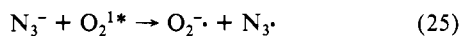


in a polar environment, regardless of whether the host surfactant is neutral or negatively or positively charged.

The enhanced production of **4** and **5** in the presence of azide ion could be attributed to the fact that one path for azide quenching can involve production of superoxide (eq 25) as recently



demonstrated.^{64,65} Thus in the aqueous media rapid protonation of the superoxide ion followed by disproportionation could produce H_2O_2 . In experiments using a 360-nm cutoff filter, we have found that irradiation of solutions containing micellar (SDS) **1** and H_2O_2 leads to enhanced production of **4**, **5**, and **6**.⁶⁶ The reason for the enhancement of **4-6** in the presence of azide in SDS compared to Brij 35 remains undetermined.

The increased prominence of the electron transfer path for photooxidation in the organized media used in this study is

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(66) There is no discernible reaction between micellar **1** and H_2O_2 in the absence of light.

noteworthy. It is not unreasonable that the behavior observed here should be quite general and perhaps indicative of similar effects in biological photooxidations occurring in various membrane protein environments. It is reasonable to anticipate that generation of superoxide on H_2O_2 in such environments could give rise to extremely complicated reaction sequences. It is tempting to suggest that the differences observed in this study on changing from a homogeneous organic solvent to aqueous surfactant assemblies parallel to some extent the differences between well-characterized singlet oxygen photooxygenations and "photodynamic action" in biological systems. The similarity of results obtained with the various micellar media and the vesicles formed from the natural lipid DPPC suggest that, at least in this instance, the micelles provide an environment similar to that for the lipid portion of biomembranes. We are currently extending these studies to other vesicle systems and to media containing other substrates susceptible to sensitized photooxidation.

Acknowledgment. We are grateful to the U.S. Army Research Office (Contract DAAG29-80-K-0066) for support of this research.

Triplet-to-Singlet Cyclopropylidene-Allene Rearrangement. A Molecular Example of Spin Angular Momentum Coupling in Orthogonal π Systems

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Abstract: Valence-bond and molecular-orbital theories are used to support each other in showing the feasibility of triplet-to-singlet cyclopropylidene-allene rearrangement. It is shown that the symmetry of the orbitals involved and the symmetry of the spin-orbit interaction operators demand an orbitally rotated state corresponding to an orthogonal allene, so as to have a nonvanishing spin-orbit matrix element. As a result, singlet *orthogonal* allene will have a favorable transmission coefficient from triplet cyclopropylidene. This is believed to be general in all perpendicular π -electron systems. Use is made of Hückel-Möbius orbitals for *both* the reactant and the product, to ensure symmetry correlation and orbital following. In addition, a method is devised to correlate an *individual* electron in a spin orbital that circumvents the conventional restriction of having to correlate a spatial orbital with *both* of the two electrons at once. This method simultaneously accounts for molecular-orbital configuration interaction and ensures the correct dissociation limit. It is also postulated that the intermediate state involves angular momentum coupling of two triplets containing a total of four electrons. The resultant singlet-state function correlates well with that of the two orthogonal π bonds of the product allene.

Cyclopropylidene has been of interest for a long time.¹ Its rearrangement into allene has been studied theoretically and experimentally until most recently.²⁻¹¹ These include *ab initio*, MINDO and INDO, etc. The interest lies not only in its place in carbene chemistry^{12,13} but also in its rearrangement mechanism.¹⁴ So far, singlet cyclopropylidene to singlet (especially planar) allene has been more thoroughly studied and understood. And it is generally accepted that opening of triplet cyclopropylidene to triplet (planar) allene is a forbidden process.² Little work appears to exist on the triplet-to-singlet rearrangement. We propose here to show by a combination of valence-bond and molecular-orbital arguments that the ring-opening rearrangement of triplet cyclopropylidene to *orthogonal* singlet allene is a symmetry-allowed and -favored process. This, we shall show, is because of the unique spin-orbit interaction leading to the perpendicular π -electron system of allene. We shall make use of the symmetry of spin and orbital angular momentum operators,¹⁵⁻²⁰

symmetry of spin functions,^{23,24} Hückel and Möbius orbitals,^{21,22} and the orbital following the idea of Zimmerman.^{21,25}

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[†] Work done while on IPA leave at the Chemical Kinetics Division, National Bureau of Standards.

