The Three Forms of Molecular Oxygen

Michael Laing
California State University, Northridge, CA 91330

Everyone is familiar with the oxygen in the air (1), and most have prepared a "pure" sample of this important element. There are many ways of doing this, and one of the best is to heat a mixture of 90 parts KClO₃ and 10 parts MnO₂ (by mass) and collect the gas that is evolved in a gas jar by downward displacement of water (2).

It is certain that pure oxygen gas is very reactive. Not only will a glowing splint burst into flame when dropped into oxygen, but heated iron filings will burn when dropped into the pure gas. This latter reaction is of course close to that of iron rusting (3), although rusting requires oxygen, water, and an electrolyte to proceed (4).

On being cooled below −183 °C oxygen condenses into a beautiful pale blue liquid with a remarkable property: it sticks to the poles of a magnet (5)! This property of being attracted to a magnetic field, called paramagnetism, is found in any molecule or material that contains unpaired electrons. So these are a few of the facts about the behavior of elemental oxygen. The question is whether the bonding model for the pair of oxygen atoms in the diatomic molecule fits these facts.

The simple molecular orbital model for diatomic molecules works beautifully (6). Figure 1 shows the energy level diagram for the O₂ molecule. Pairs of electrons are assigned to the σ and the two π bonding orbitals (BO), and one electron is assigned to each of the two π* antibonding orbitals (AB), the latter two electrons having their spins parallel as required by Hund's rule (7). These two electrons obey the "maximum multiplicity, minimum energy" rule, and they are clearly of parallel spin. Thus, the O₂ molecule has two unpaired electrons and is paramagnetic. This explanation of the paramagnetism of oxygen was the great triumph of the molecular orbital model.

But what prevents us from assigning the two electrons to the same orbital but with opposite spin (Fig. 2)? And what of keeping the two electrons in different π* orbitals but assigning opposite spins to them (Fig. 3)?

The three electron distributions described above are clearly different. The first, the ground state, has two unpaired electrons and is paramagnetic, while the other two have no unpaired electrons and are both diamagnetic. In other words, the simple molecular orbital picture of bonding in diatomic molecules predicts that three forms of oxygen molecules could exist. The oxygen molecules with the electron configurations illustrated in Figures 2 and 3 have all electrons paired so they will not be attracted by a magnetic field. Therefore, they will differ from the paramagnetic form shown in Figure 1 and so should be detectable. Furthermore, they should have different chemical properties. Even though the two nuclei are identical in each case, the form with two unpaired electrons will differ in chemical reactivity from the one in which all electrons are paired. Also, because the electron configurations are different, these three forms must differ in energy. Unfortunately, we cannot deduce their relative energies other than to say that the form with two unpaired electrons will be lowest in energy (Fig. 4), in keeping with Hund's rule (7).

We can also ponder on the O–O bond lengths in the three different electronic states: will they be the same or different? In each state there are six bonding electrons and two antibonding electrons. Clearly the formal bond order in each case will be 2. We are therefore led to predict that the three forms would have similar O–O bond lengths, with the bond lengths in the forms with all electrons paired predicted to be somewhat longer than in the paramagnetic form.

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1 On leave from University of Natal, Durban, South Africa.
The question to ask now is: does the oxygen molecule actually exist in more than one electronic form? The answer is emphatically yes. All three states have been detected. The commonest form, the ground state with two unpaired electrons, is termed a triplet and given the symbol $^3\Sigma$. The other two forms with paired electrons are called singlet states and are termed "excited" because they are higher in energy than is the triplet ground state. They are given the symbols $^1\Delta$ and $^1\Sigma$, with $^1\Delta$ lower in energy than $^1\Sigma$ (7).

The singlet $^1\Delta$ form exists not as a theoretical curiosity but as a useful material, valuable as a reagent in organic chemistry (8). There are several detailed reviews that describe its preparation, physical characteristics, and reactions (9). This chemically useful $^1\Delta$ form can be prepared either by reacting hydrogen peroxide with sodium hypochlorite or by excitation of ordinary $^3\Sigma$ triplet oxygen with ultraviolet light in the presence of a sensitizing dye. Concentrations of up to 10% in the gas phase can be obtained, and the lifetime of the singlet $^1\Delta$ form can be between 1 s and 45 min, depending on the concentration of the gas and whether the phase is gaseous or condensed.

