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The Lowest Singlet and Triplet States of the Oxylallyl Diradical

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The Lowest Singlet and Triplet States of the Oxylallyl Diradical

Abstract
Photodetachment of the oxyallyl radical anion leads to formation of the oxyallyl diradical, an elusive transient molecule involved in many organic reactions. As described by W. C. Lineberger et al. in their Communication on page 8509 ff., the photoelectron spectrum reveals that the oxyallyl ground state is singlet and the lowest triplet state is only 55 meV higher in energy. The spectral profile indicates that the planar singlet state is the transition state for ringopening of cyclopropanone, whilst the CCC bending motion is activated upon photodetachment to the triplet state.

Keywords
oxylallyl, diradical, states, lowest, triplet, singlet

Disciplines
Life Sciences | Physical Sciences and Mathematics | Social and Behavioral Sciences

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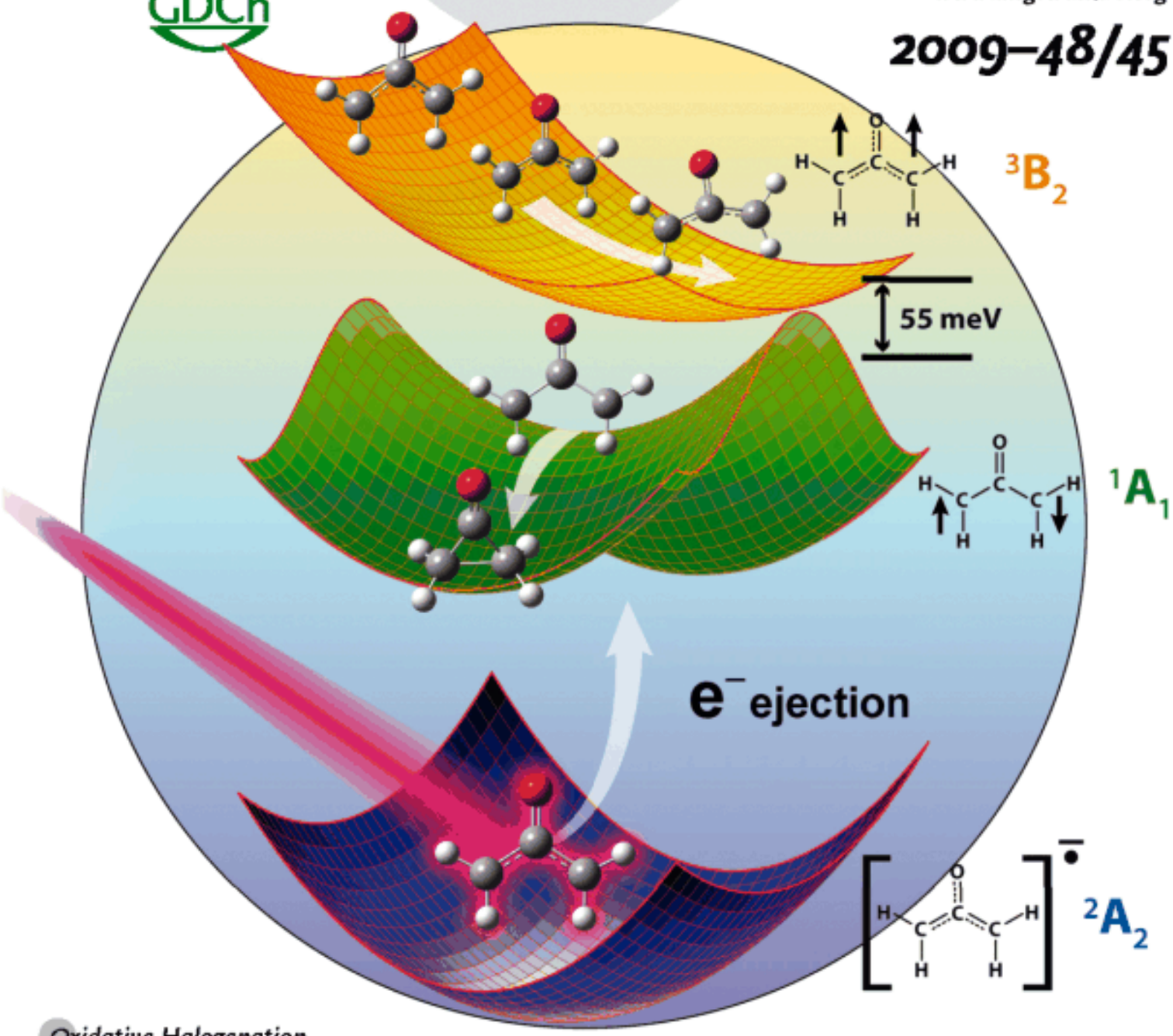

