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Dioxygen: What Makes This Triplet Diradical Kinetically Persistent?

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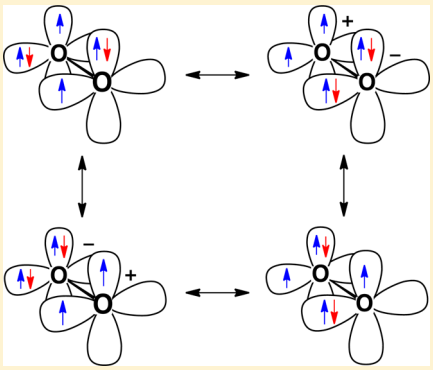
Supporting Information

ABSTRACT: Experimental heats of formation and enthalpies obtained from G4 calculations both find that the resonance stabilization of the two unpaired electrons in triplet O_2, relative to the unpaired electrons in two hydroxyl radicals, amounts to 100 kcal/mol. The origin of this huge stabilization energy is described within the contexts of both molecular orbital (MO) and valence-bond (VB) theory. Although O_2 is a triplet diradical, the thermodynamic unfavorability of both its hydrogen atom abstraction and oligomerization reactions can be attributed to its very large resonance stabilization energy. The unreactivity of O_2 toward both these modes of self-destruction maintains its abundance in the ecosphere and thus its availability to support aerobic life. However, despite the resonance stabilization of the π system of triplet O_2, the weakness of the O−O σ bond makes reactions of O_2, which eventually lead to cleavage of this bond, very favorable thermodynamically.



INTRODUCTION

Dioxygen, O_2, is the only molecule in abundance in our environment that is paramagnetic, with a triplet ground state. That does make one sit up. Certainly, we have in the laboratory (or in our infatuation with the internal combustion engine) made other paramagnetic molecules—doublets and triplets most prominently. But, for good reasons, they are not around us in great concentrations. Their unpaired electrons encourage these radicals and diradicals to stabilize themselves by forming bonds to each other.

However, oxygen (throughout this paper we will use the word oxygen for the O_2 molecule, which is properly called dioxygen) is abundant. In fact, this triplet diradical constitutes 20.94% of the earth's atmosphere.[1] Although chemists have learned to kinetically stabilize other radicals and diradicals by encumbering them with sterically demanding substituents,[2] oxygen is naked. What causes this triplet diradical to persist?

Oh, yes, oxygen is absolutely essential for many forms of life on our planet. And yet, and yet, when oxygen first came in large amounts into the earth's atmosphere,[3] presumably produced by photosynthetic bacteria, around 2.3 billion years ago, it occasioned a major killing off of the life forms that had evolved prior to that date.[4] The life forms that evolved subsequently must have evolved the way they did, in order to cope with, and utilize, molecular oxygen.

Is oxygen "stable"? Is oxygen reactive? Chemists know that there is a distinction between thermodynamics and kinetics. However, the Bell−Evans−Polanyi principle connects the two and indicates that, in general, the relative rates of two reactions are related to which of the two is thermodynamically more favorable.[5] Therefore, in this paper we will focus on the enthalpies of the reactions of oxygen and of the molecules that are related to it. We will use enthalpic terms—exothermic, endothermic—when we write about thermodynamic stability. We will use the more qualitative terms, persistent and reactive, to describe kinetic proclivities.

Is oxygen stable thermodynamically? By itself, apparently it is, but why this triplet diradical does not react with itself to form oligomers is one of the questions that are addressed in this manuscript.

Is oxygen stable in the presence of other elements? The answer is clearly overall negative. With the exception of gold, absolutely every element reacts exothermically with oxygen.[6,7] In that sense, oxygen is energy-rich;[8] and not for nothing is it a choice liquid propellant for rockets.[9] Almost every compound in our bodies, in all living things, with the exception of some inorganic ions such as phosphate and carbonate, is subject to combustion with oxygen. We can burn, and not just with passion.

But, of course, we do not burn. That hydrogen balloon we explode in a general chemistry class does not go off until a flame or spark enters the scene, to allow the reaction to proceed to its thermodynamic nirvana, water. Paper, the making of our civilization (well, at least until now), will not enflame until Fahrenheit 451.[10] Clearly, oxygen, that molecule which reacts exothermically with almost anything, also has a reasonably high activation barrier to reaction with the same anything.

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In fact, the barrier to the reaction of oxygen with the C−H bonds in any organic molecule is astoundingly high.[11] But why? O_2 in its triplet ground state is a diradical! Think of what you know of how easily a chlorine atom or a hydroxyl radical abstracts hydrogen atoms from alkanes.[12] Like monoradicals, most diradicals are generally extremely reactive.[13]

Let us put the startling exceptionalism of oxygen another way: How can a molecule constitute one-fifth of the earth's atmosphere, when it is in continual intimate contact with hundreds of thousands of molecules with which its reaction would be downhill in enthalpy? Phenomenologically, the answer to that question is obviously that O_2 must have high barriers to reactions with most molecules. Why that is so, and in particular why oxygen has a high barrier to reactions involving the abstraction of hydrogen atoms, is one of the questions that this paper will consider.

An example of the unreactivity of $^{\bullet}OO^{\bullet}$ ($^{\bullet}OO^{\bullet}$ is the notation that we will use throughout this manuscript, in order to emphasize that O_2 is a triplet diradical) toward hydrogen atom abstraction is provided by one of the first steps in common autoxidation reactions. Of course, combustion and oxidation mechanisms are unfailingly complex, with a multitude of possible steps following initiation, which typically occurs by formation or introduction of a radical.[14−17] Chain propagation steps follow, and many different types of radicals can play a role.

However, we focus here on the hydrogen abstraction step in autoxidation reactions (eq 1). This step involves peroxyl radicals, $ROO^{\bullet}$, not the much more plentiful $^{\bullet}OO^{\bullet}$ diradicals, which only participate in radical coupling in the second chain-propagating step (eq 2).[18]

$$ROO^{\bullet} + RH \rightarrow ROOH + R^{\bullet} \quad (1)$$

$$R^{\bullet} + {}^{\bullet}OO^{\bullet} \rightarrow ROO^{\bullet} \quad (2)$$

Radical coupling, of which eq 2 is an example, is a common, usually almost barrierless reaction of two radicals, when the radicals are not sterically protected. But $^{\bullet}OO^{\bullet}$ diradicals do not bond strongly with each other, to form dimers, trimers, or higher oligomers.[19] There have been numerous studies, both experimental and theoretical, of dimers, trimers, tetramers, and higher aggregates of O_2. The consensus that has emerged is that these are weakly bound (yet quite detectable and capable of being studied spectroscopically) by predominantly dispersion forces.[20,21] Thus, $^{\bullet}OO^{\bullet}$ remains a diatomic gas under ambient earth conditions, rather than being sequestered in oligomers. In this regard oxygen is quite different from sulfur, for which the most stable form is not triplet S_2 ($^{\bullet}SS^{\bullet}$), but the tetramer, S_8.