Singlet $^1\Delta$ oxygen undergoes two-electron reactions (analogous to those of ethylene), unlike paramagnetic triplet $^3\Sigma$ oxygen, which takes part in free radical processes.

The reactions of $^1\Delta$ singlet oxygen are important because they represent very smooth methods of introducing oxygen into an organic compound in a highly stereospecific fashion. There are three common modes of reaction of $^1\Delta$ oxygen: the ene reaction, the Diels–Alder type of cycloaddition, and the addition to an activated double bond. All three types have been used in organic synthesis involving oxidation of olefins, especially in the field of natural products (10). Examples of each type of reaction of $^1\Delta$ oxygen, abbreviated $^1\text{O}_2$, are given below.

**The Ene Reaction**
This reaction involves the migration of a double bond to form an allylic hydroperoxide, which in turn can be dehydrated to yield an unsaturated ketone.

\[
\text{R-R} \quad \text{O-O} \quad \text{H}_{\text{O}} \quad \text{R-R}
\]

(1)

Alternatively, the hydroperoxide group can be reduced to OH to form an allylic alcohol.

**Diels–Alder Type of Addition**
Here the $^1\text{O}_2$ adds across two double bonds to form a six-membered ring, which in turn can be decomposed to give two carbonyl groups.

\[
\text{O-O} \quad \text{R}^{*} \quad \text{O-O} \quad \text{R}^{*} \quad \text{O-O} \quad \text{R}^{*}
\]

(2)

One of the first examples of this type of addition is the classic synthesis of (±)-ascaridole (2) in near quantitative yield from α-terpene (1).

**Addition to an Activated Double Bond**
In this reaction the $^1\text{O}_2$ adds directly across the double bond to yield a four-membered 1,2-dioxetane ring, which in turn can be cleaved to yield a di-aldehyde type of structure.

Note that both C-C and O-O bonds are cleaved simultaneously. An interesting example of this reaction is the synthesis of a musk fragrance (3).

Quite apart from its importance in synthetic organic chemistry, singlet oxygen plays an important role in autoxidation (i.e., photodegradation of polymers and vulcanized rubber in air). Notice, too, the implications for biology and life forms that are dependent on oxygen transpiration. The same photosensitizing dyes that yield $^1\Delta$ singlet oxygen also sensitize the oxidative destruction of nucleic acids and enzymes and can produce skin cancer. In addition, many of the carcinogenic polycyclic aromatic hydrocarbons are known to be good photosensitizers with the ability to generate singlet oxygen. Furthermore, the reactions of certain oxygenases so resemble that of $^1\Delta$ oxygen that it becomes a prime candidate as the reactive species in these enzymatic reactions (11).

One of the unique aspects of this $^1\Delta$ singlet form of oxygen is that it can be detected visually because it takes part in reactions that yield "cold light", a process called chemiluminescence (12). The best known reaction of this class is the reaction of luminol that gives a beautiful blue glow in the dark (13).

Finally, we come back to the question of the O-O bond lengths. They were in fact measured many years ago by a careful analysis of the ultraviolet absorption spectrum of oxygen gas. The experimentally determined bond lengths are: $^3\Sigma$ (ground state) 1.2074 Å, $^1\Delta$ (lowest excited state) 1.2155 Å, $^1\Sigma$ (second excited state) 1.2268 Å (14). Three things are evident: (1) all of the bond lengths are similar (in keeping with the formal bond order being 2 in each case); (2) the bond lengths are longer in the excited states; and (3) the $^1\Delta$ state has the shorter of the bond lengths of the two excited states. All three observations are in line with what might have been predicted.

We may conclude by saying that a logical application of the simple rules of the molecular orbital bonding theory for diatomic molecules (6) led us to predict the existence of three spin isomers of the oxygen molecule: one triplet form with two unpaired electrons and two singlet forms with all electrons paired. In addition, the experimental chemist has shown that the reactivity of the singlet $^1\Delta$ form differs enough from that of the usual triplet $^3\Sigma$ form to be useful in organic synthesis.

**Acknowledgment**
I thank my friend Ernest Bovey whose interest in the topic led me to write this article.

**Literature Cited**
3. Ref. 1b, p 189.
4. Ref. 2a, p 311.