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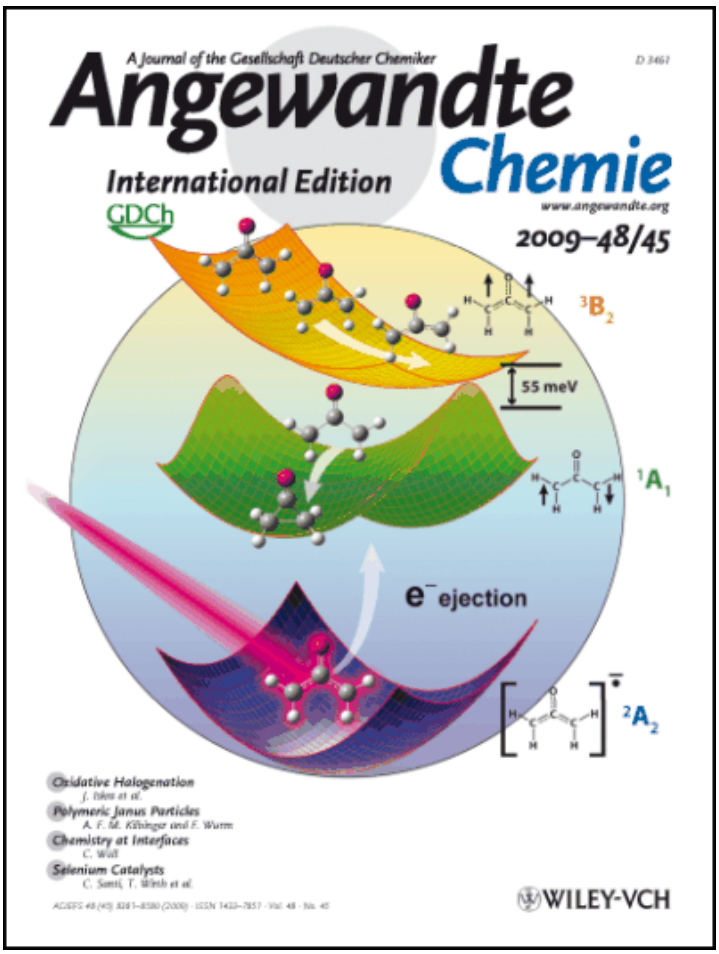

Photodetachment of the oxyallyl radical anion leads to formation of the oxyallyl diradical, an elusive transient molecule involved in many organic reactions. As described by W. C. Lineberger et al. in their Communication on page 8509 ff., the photoelectron spectrum reveals that the oxyallyl ground state is singlet and the lowest triplet state is only 55 meV higher in energy. The spectral profile indicates that the planar singlet state is the transition state for ring-opening of cyclopropanone, whilst the CCC bending motion is activated upon photodetachment to the triplet state.

VIP Diradicals

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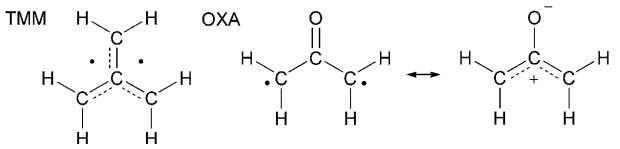
The Lowest Singlet and Triplet States of the Oxyallyl Diradical**

*Takatoshi Ichino, Stephanie M. Villano, Adam J. Gianola, Daniel J. Goebbert, Luis Velarde, Andrei Sanov, Stephen J. Blanksby, Xin Zhou, David A. Hrovat, Weston Thatcher Borden, and W. Carl Lineberger**

Oxyallyls are reactive intermediates, whose participation has been postulated in the ring opening of cyclopropanones[1] and allene oxides,[2] in the Favorskii rearrangement,[3] and in a variety of synthetically useful transformations.[4] The parent oxyallyl (OXA) can be viewed as a derivative of trimethylenemethane (TMM), in which one methylene group is replaced by an oxygen atom (Scheme 1).



Scheme 1. Trimethylenemethane (TMM) and oxyallyl (OXA).

