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The Oxyallyl Diradical: Observation of the Singlet and Triplet State by Negative-Ion Photoelectron Spectroscopy**

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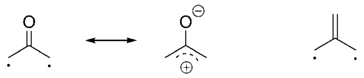
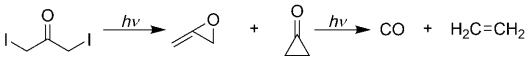
The oxyallyl diradical **1** has so far escaped direct spectroscopic observation. This is remarkable in view of its possible involvement as a reactive intermediate in a number of organic transformations, such as the Favorskii rearrangement,[1] cyclopropanone stereomutation,[2] and photochemical rearrangement of cyclohexadienones,[3] to name a few. Triplet oxyallyl ^{3}**1** was predicted to be a rather stable C_3H_4O isomer on the triplet potential energy hypersurface in a thermodynamic *and* kinetic sense.[4] The elusive nature of **1** is all the more remarkable as the related non-Kekulé hydrocarbon, trimethylenemethane (TMM, **2**), was synthesized and characterized in its triplet ground state by EPR spectroscopy in the seminal work of Dowd more than 40 years ago.[5]



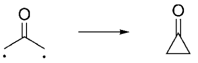
1 **2**

The failure to directly observe **1** is not because of a halfhearted experimental endeavor. Indeed, a number of unsuccessful attempts have been reported; among them is the photolysis of 1,3-diiodoacetone [Eq. 1].[6] Cyclopropanone (**3**) and allene oxide (**4**), instead of **1**, can be unambiguously identified among other species. These compounds decompose into ethylene and carbon monoxide after longer irradiation times.[6] This experiment suggests a reason for the inability to observe the oxyallyl diradical: the energy barrier for the ring-closure reaction to give cyclopropanone [Eq. 2] might be too low.



4 **3**

(1)



1 **3**

(2)

Often when nature sets the limits for experimental methods, theory can provide further insight. Borden and coworkers laid the foundation for an understanding of the oxyallyl diradical.[7] In TMM (**2**) there are two degenerate nonbonding molecular orbitals (NBMOs) and as these are nondisjoint, a triplet ground state results.[5] The presence of the oxygen atom in **1** lifts the degeneracy of these NBMOs; as a consequence, the singlet ($^1A_1$, ^{1}**1**) and triplet ($^3B_2$, ^{3}**1**) states become almost degenerate.

What is more important is that the singlet oxyallyl diradical can easily undergo a ring-closure reaction. Indeed, it is not even clear if the compound in its singlet state corresponds to a minimum on the C_3H_4O potential energy surface. Borden and co-workers arrive at an energy barrier for disrotatory ring closure of 0.33 kcal mol^{-1}, by employing the CASSCF level of theory using explicit correlations of four electrons in four orbitals.[7] Furthermore, investigations by Schröder, Schwarz, and co-workers note an annoying dependence of the number of imaginary vibrational frequencies upon the size of the active space.[4] These authors therefore conclude that the nature of the singlet oxyallyl diradical—minimum or (higher order) saddle point—is unclear, but that "it is very likely to escape all attempts of its generation and identification by neutralization-reionization mass spectrometry."[4]

The decisive properties for stability and observability of the oxyallyl ^{3}**1** are the energy difference between singlet and triplet states, and the probability of hopping onto the unstable singlet surface. To arrive at a reliable singlet–triplet gap, Schröder, Schwarz, and co-workers systematically increased the level of theory by using multireference techniques in the context of perturbation theory, configuration interaction, and averaged coupled-pair functional (MR-ACPF) formulations.[4] All these methods agree upon a triplet ground state of **1**, but the singlet–triplet energy difference becomes smaller with increasing sophistication, arriving at 0.3 kcal mol^{-1} at the MR-ACPF/cc-pVTZ level of theory.[4] As the computed spin-

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orbit coupling element turned out to be extremely small (0.05 cm^{-1}) and as this mechanism is expected to provide the strongest contribution to the probability of transition from the "stable" triplet to the "unstable" singlet state, it was concluded that the "triplet lifetime may suffice for its detection."[4]

The detection of the triplet and the singlet state of **1** has now been achieved by Lineberger and co-workers using negative ion photoelectron spectroscopy (NIPES).[8] It was therefore possible to address the fundamental issues of the oxyallyl diradical from an experimental perspective for the first time: the size of the singlet–triplet energy gap and the nature of singlet oxyallyl diradical. The oxyallyl system was produced by photodetachment from the mass-selected oxyallyl radical anion. This in turn was synthesized from the reaction of the atomic oxygen radical anion with acetone. In the photoelectron spectra the authors observe a number of peaks with different spacings: one series with a spacing of (405 ± 10) cm^{-1} is assigned to the triplet state of oxyallyl diradical. Based on computations, the observed vibrational progression is due to the CCC bending mode that is activated as the bond angles in the radical anion and neutral triplet differ significantly. Another series with a spacing of (1680 ± 50) cm^{-1} is ascribed to the vibrational progression of the CO stretching vibration in the singlet oxyallyl diradical due to shortening of the CO bond upon electron loss. This large value for the CO stretching vibration suggests a substantial CO double bond character in the singlet oxyallyl diradical.[7b]

The origins of the assigned NIPES bands suggest that the oxyallyl diradical has a singlet electronic ground state with an adiabatic singlet–triplet energy gap of 1.3 kcal mol^{-1}. This energetic preference for the singlet state is in contrast to the most sophisticated calculations available.[4] Possible reasons for the discrepancy may be associated with neglecting the dynamic correlation in the calculation of the oxyallyl structures used for the energy refinement and the limitations in the applied one-electron basis sets.

Is the singlet oxyallyl diradical a reactive intermediate or a transition state? This question has also been answered by the recent NIPES study.[8] The broadness of the peaks in the photoelectron spectrum associated with the singlet oxyallyl diradical can be attributed to lifetime broadening, a phenomenon that results from the transition-state nature of the species. This result is in agreement with newly performed calculations that include electron correlation at the CASPT2 level of theory and that arrive at a barrierless formation of cyclopropanone from the singlet oxyallyl diradical. CASPT2 calculations with the aug-cc-pVTZ basis set also found the singlet to be lower in energy than the triplet by 1.3 kcal mol^{-1}, essentially in exact agreement with the experimental value.[9]

The recent study by Lineberger and co-workers answers the essential questions with respect to the oxyallyl diradical: the singlet state is slightly lower in energy than the triplet state, but it does not correspond to a minimum on the potential energy surface. The experiment by Lineberger and co-workers is therefore another example in which NIPES allows the observation of transition states. In hindsight it is indeed ironic that after the successful synthesis of **3** in 1966,[10] an open oxyallyl structure was considered.[11]

Another interesting small and elusive molecule with a similar potential energy surface is ethylene dione, OCCO. Like the oxyallyl diradical, it is computed to have a triplet state that is stable towards dissociation. The singlet state is higher in energy by more than 10 kcal mol^{-1}, but does not correspond to an energy minimum. It is indeed unbound and its population results in the dissociation into two CO molecules. As this unbound surface crosses the triplet surface in the vicinity of its minimum, ethylenedione is also an "intrinsically short-lived molecule".[12] It remains to be seen if NIPES investigations can provide additional insight into the properties of this long sought after species.

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