In this paper, we use a combination of thermodynamic data, where available, and high level calculations to investigate the reason for the unreactivity of triplet $^{\bullet}OO^{\bullet}$ toward (a) hydrogen abstraction and (b) oligomerization. Triplet $^{\bullet}SS^{\bullet}$ provides a suitable comparison with triplet $^{\bullet}OO^{\bullet}$ in both types of reactions. We also investigate the origin of the large enthalpy release that is associated with reactions that result in the eventual cleavage of the O−O σ bond in O_2.

METHODOLOGY

Where available, heats of formation of reactants and products in several reactions of $^{\bullet}OO^{\bullet}$ were obtained from Argonne National Laboratory's Active Thermochemical Tables (ATcT).[22] From these values of $\Delta_f H°(298.15\ K)$, the enthalpies of reaction, $\Delta H(298.15\ K)$, were calculated. Fortunately, the relevant heats of formation are reasonably abundant for the O/H molecules discussed in this manuscript, due to their importance in combustion and atmospheric chemistry. The Active Thermochemical Tables represent a systematic approach to thermochemistry, combining experiment and theory. Previous experience has shown that the enthalpies of reactions, computed with ATcT heats of formation, are in excellent agreement with the values obtained from high level calculations.[23]

Enthalpies of reactants and products were also computed at the G4 level of theory,[24] and these enthalpies were used to obtain G4 values of $\Delta H(298.15\ K)$ for all of the reactions in this paper. Where comparisons of the calculated G4 values with the largely experimental ATcT values of $\Delta H(298.15\ K)$ are possible (e.g., in the first four reactions in Table 1), the agreement between the two types of values is within ±1.0 kcal/mol. Therefore, it seems reasonable to suppose that the G4 values of $\Delta H(298.15\ K)$ for all of the reactions in this paper are probably quite accurate.

Table 1. Enthalpies of Reaction, $\Delta H(298.15\ K)$ in kcal/mol, Obtained from Experimental Heats of Formation, $\Delta_f H°(298.15\ K)$, and from G4 Calculations

		$\Delta H(298.15\ K)$	
reaction label	reaction	G4 value	ATcT value
A	$^{\bullet}OH + H_2O_2 \rightarrow H_2O + {}^{\bullet}OOH$	−31.6	−31.0
B	$^{\bullet}OH + {}^{\bullet}OOH \rightarrow H_2O + {}^{\bullet}OO^{\bullet}$	−69.0	−69.2
C	$2\ {}^{\bullet}OOH \rightarrow HOOH + {}^{\bullet}OO^{\bullet}$	−37.4	−38.2
D	$2\ {}^{\bullet}OH + HOOH \rightarrow 2H_2O + {}^{\bullet}OO^{\bullet}$	−100.6	−100.2
E	$3\ {}^{\bullet}OO^{\bullet} \rightarrow O_6$ (cyclic)	+79.4	
F	$4\ {}^{\bullet}OO^{\bullet} \rightarrow O_8$ (cyclic)	+94.6	
G	$2\ {}^{\bullet}OOH \rightarrow HOOOOH$	−15.4	
H	$^{\bullet}SH + H_2S_2 \rightarrow H_2S + {}^{\bullet}SSH$	−17.5	
I	$^{\bullet}SH + {}^{\bullet}SSH \rightarrow H_2S + {}^{\bullet}SS^{\bullet}$	−33.4	
J	$2\ {}^{\bullet}SSH \rightarrow HSSH + {}^{\bullet}SS^{\bullet}$	−15.9	
K	$2\ {}^{\bullet}SH + HSSH \rightarrow 2H_2S + {}^{\bullet}SS^{\bullet}$	−50.9	
L	$3\ {}^{\bullet}SS^{\bullet} \rightarrow S_6$ (cyclic)	−70.8	
M	$4\ {}^{\bullet}SS^{\bullet} \rightarrow S_8$ (cyclic)	−103.0	
N	$2\ {}^{\bullet}SSH \rightarrow HSSSSH$	−41.2	

RESULTS AND DISCUSSION

The experimental and G4 values of $\Delta H(298.15\ K)$ for the reactions discussed in this manuscript are assembled in Table 1. The experimental values of $\Delta_f H°(298.15\ K)$ and the G4 enthalpies of the reactants and products, from which the G4 $\Delta H(298.15\ K)$ values in Table 1 were derived, are given in Table S1.

Hydroperoxyl Radical ($^{\bullet}OOH$). The three-electron, two-center π bonds in the O_2 molecule (about which we will have much more to say) are like those in the hydroperoxyl radical ($^{\bullet}OOH$). Actually, it is useful to travel to $^{\bullet}OO^{\bullet}$ via $^{\bullet}OOH$, so we begin by computing the resonance stabilization of the $^{\bullet}OOH$ radical. This important species has a $^2A''$ ground state. It is a π radical, with O−O 1.33 Å, O−H 0.97 Å, and an OOH angle of 104.3°.[25] The stabilization energy of $^{\bullet}OOH$ can be defined by the enthalpy of the reaction

$$^{\bullet}OH + H_2O_2 \rightarrow H_2O + {}^{\bullet}OOH \quad (3)$$

in which the localized hydroxyl radical is converted to the delocalized peroxyl radical. Equation 3 in the text is equation A

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in Table 1. (We will consistently use letters to label chemical equations in Table 1, and numbers for those that appear in the text.) Entry A in Table 1 shows that an O−H bond in H_2O_2 is ca. 31−32 kcal/mol weaker than an O−H bond in H_2O, presumably due to the resonance stabilization of •OOH, relative to •OH.

