly and disassembly of a supramolecular dendrimer in solution for the first time.

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