TMM has been the subject of many theoretical and experimental studies.[5] ESR measurements by Dowd and co-workers showed that TMM has a triplet ground state.[6] This fact is in accord with Hund's rule, since triplet TMM has a degenerate pair of half-filled, nonbonding π molecular orbitals (MOs), ψ_2 and ψ_3, that are nondisjoint[7] (i.e., they share common atoms, Figure 1). Lineberger and co-workers determined the energy difference between the triplet and the lowest, planar, singlet states to be (16.1 ± 0.2) kcal mol^{-1} in photoelectron spectroscopic measurements.[8] There is excellent agreement between this experimental investigation[8] and prior ab initio calculations[9] with respect to the singlet–triplet (S–T) energy separation.

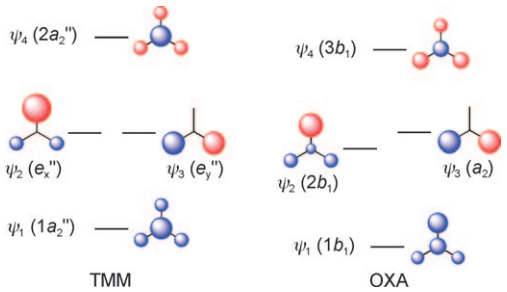


Figure 1. Schematic representation of the π MOs (top lobes only) of TMM (D_{3h} symmetry) and OXA (C_{2v}). In the OXA radical anion, MOs are doubly occupied up to $2b_1$, and a_2 is singly occupied.

The oxygen substitution in OXA strongly lifts the degeneracy of ψ_2 and ψ_3 in TMM, stabilizing the $2b_1$ MO relative to the a_2 MO (Figure 1).[10] The best ab initio calculations have predicted that the S–T splitting in OXA should be close to zero, with the singlet state possibly even slightly lower than the triplet state.[11] The calculations also indicate that singlet OXA has a strong C–O π bond;[10] that is, the first of the two resonance structures, shown in Scheme 1, provides a much better description of the lowest singlet state of OXA than the second resonance structure, which is zwitterionic. In contrast to these theoretical efforts to understand the electronic structure, no direct experimental detection of OXA has been reported to date.

Herein, we report the photoelectron spectrum of the OXA radical anion. The spectrum gives the relative energies of the lowest singlet and triplet states of OXA and provides information about important vibrations in each state.

The OXA radical anion was synthesized in helium buffer gas through the reaction of the atomic oxygen radical anion ($O^{\bullet-}$) with acetone. Photodetachment from the mass-selected OXA radical anion was effected with a UV laser (351.1 nm, 3.531 eV).[12,13] Figure 2 displays the photoelectron spectra, taken at different values of the angle θ formed by the electric field vector of the laser beam and the photoelectron momentum vector. The photoelectron intensity can be expressed as given in Equation (1):[14]

$$I(\theta) = \frac{\sigma_0}{4\pi}[1 + \beta P_2(\cos\theta)] \quad (1)$$

Here, σ_0 and β are the total cross section and the anisotropy parameter, respectively, and $P_2(\cos\theta)$ is the second Legendre

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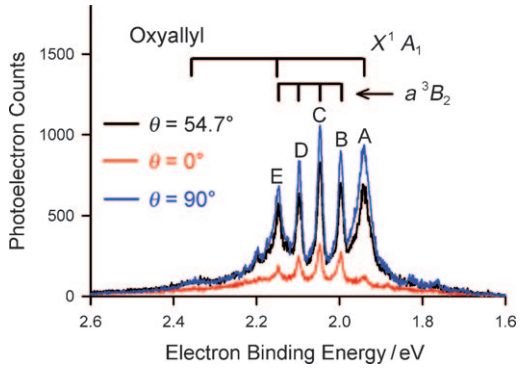

Figure 2. Photoelectron spectra of the OXA radical anion.

polynomial. Depending on the MO from which detachment takes place, a unique angular distribution of photoelectrons is observed, and this angular dependence is characterized by the β parameter ($-1 \leq \beta \leq 2$).

Peaks B, C, D, and E exhibit identical peak spacings of (405 ± 10) cm^{-1}. Peak A shows two features that distinguish it from these other four peaks. First, the β value for peak A is more negative than those for the other peaks. Its relative intensity diminishes to a greater extent than those of the other peaks at $\theta = 0°$. Second, peak A is much broader than peaks B–E. These observations lead us to believe that peak A and peaks B–E are associated with two different electronic states of OXA.