The qualifier "presumably" is used for good reasons. As usual in thermodynamic considerations of stability, reasonable men and women can, and often do, turn the horse around.[26] For example, some of the exothermicity of the reaction A could also be attributed to some destabilizing feature of one of the reactants, hydrogen peroxide. Lone pair repulsion might serve admirably, but the *gauche* conformation of H_2O_2 minimizes the destabilizing overlap between the pairs of electrons on the two oxygens and replaces it with the more stabilizing hyperconjugative interactions between the lone pairs and the O−H σ^* orbitals.[27] Therefore, we attribute most, if not all, of the exothermicity of reaction A in Table 1 to the resonance stabilization of •OOH.

The resonance stabilization of •OOH is due to the presence of a three-electron, two-center π bond between the oxygens.[28] In such a bond two oxygen electrons occupy a π MO that is O−O bonding, and the unpaired electron occupies a π^* MO that is O−O antibonding. Consequently, there is, on net, one bonding electron in the three-electron, two-atom π bond in •OOH; and this π bonding electron serves to stabilize •OOH, relative to •OH.

In valence bond (VB) theory, the resonance stabilization in a three-electron, two-center π bond is attributed to a contribution from the second resonance structure in Figure 1. In this type of

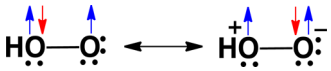

Figure 1. Resonance stabilization of the hydroperoxyl radical by three-electron, two-center bonding. For the sake of visual clarity, we have colored the α-spin electrons blue and β-spin electrons red in this and in subsequent figures.

resonance stabilization, one nonbonding π electron on the oxygen that has an octet of electrons in the first structure in Figure 1 is delocalized in the second structure into the singly occupied 2p-π AO on the other oxygen. If the unpaired electron is assumed to have α-spin, the electron that is delocalized into the AO occupied by this electron must, of course, have β-spin.

We will subsequently return to a detailed discussion of the MO and VB descriptions of the three-electron, two-center, π bonding in •OO•.

The Dioxygen Triplet Diradical (•OO•). The •OO• triplet diradical has two orthogonal sets of π MOs. Therefore, on breaking the O−H bond in HOO• to form •OO•, one might have expected that the reaction

$$\text{•OH} + \text{•OOH} \rightarrow H_2O + \text{•OO•} \quad (4)$$

like the reaction in eq 3, would be exothermic by 31−32 kcal/mol, because in the reaction in eq 4 a second three-electron, two-center π bond can be formed between the oxygens.

However, the reaction in eq 4, which is reaction B in Table 1, is both calculated and found experimentally to be exothermic by 69 kcal/mol. Indeed, reaction C in Table 1, which is the difference between reactions B and A, shows that breaking the O−H bond in •OOH, to form •OO•, actually requires 37−38 kcal/mol less enthalpy than breaking an O−H bond in HOOH, to form •OOH.

Looked at in reverse, this result means that hydrogen atom abstraction by •OO• is 37−38 kcal/mol less favorable enthalpically than hydrogen atom abstraction by •OOH. Therefore, applying the Bell−Evans−Polanyi principle,[5] it is certainly understandable that ROO• can abstract a hydrogen from R−H in the first chain propagating reaction of an autoxidation reaction (eq 1), but •OO• apparently does not abstract a hydrogen from R−H, even when •OO• is present in very large excess.

In this connection we wish to mention a detailed study of the $2H_2 + O_2 \rightarrow 2H_2O$ reaction by Filatov, Reckien, Peyerimhoff, and Shaik.[29] Their paper was informed by oxidation modes in metal−oxene and mono-oxygenase enzymes that the Shaik group had studied. Both the triplet and singlet surfaces for the abstraction of a hydrogen atom from H_2 by O_2 were calculated, and it was found that this reaction encounters very large barriers of 60.7 and 66.4 kcal/mol, respectively, for the triplet and the singlet states of O_2.

How much of the 60.7 kcal/mol calculated barrier height to abstraction of a hydrogen atom from H_2 by triplet •OO• is simply due to thermochemistry? Filatov et al. calculate that this reaction is energetically unfavorable by 58.0 kcal/mol.[29] Therefore, more than 95% of the calculated barrier height is due to the unfavorable energetics of this hydrogen abstraction reaction. It is clear that the kinetics of this reaction are dominated by its thermochemistry.

Returning to reaction C in Table 1, it can also be interpreted as indicating that the electron delocalization in •OO• is 37−38 kcal/mol more stabilizing than the electron delocalization in two molecules of •OOH. Either MO or VB theory can be used to explain the reason for the extra stability of O_2; and, as discussed in the following sections, the two explanations turn out to be similar.

However, it should first be noted that it is to Linus Pauling that we owe the recognition of the special thermodynamic stability of the two, three-electron, π bonds in O_2, relative to the strength of the O−O σ bond.[30,31] In section 2 of the Supporting Information for this manuscript we describe how Pauling viewed O_2.

Resonance Structures for the •OO• Diradical. Shown in Figure 2 are the four resonance structures that arise from assigning six electrons—four of α-spin and two of β-spin—to the four $2p_x$ and $2p_y$ π AOs in the triplet ground state of the oxygen molecule. As shown in Figure 2, one α-spin electron occupies each 2p-π AO. The β-spin electron in each of the two

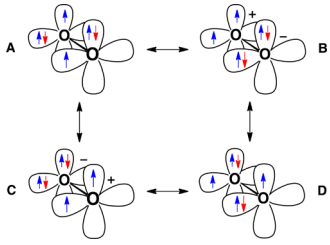

Figure 2. Possible distributions, **A**−**D** of the two β-spin electrons in the two orthogonal π systems of triplet •OO•. The four α-spin electrons each occupy one of the four 2p-π AOs; so, as shown in resonance structures **A**−**D**, it is only the β-spin electrons that are delocalized.

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orthogonal π systems is delocalized over the 2p-π AOs of both oxygen atoms.[32]

The two zwitterionic structures, **B** and **C**, represent delocalization of the β-spin electrons in the two orthogonal π systems in a fashion similar to that shown in the second resonance structure for peroxyl radical in Figure 1. Thus, if resonance structures **A**, **B**, and **C** represented accurately the $^{\bullet}OO^{\bullet}$ wave function, one would expect that the stabilization provided by electron delocalization in $^{\bullet}OO^{\bullet}$ would be about the same as that in two peroxyl radicals. Therefore, the enthalpy of reaction C in Table 1 would be close to zero, instead of having its actual value of 37−38 kcal/mol.

It is the contribution from resonance structure **D** in Figure 1 that makes the delocalization energy of $^{\bullet}OO^{\bullet}$ 37−38 kcal/mol larger than that that of two molecules of $^{\bullet}OOH$. In structure **D**, as in structure **A**, there is no charge separation, as there is in resonance structures **B** and **C**. Therefore, resonance structures **A** and **D** in Figure 2 are expected to dominate the wave function for the electrons in the two orthogonal π systems.

The picture in Figure 2 of the bonding in O_2 is patently a VB description; and it seems, at first, to have no relation to the MO representation of the triplet state of the O_2 molecule. The correspondence between the VB and MO pictures is delineated in the next section.

The MO Wave Function for Triplet $^{\bullet}OO^{\bullet}$ and the Importance of Including Electron Correlation in this Wave Function. The MO description of triplet O_2 begins with two, orthogonal, bonding π MOs,[33]

$$\pi_x = \frac{1}{\sqrt{2}}(\phi_{1x} + \phi_{2x})$$
$$\pi_y = \frac{1}{\sqrt{2}}(\phi_{1y} + \phi_{2y}) \quad (5)$$

and their antibonding π^* partners,[34]

$$\pi_x^* = \frac{1}{\sqrt{2}}(\phi_{1x} - \phi_{2x})$$
$$\pi_y^* = \frac{1}{\sqrt{2}}(\phi_{1y} - \phi_{2y}) \quad (6)$$

An α- and a β-spin electron are assigned to each of the bonding π MOs, and an α-spin electron is assigned to each of the antibonding π^* MOs. Thus, the restricted, open-shell, Hartree−Fock (ROHF) wave function for triplet O_2 can be written

$$\Psi(\mathrm{ROHF}) = |...\pi_x^{\alpha}\pi_x^{\beta}\pi_y^{\alpha}\pi_y^{\beta}\pi_x^{*\alpha}\pi_y^{*\alpha}\rangle \quad (7)$$

Since the MOs for two electrons of the same spin can be added or subtracted, without changing a many-electron wave function, the pair of α-spin electrons in the π and π^* MOs in each of the two orthogonal π systems of triplet $^{\bullet}OO^{\bullet}$ can be taken to be localized, one in each AO, as shown in each of the four resonance structures in Figure 2. Since only the β-spin electrons are delocalized, the ROHF wave function in eq 7 can be abbreviated as

$$\Psi(\mathrm{ROHF}) = |...\pi_x^{\beta}\pi_y^{\beta}\rangle \quad (8)$$

eq 8 shows that in Ψ(ROHF) the two β-spin electrons, one in π_x and one in π_y, move independently of each other. Therefore, all four of the structures in Figure 2 have equal weights in the ROHF wave function for the triplet $^{\bullet}OO^{\bullet}$ diradical.

Although the ROHF wave function for $^{\bullet}OO^{\bullet}$ fails to weight structures **A** and **D** more heavily than structures **B** and **C**, the ROHF wave function does make the delocalization energy, calculated for $^{\bullet}OO^{\bullet}$, larger than that for two molecules of $^{\bullet}OOH$. When the energy of reaction C in Table 1,

$$2HOO^{\bullet} \rightarrow HOOH + {}^{\bullet}OO^{\bullet} \quad (9)$$

is computed at the ROHF/aug-cc-pVTZ level of theory, the reaction is determined to be energetically favorable by 22.5 kcal/mol. However, this ROHF energetic favorability is about 15 kcal/mol less than both the experimental and the G4 exothermicities of reaction C in Table 1.

In order to weight more heavily the contribution of the non-zwitterionic structures, **A** and **D**, in the wave function for triplet $^{\bullet}OO^{\bullet}$, correlation between the motions of the β-spin electrons can be introduced by adding a second configuration to the ROHF wave function. The configuration that needs to be added can be abbreviated as $|...\pi_x^{*\beta}\pi_y^{*\beta}\rangle$, in which each β-spin electron is assigned to the antibonding π^* MO of one of the two orthogonal π systems (eq 6). The resulting two-configuration (TC)SCF wave function for the β-spin electrons in triplet $^{\bullet}OO^{\bullet}$ is then

$$\Psi(\mathrm{TCSCF}) = |...\pi_x^{\beta}\pi_y^{\beta}\rangle - \lambda^2|...\pi_x^{*\beta}\pi_y^{*\beta}\rangle \quad (10)$$

where the mixing coefficient, λ^2, must be optimized variationally.

In eq 10, two electrons are excited from bonding π MOs in the first configuration to antibonding π^* MOs in the second configuration. Therefore, the energy of the second configuration is considerably higher than that of the first. Consequently, the mixing coefficient, λ^2, in eq 10 is certainly much less than 1.

The spatial part of the TCSCF wave function in eq 10 can be factored; and an unnormalized version of the spatial part of the TCSCF wave function in eq 10 can be rewritten as

$$\Psi(\mathrm{TCSCF}) = |...(\pi_x + \lambda\pi_x^*)(\pi_y - \lambda\pi_y^*)\rangle + |...(\pi_x - \lambda\pi_x^*)(\pi_y + \lambda\pi_y^*)\rangle \quad (11)$$

Substituting for π from eq 5 and for π^* from eq 6, eq 11 becomes

$$\Psi(\mathrm{TCSCF}) = |...[(1+\lambda)\phi_{1x} + (1-\lambda)\phi_{2x}][(1-\lambda)\phi_{1y} + (1+\lambda)\phi_{2y}]\rangle + |...[(1-\lambda)\phi_{1x} + (1+\lambda)\phi_{2x}][(1+\lambda)\phi_{1y} + (1-\lambda)\phi_{2y}]\rangle \quad (12)$$

It can easily be seen that the TCSCF wave function in eq 12 correlates the motions of the β-spin electrons in the two orthogonal π systems of $^{\bullet}OO^{\bullet}$, because in the limit where λ = 1, eq 12 becomes

$$\Psi(\mathrm{TCSCF}) = |...\phi_{1x}\phi_{2y}\rangle + |...\phi_{2x}\phi_{1y}\rangle \quad (13)$$

The TCSCF wave function in eq 13 correlates the β-spin electrons in the two different π systems of O_2 perfectly, by always keeping these electrons on different oxygen atoms, one electron on oxygen 1 and the other on oxygen 2, thus minimizing the Coulombic repulsion between them. Therefore, if λ = 1, only the two non-zwitterionic electron distributions, **A** and **D**, in Figure 1 would be present in $^{\bullet}OO^{\bullet}$.[35]

However, λ = 1 means that the π and π^* MOs of $^{\bullet}OO^{\bullet}$ would be equally occupied. Then there would be no π bonding in either of the two orthogonal π systems of $^{\bullet}OO^{\bullet}$. Clearly, λ = 1 is a limit that will not be reached in the TCSCF wave function for O_2.