B3LYP/6-311++G(d,p) calculations[15] predict that the electron binding energy (eBE) of the OXA radical anion, relative to the triplet ($^3B_2$) state of OXA, is 1.979 eV, which matches quite well with the eBE of peak B. The C-C-C bond angles of $^3B_2$ OXA and of the $^2A_2$ ground state of the radical anion at their equilibrium geometries are calculated to be 121.9° and 114.4°, respectively. Thus, photodetachment to form $^3B_2$ OXA is expected to activate the C-C-C bending motion. The corresponding normal mode of $^3B_2$ OXA has a harmonic vibrational frequency of 408 cm^{-1} according to the DFT calculations. Therefore, it is concluded that peaks B–E represent a vibrational progression in the C-C-C bending mode of $^3B_2$ OXA.

The singlet ($^1A_1$) state of OXA cannot be adequately described by a single electronic configuration.[10,11] Therefore, (4,4)CASSCF and CASPT2 calculations[15] were performed on this state, which we associate with peak A. The CASSCF/cc-pVTZ calculations find that the planar $^1A_1$ state is a very shallow energy minimum, which vanishes when zero-point corrections are made to the energy of $^1A_1$ OXA and to that of the transition state for its disrotatory ring closure to cyclopropanone. Upon inclusion of dynamic electron correlation at the CASPT2 level of theory, a scan along the b_1 coordinate for the ring closure finds that formation of cyclopropanone from $^1A_1$ OXA is barrierless. Thus, the broad width of peak A can be attributed to lifetime broadening arising from the transition-state nature of $^1A_1$ OXA.

The spectrum also exhibits a broad band at the base of peak E. This broad band is located at (1680 ± 50) cm^{-1} relative to peak A, and another broad band can be seen at higher eBE, with the same spacing, relative to peak E. CASSCF calculations predict a shortening of the C–O bond by 0.057 Å upon electron loss from the $^2A_2$ state of the radical anion to form $^1A_1$ OXA.[16] Thus, it is reasonable to suppose a manifestation of a vibrational progression in C–O stretching for the $^1A_1$ state in the spectrum. It should be noted that acetone has a fundamental frequency of 1731 cm^{-1} for the C–O stretching mode;[17] hence, the observed peak spacing confirms the theoretical prediction of substantial C–O double-bond character in $^1A_1$ OXA.[10] The observation of $^1A_1$ OXA attests to the utility of negative ion photoelectron spectroscopy as a means of studying transition states.[18]

In summary, both the ground and first excited states of OXA have been observed in the photoelectron spectrum of the corresponding radical anion. The electron affinity of OXA is (1.942 ± 0.010) eV. The ground state is $^1A_1$, but the adiabatic energy of the $^3B_2$ state is only (55 ± 2) meV (1.3 kcal mol^{-1}) higher than that of the singlet ground state. The spectrum indicates that the $^1A_1$ state has a strong C–O π bond and undergoes barrierless ring closure to form cyclopropanone. The results of previous electronic structure calculations[10,11] and those of the calculations conducted in the present study are in excellent agreement with the experimental findings reported herein.

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Keywords: oxyallyl compounds · photoelectron spectroscopy · radicals · reactive intermediates

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[13] The acetylcarbene radical anion is an isomer of the OXA radical anion, and it is a minor product of the reaction of $O^{\cdot-}$ with acetone (see J. H. J. Dawson, A. J. Noest, N. M. M. Nibbering, *Int. J. Mass Spectrom. Ion Processes* **1979**, *30*, 189–191; M. X. Lin, J. J. Grabowski, *Int. J. Mass Spectrom.* **2004**, *237*, 149–165). Photodetachment from this minor ion product is responsible for the weak background signals in the spectrum shown in Figure 2, as confirmed by independent measurements of isotopically labeled ions. A more detailed account of the analysis of the spectrum will be given in a full paper.

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[16] In the second configuration of the CASSCF wavefunction for $^1A_1$ OXA, the pair of electrons in the $2b_1$ MO in the dominant configuration are transferred into the a_2 MO. Consequently, the occupation number of the $2b_1$ MO is smaller in $^1A_1$ OXA than in the $^2A_2$ state of the radical anion (1.44 vs 1.93). Since, as shown in Figure 1, $2b_1$ is C–O antibonding, the difference in occupation of this MO explains why $^1A_1$ OXA has a shorter C–O bond than the $^2A_2$ state of the radical anion.

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