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In an actual TCSCF calculation on triplet •OO•, λ is variationally optimized, so that the energy of the TCSCF wave function is minimized by finding the best compromise between maximizing bonding in the two orthogonal π systems and minimizing the Coulombic repulsion between the β-spin electrons in them. Going from an ROHF calculation on •OO• to a TCSCF calculation lowers the calculated energy of triplet •OO• by 20.7 kcal/mol and thus almost doubles the energetic favorability of the reaction in eq 9, from 22.5 to 43.2 kcal/mol.

Using the TCSCF energy for •OO• in eq 10 overestimates by 5−6 kcal/mol the stabilization of •OO• by electron delocalization. Nevertheless the TCSCF value of 43.2 kcal/mol for the energy of the reaction in eq 9 comes much closer to the G4 and experimental values of 37−38 kcal/mol than does the ROHF value of only 22.5 kcal/mol. As already noted, correlation between the β-spin electrons in the two π systems of •OO• is totally absent from the ROHF wave function for triplet •OO•, and this type of electron correlation plays an important role in the stabilization of triplet •OO• by the pair of three-electron, two-center π bonds that this diradical contains.

VB Description of the Origin of the Thermodynamic Stability of the Triplet •OO• Diradical. VB theory, like MO theory, does come to the conclusion that O_2 is a diradical with a triplet ground state.[36−41] The malignment of VB theory for its supposed failure of characterizing the ground state of O_2 is undeserved. Indeed, advanced VB calculations on O_2 lead to results that are as accurate as advanced wave function methods (*vide infra*). MO theory and valence bond theory can, in fact, be connected to each other through the so-called Generalized Valence Bond (GVB) theory, pioneered by Goddard and coworkers.[42,43]

How does VB theory account for the 37−38 kcal/mol greater stabilization by electron delocalization of triplet •OO•, relative to two molecules of •OOH?

The four structures in Figure 2 represent the most important resonance structures for triplet •OO•. VB calculations by McWeeny[44] found that the optimal VB wave function is

$$\Psi(\mathrm{VB}) = 0.59(\mathbf{A} + \mathbf{D}) - 0.23(\mathbf{B} + \mathbf{C}) \quad (14)$$

Not surprisingly, the non-zwitterionic structures, **A** and **D**, have a much higher weight than the zwitterionic structures, **B** and **C**, in this wave function.

Why are structures **B** and **C** present in Ψ(VB) in eq 14 if they are much higher in energy than structures **A** and **D**? As pointed out by Harcourt in 1992,[45] structures **B** and **C** differ from structures **A** and **D** by the shift of just one electron; whereas, **A** and **D** (and **B** and **C**) differ from each other by the shift of two electrons. In VB theory, greater stabilization results from one-electron than from two-electron shifts between resonance structures. Therefore, the interaction of structures **A** and **D** with **B** and **C** provides more resonance energy than the interaction of structures **A** and **D** with each other.

Harcourt computed the energy of the VB wave function in which structures **A**, **B**, **C**, and **D** were constrained to have equal weights. This constrained VB wave function was calculated by Harcourt to be 25.9 kcal/mol higher in energy than the VB wave function in eq 14, in which the coefficients of the resonance structures are optimized.

Since the VB wave function in eq 14 should be similar to the TCSCF MO wave function in eq 10, and since the VB wave function with all of the coefficients constrained to be equal should be equivalent to the ROHF wave function in eq 8, it is not surprising that Harcourt's energy difference of 25.9 kcal/mol between the unconstrained and constrained VB wave functions is similar in size to the energy difference of 20.7 kcal/mol between the TCSCF and ROHF MO wave functions.

Harcourt also computed the energy of the VB wave function consisting only of structures **A**−**C** and omitting structure **D**. This should correspond to an •OO• molecule in which the stabilization should be approximately the same as that in two molecules of •OOH. Harcourt's 1992 calculations found the energy difference between this incomplete VB wave function and the VB wave function in eq 14 to be 25.6 kcal/mol. This energy difference is about 11−12 kcal/mol smaller than the experimental and G4 enthalpies of reaction C in Table 1, which find the delocalization energy in triplet •OO• to be 37−38 kcal/mol larger than that in two molecules of •OOH.

Harcourt also compared the energy of the VB wave function in eq 14 with the energy calculated for just structure **A**, which has no resonance stabilization. He found that delocalization stabilizes the VB wave function in eq 14 by 77.2 kcal/mol, relative to structure **A**. Using a much better basis set, Su et al. calculated that a VB wave function consisting of structures **A**−**D** is 102.6 kcal/mol lower than structure **A** alone.[40] As discussed in the next section, both G4 calculations and experimental heats of formation find that the total resonance energy of triplet •OO• is very close to the VB value, computed by Su et al.

The Resonance Energy of •OO•. Summing reactions A and B in Table 1 gives

$$2\ {}^{\bullet}\mathrm{OH} + \mathrm{HOOH} \rightarrow 2\mathrm{H_2O} + {}^{\bullet}\mathrm{OO}^{\bullet} \quad (15)$$

which is reaction D in Table 1. The enthalpy of this reaction is −100.6 kcal/mol, as computed by G4, and −100.2 kcal/mol from experimental heats of formation.

The very high exothermicity of this reaction can be viewed as being due to the difference in energy between having two unpaired electrons localized on two hydroxyl radicals and having them in a pair of two-center, three-electron bonds in an oxygen molecule. Thus, the enthalpy of the reaction in eq 14 (equation D in Table 1) seems to be a reasonable definition of the delocalization or resonance energy of O_2.[46]

Of course, resonance energies always depend on the reference state. If one were to use, instead of equation D, equation C of Table 1 to define the resonance energy of •OO•, one would get 37−38 kcal/mol, with the reference now being two •OOH radicals. As shown in equation A, each •OOH radical is resonance-stabilized by 31−32 kcal/mol. Thus, the 100 kcal/mol figure for the resonance stabilization of •OO• contains contributions from the stabilization by each of the two, orthogonal, three-electron bonds in this diradical, plus the additional, synergistic, stabilization that comes from the presence of both three-electron bonds in the same molecule.

Accepting that eq 15 (equation D of Table 1) is a good measure of the resonance stabilization of the oxygen molecule means that the 100 kcal/mol resonance energy of triplet •OO• is approximately three times the size of Kistiakowski's value of 36.5 kcal/mol for the resonance energy of benzene, relative to the double bonds in three molecules of cyclohexene.[47] Who would have guessed that the resonance stabilization of •OO• is this large?

Why O_6 and O_8 Are Not the Thermodynamically Most Stable Allotropes of Oxygen. The ca. 100 kcal/mol resonance energy of triplet •OO• is the reason that G4 calculations predict its trimerization to cyclic O_6 in reaction E

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of Table 1[48] and its tetramerization to cyclic O_8 in reaction F to be endothermic by, respectively, 79.4 and 94.6 kcal/mol. Although both O_6 and O_8 are local minima, their formation from triplet O_2 is calculated to be highly unfavorable enthalpically.[49,50]

In section S3 of the Supporting Information we describe the energetics of cyclic O_4, which is calculated to be both thermodynamically and kinetically unstable toward fragmentation to two molecules of triplet O_2. The G4 value for the endothermicity of the dimerization of triplet O_2 to cyclic O_4 is 93.6 kcal/mol. Although the strain in the O_4 ring certainly contributes to the unfavorability of this reaction, it should be noted that the G4 enthalpy of reaction F in Table 1, for the tetramerization of O_2 to cyclic O_8, is calculated to be 94.6 kcal/mol, even slightly more unfavorable. Note that the O_2 oligomers discussed in this section are not the van der Waals complexes mentioned earlier[20] but metastable molecules with covalent O−O σ bonds.

Here we focus our detailed analysis on the formation of cyclic O_6. The trimerization of O_2 involves the formation of three new O−O σ bonds, but at the sacrifice of 3 × 100.6 = 301.8 kcal/mol of resonance energy. If the difference between 301.8 kcal/mol and the 79.4 kcal/mol endothermicity of the trimerization reaction in equation E of Table 1 is assumed to be three times the average enthalpy of each of the three O−O σ bonds that are made in the trimerization reaction,[51] the average enthalpy of each of these three O−O bonds is (301.8−79.4)/3 = 74.1 kcal/mol.

As a check on this value of the average O−O bond enthalpy in the chair conformation of O_6, we have computed the G4 value for the bond dissociation enthalpy of the central O−O bond of a chairlike geometry of HOO−OOH to two molecules of $^{\bullet}$OOH.[52] This is the reverse of reaction G in Table 1. The calculated enthalpy of the reverse reaction is 15.4 kcal/mol.

However, reaction A of Table 1 indicates that each of the two $^{\bullet}$OOH molecules formed by the reverse of reaction G in Table 1 is resonance-stabilized by 31.6 kcal/mol, relative to a localized hydroxyl radical. Therefore, without the resonance stabilization of the two $^{\bullet}$OOH radicals, the BDE of the central bond of HOO-OOH would be 2 × 31.6 + 15.4 = 78.6 kcal/mol. Thus, the BDE of the central O−O bond of HOO−OOH to two, hypothetical, localized, $^{\bullet}$OOH radicals is slightly higher than the average O−O BDE of 70.1 kcal/mol in the more rigidly constrained chair conformation of O_6, but only by 4.5 kcal/mol.[53]

Why Does Triplet $^{\bullet}$SS$^{\bullet}$ Form Oligomers? Reactions L and M of Table 1 show that, in agreement with experiment, the oligomerization of $^{\bullet}$SS$^{\bullet}$ to S_6 and S_8 is predicted by G4 calculations to be thermodynamically favorable. The calculated enthalpy changes are −70.8 kcal/mol for trimerization of triplet $^{\bullet}$SS$^{\bullet}$ to S_6 and −103.0 kcal/mol for tetramerization to S_8.

If the very high resonance energy of triplet $^{\bullet}$OO$^{\bullet}$ is what keeps it from trimerizing to cyclic O_6 and O_8, is oligomerization of triplet $^{\bullet}$SS$^{\bullet}$ to cyclic S_6 and S_8 thermodynamically favorable because triplet $^{\bullet}$SS$^{\bullet}$ has a much lower resonance energy than triplet $^{\bullet}$OO$^{\bullet}$? Comparisons of the G4 enthalpies of reactions H−K in Table 1 with the enthalpies of reactions A−D indicate that π bond formation is only about half as stabilizing for S−S π bonds as for O−O π bonds.[54,55]

Of particular interest is that the resonance energy of triplet $^{\bullet}$SS$^{\bullet}$, as given by reaction K of Table 1, is only 50.9 kcal/mol. Thus, the resonance energy of triplet $^{\bullet}$SS$^{\bullet}$ is about 50 kcal/mol less than that of 100 kcal/mol in triplet $^{\bullet}$OO$^{\bullet}$, as given by reaction D in Table 1.

The difference between the G4 enthalpies of the trimerization reactions of O_6 and S_6 in Table 1 amounts to 79.4 − (−70.8) = 150.2 kcal/mol. This is almost exactly the same as three times the difference of 50 kcal/mol between the resonance energies of O_2 and S_2. Therefore, the 50 kcal/mol difference between the resonance energies of O_2 and S_2 can account quantitatively for the difference of 150 kcal/mol between the enthalpies of their trimerization reactions.

Since this is the case, it must be that the average S−S σ BDE in cyclic S_6 is nearly the same as the average O−O σ BDE in cyclic O_6. In order to confirm that these two BDEs are nearly the same, we computed the enthalpy for dissociation of the S−S bond in the chairlike conformation of HSS−SSH. As shown in Table 1 for reaction N, this S−S BDE is 41.2 kcal/mol.

However, the two HSS$^{\bullet}$ radicals formed are each resonance-stabilized to the extent of 17.5 kcal/mol, as given by reaction H in Table 1. Therefore, the S−S σ BDE of the chairlike conformation of HSS−SSH to two, hypothetical, unstabilized, $^{\bullet}$SSH radicals would be 2 × 17.5 + 41.2 = 76.2 kcal/mol. This S−S σ BDE is almost the same as the σ BDE of 78.6 kcal/mol for the cleavage of the O−O bond in the chairlike conformation of HOO−OOH, without the stabilization energy of the two $^{\bullet}$OOH radicals formed.

The similarity of these intrinsic S−S and O−O σ BDEs strongly supports the hypothesis that the 150 kcal/mol difference between the G4 heats of the trimerization reactions of triplet $^{\bullet}$OO$^{\bullet}$ and triplet $^{\bullet}$SS$^{\bullet}$ is due to the 150 kcal/mol difference between the resonance energies of three moles of O_2 and three moles of S_2.

Why Are the Reactions of O_2 To Form Water Highly Exothermic? In the foregoing sections of this manuscript, we have stressed that thermochemistry makes $^{\bullet}$OO$^{\bullet}$ remarkably unreactive toward hydrogen atom abstraction. For example, as already noted, reaction D of Table 1 shows that abstraction of two hydrogen atoms by triplet $^{\bullet}$OO$^{\bullet}$ is ca. 100 kcal/mol less favorable enthalpically than the same reaction of two $^{\bullet}$OH radicals. In fact, as discussed above, this comparison provides a reasonable definition of the resonance energy of the pair of three-electron, two-center bonds in $^{\bullet}$OO$^{\bullet}$, including the 37−38 kcal/mol synergistic interaction between them in equation C of Table 1.

As shown in reaction O of Table 2, the 100 kcal/mol resonance energy of $^{\bullet}$OO$^{\bullet}$ makes the reaction of $^{\bullet}$OO$^{\bullet}$ with H_2, to form HOOH, exothermic by only about 32 kcal/mol. However, as every general chemistry student learns, the reaction of $^{\bullet}$OO$^{\bullet}$ with two moles of H_2, to form two moles of water, is hugely exothermic. As shown in reaction Q of Table 2, the overall exothermicity amounts to about 115 kcal/mol, a

Table 2. Enthalpies of Reaction, ΔH(298.15 K) in kcal/mol, Obtained from Experimental Heats of Formation, $\Delta_f H°$(298.15 K), and from G4 Calculations

		ΔH(298.15 K)	
reaction label	reaction	G4 value	ATcT value
O	H_2 + $^{\bullet}$OO$^{\bullet}$ → HOOH	−31.6	−32.4
P	H_2 + HOOH → $2H_2O$	−83.3	−83.2
Q	$2H_2$ + $^{\bullet}$OO$^{\bullet}$ → $2H_2O$	−114.9	−115.6
R	H_2O_2 → 2 $^{\bullet}$OH	48.9	49.4

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factor of 3.6 more than the exothermicity of reaction O in Table 2.

The reason for the much greater exothermicity of reaction Q than reaction O is that reaction P, the formation of two moles of water from the reaction of the hydrogen peroxide with H_2, is exothermic by 83 kcal/mol. Since reactions O and P both involve the breaking of the bond in H_2 and the formation of two O−H bonds, what accounts for the 51 kcal/mol greater exothermicity of reaction P than reaction O in Table 2?

The answer is not hard to find. Breaking the pair of three-electron, two-center π bonds in O_2 costs 100 kcal/mol, as shown by reaction D in Table 1. However, reaction R in Table 2 shows that breaking the weak O−O σ bond in HOOH costs only 49 kcal/mol. The difference of 51 kcal/mol accounts very nicely for the difference in enthalpy between reaction O in Table 2, which breaks the pair of strong, three-electron, two-center π bonds in $^{\bullet}OO^{\bullet}$, and reaction P, which breaks the weak O−O σ bond in HOOH. Thus, what makes $^{\bullet}OO^{\bullet}$ a very unusual molecule is not only its triplet ground state but also that, as first pointed out by Pauling,[56] the π bonding in this diradical is actually stronger than the σ bonding.[57]

This is the reverse of the situation in organic molecules. For example, using the heats of formation in the ATcT,[22] the enthalpy of the reaction

$$H_2C{=}CH_2 + H_3C{-}CH_3 \rightarrow 2H_3C{-}CH_2^{\bullet} \quad (16)$$

is ΔH = 64.9 kcal/mol. The enthalpy of the reaction in eq 16 is the Benson definition of the strength of the π bond in ethylene.[58] The difference between the enthalpy of this reaction and that of ΔH = 174.8 kcal/mol for the reaction

$$H_2C{=}CH_2 \rightarrow 2\,{}^3CH_2 \quad (17)$$

is 109.9 kcal/mol; and this can be taken to be the energy of the σ bond in ethylene. Thus, the σ bond of ethylene is 45.0 kcal/mol stronger than the π bond, which is the exact opposite of the situation in $^{\bullet}OO^{\bullet}$.

The strong π bonding in $^{\bullet}OO^{\bullet}$ is, as discussed in this manuscript, the reason that this triplet diradical is persistent. On the other hand, the weak σ bond allows the formation of two molecules of H_2O from $^{\bullet}OO^{\bullet}$ to deliver large amounts of energy. The unusual combination of these two properties is what gives $^{\bullet}OO^{\bullet}$ the ability to support the existence of aerobic life on this planet.

CONCLUSIONS

The 37−38 kcal/mol exothermicity, calculated by G4 and deduced from experimental heats of formation, for reaction C in Table 1 provides a simple rationalization for the experimental fact that triplet $^{\bullet}OO^{\bullet}$ does not abstract hydrogen atoms, to form $^{\bullet}OOH$, under reaction conditions in which peroxyl radicals ($^{\bullet}OOH$) do abstract hydrogen atoms, to form HOOH.

The ca. 100 kcal/mol of resonance stabilization of triplet $^{\bullet}OO^{\bullet}$, relative to the localized radical centers in two hydroxyl radicals (reaction D in Table 1), explains why trimerization of triplet $^{\bullet}OO^{\bullet}$ is computed to be endothermic by 79.4 kcal/mol. On the other hand, the 51 kcal/mol resonance energy of triplet $^{\bullet}SS^{\bullet}$, relative to the localized radical centers in two thiyl radicals (reaction K in Table 1), is only about half that of triplet $^{\bullet}OO^{\bullet}$; and this difference in stabilization energies is responsible for the fact that trimerization of triplet $^{\bullet}SS^{\bullet}$ is computed to be exothermic by 70.8 kcal/mol.

The very large resonance stabilization of triplet $^{\bullet}OO^{\bullet}$ is largely a consequence of the pair of two-center, three-electron bonds in this diradical. However, the overall resonance stabilization of O_2 is 100 kcal/mol, which is between 37 and 38 kcal/mol greater than the resonance stabilization of two molecules of $^{\bullet}OOH$. In MO theory most of this additional stabilization of triplet $^{\bullet}OO^{\bullet}$ comes from correlation between a pair of electrons, with opposite spins to those of the unpaired electrons, each of which occupies the bonding π MO of one of the two orthogonal π systems in this diradical. Correlation between the motions of these two electrons minimizes their Coulombic repulsion energy.

In VB theory the explanation of the very large stabilization of triplet $^{\bullet}OO^{\bullet}$ is similar to that given in MO theory. Two non-zwitterionic resonance structures dominate the higher energy zwitterionic structures in the VB wave function for triplet $^{\bullet}OO^{\bullet}$.

The 100 kcal/mol resonance energy of the triplet $^{\bullet}OO^{\bullet}$ diradical, which stabilizes it kinetically against both hydrogen atom abstraction and oligomerization, can be viewed as an important reason why O_2 is abundant in the atmosphere of earth. The fact that O_2 currently constitutes 20.94% of earth's atmosphere makes it readily available to participate in the oxidation reactions that form CO_2 and H_2O from organic molecules.

The weakness of the σ bond in $^{\bullet}OO^{\bullet}$ and in the peroxides formed from it makes the oxidation reactions that generate CO_2 and H_2O from the reactions of $^{\bullet}OO^{\bullet}$ with organic molecules highly exothermic, despite the large loss of resonance energy that is associated with addition reactions to this triplet diradical. Consequently, it is the unusual combination of strong π bonding and weak σ bonding in $^{\bullet}OO^{\bullet}$ that enables this molecule to provide the chemical energy that sustains all of the aerobic forms of life on earth.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b04232.

Experimental heats of formation, what Linus Pauling had to say about $^{\bullet}OO^{\bullet}$, O_4 cyclic dimer of O_2, O_6 and O_8 cyclic oligomers of O_2, examples of unreactivity of O_2, and what accounts for the large difference between the O−O σ BDEs in O_2 and in HOOH (PDF)

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(50) There is also a substantial literature on the bonding (and loss of magnetism, and coloration) that develops in oxygen under pressure. Leading references here are: (a) Meng, Y.; Eng, P. J.; Tse, J. T.; Shaw, D. M.; Hu, M. Y.; Shu, J.; Gramsch, S. A.; Kao, C.; Hemley, R. J.; Mao, H. *Proc. Natl. Acad. Sci. U. S. A.* **2008**, *105*, 11640−11644. (b) Lundegaard, L. F.; Weck, G.; McMahon, M. I.; Desgreniers, S.; Loubeyre, P. *Nature* **2006**, *443*, 201.

(51) A more precise analysis would have to include the changes that occur when the σ bonds of three O_2 molecules are transformed into three of the σ bonds of O_6.

(52) (a) The hydrogen tetraoxide molecule (HOOOOH) has been synthesized and characterized by Raman spectroscopy: Levanov, A. V.; Sakharov, D. V.; Dashkova, A. V.; Antipenko, E. E.; Lunin, V. V. *Eur. J. Inorg. Chem.* **2011**, *2011*, 5144−50. (b) The results of calculations of the equilibrium constant for the dimerization of HOO$^\bullet$ to HO_4H have been reported: Sprague, M. K.; Irikura, K. K. *J. Phys. Chem. A* **2015**, *119*, 7052−62 and references cited therein. (c) The dimerization of two peroxyl radicals, $^\bullet$OOR, to form the tetraoxide, ROOOOR, is, in fact, the chain terminating step in autooxidation reactions. For a very interesting theoretical study of why the fate of the tetraoxide depends on whether R contains a secondary or tertiary carbon attached to O, see: Lee, R.; Gryn'ova, G.; Ingold, K. U.; Coote, M. L. *Phys. Chem. Chem. Phys.* **2016**, *18*, 23673−79.

(53) It should be noted that the average O−O bond energy in O_6 and the value of what the BDE of the central bond in HOO−OOH would be, without the resonance stabilization of the $^\bullet$OOH radicals formed when this bond breaks, are both considerably larger than the O−O BDE of 48.9 kcal/mol in H_2O_2 (reaction R in Table 2). Donation of lone pairs of electrons from the oxygens α to an O−O bond into the σ^* orbital of the bond provides stabilization of the lone pairs on the oxygens that flank each of the O−O bonds in O_6 and in HOO−OOH.

(54) Using the Wolfsberg−Helmholtz approximation for estimating the strengths of bonding interactions, most or all of this difference in S−S and O−O π bond strengths can be attributed to the fact that sulfur is less electronegative than oxygen. Wolfsberg, M.; Helmholz, L. J. *J. Chem. Phys.* **1952**, *20*, 837.

(55) Nevertheless, Pratt and co-workers have found that hydropersulfides (RSSH) react exothermically with peroxyl radicals to form hydroperoxyls and persulfide radicals: Chauvin, J.-P. R.; Griesser, M.; Pratt, D. A. *J. Am. Chem. Soc.* **2017**, *139*, 6484−93. Indeed, using the G4 energies in Table S1 of the Supporting Information, the reaction $^\bullet$OOH + HSSH → HOOH + $^\bullet$SSH is calculated to be exothermic by 13.5 kcal/mol, despite the fact that comparison of reactions A and H in Table 1 indicates that the $^\bullet$OOH radical has 14 kcal/mol greater resonance stabilization than the $^\bullet$SSH radical. The explanation for the finding that the more resonance stabilized radical reacts to form the less resonance stabilized radical is that an S−H bond (e.g., in H_2S) is, according to the heats of formation in Table S1, 28 kcal/mol weaker than an O−H bond (e.g., in H_2O).

(56) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, 1960; p 92.

(57) The ATcT value of $\Delta_f H°(298.15\ K)$ for an oxygen atom is 59.6 kcal/mol,[22] which means that the BDE of triplet $^\bullet$OO$^\bullet$ to two atoms of ^{3}P $^\bullet$O$^\bullet$ is 119.2 kcal/mol. If the π BDE in $^\bullet$OO$^\bullet$ is 100 kcal/mol, then the BDE of the σ bond is only 19 kcal/mol, which is about 30 kcal/mol less than that of the O−O σ bond in HOOH in reaction R of Table 2. One of the contributors to this large difference in O−O σ BDEs is discussed in section S-6 of the Supporting Information.

(58) (a) Benson, S. W. *J. Chem. Educ.* **1965**, *42*, 502. (b) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976; pp 63−65. (c) Benson's thermochemical value of the π BDE in ethylene is essentially the same as the value that was obtained from the kinetics of the *E*−*Z* isomerization of ethylene-1,2-d_2 by: Douglas, J. E.; Rabinovitch, B. S.; Looney, F. S. *J. Chem. Phys.* **1955**, *23*, 315.

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