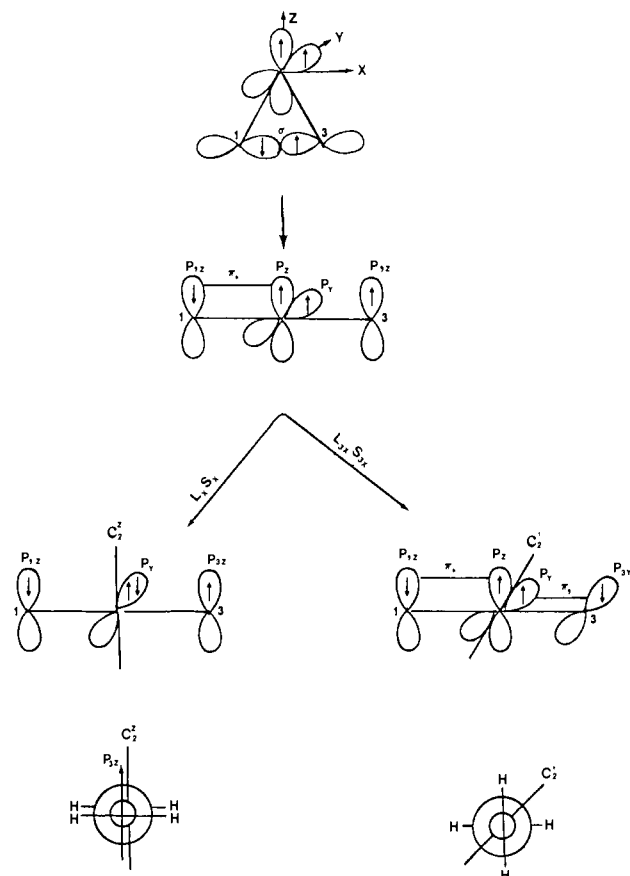


Figure 1. Valence-bond view of triplet cyclopropylidene rearrangement to singlet planar allene (lower left) and to singlet orthogonal allene (lower right).

We take the cyclopropylidene carbon skeleton to be on the xz plane (Figure 1) with the z axis passing through the center atom and bisecting the line formed by the "end atoms" C-1 and C-3. The system initially has C_{2v} symmetry. In the reaction when C_2^z symmetry only is meaningful (e.g., conrotatory opening of the ring) the irreducible symmetry representations are a and b , when only σ_v^{yz} is meaningful (e.g., disrotatory ring opening) the representations are a' and a'' , and when C_{2v} is conserved (e.g., nonrotatory ring opening to planar allene) the representations are a_1 , a_2 , b_1 , and b_2 . The two unpaired electrons of triplet cyclopropylidene may be considered to reside in the two sp^2 -hybrid valence-bond orbitals at the center carbon atom, $\phi_0 \cong \frac{1}{2}(P_z + P_y)$ and $\phi_2 \cong \frac{1}{2}(P_z - P_y)$, where the s orbital is omitted for brevity and the orbitals are not normalized. They may also be considered to reside in $P_z \cong \phi_0 + \phi_2$ and $P_y \cong \phi_0 - \phi_2$.

We start with the valence-bond picture of the ring opening and take the two unpaired electrons of the triplet to reside on P_z and P_y . By orbital symmetry, the triplet state is necessarily 3B (in C_2 point group but ${}^3A'$ in C_s and 3B_2 in C_{2v}) and is designated

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with a subscript c as it comes mainly from the center atom, viz.

$${}^3B_c = \frac{1}{\sqrt{2}}(P_y(1) P_z(2) - P_y(2) P_z(1)){}^3\tau$$

$$= \frac{1}{\sqrt{2}}(\phi_0(1) \phi_2(2) - \phi_0(2) \phi_2(1)){}^3\tau \quad (1)$$

where ${}^3\tau$'s are the triplet spin wave functions $\alpha_1\alpha_2$, $\beta_1\beta_2$, and $(1/\sqrt{2})(\alpha_1\beta_2 + \beta_1\alpha_2)$.

When the ring opens (assuming in a nonrotatory manner for the sake of discussion), the broken σ_{13} bond with two-electron 1A symmetry will lead to P_{1z} and P_{3z} orbitals at the end atoms C-1 and C-3. These two orbitals with two electrons will again form a singlet 1A_e where e stands for the end atoms. The orbital (e.g., P_{1z}) with the correct antiparallel (e.g., β) spin will form a π_z bond with the center P_z electron of the triplet (Figure 1). The other electron in P_{3z} will not bond with the remaining electron in P_y of the triplet because the orbitals are orthogonal and the spins are parallel. However, the intervention of the spin-orbit interaction operator $l_{3x}S_{3x}$ will "rotate" the P_{3z} orbital to P_{3y} and flips the spin to be antiparallel to that in P_y . The ensuing bonding between P_{3y} and P_y gives rise to the π_y bond, orthogonal to the already-formed adjacent π_z bond. This is the orthogonal allene which in the ground state is necessarily of 1A symmetry (although the C_2 symmetry axis now is midway between y and z rather than along z). The symmetry of the product, orthogonal allene, in fact dictates that the x component (instead of the z component) of the spin-orbit interaction operator be used, so that l_x which is of B symmetry will naturally convert the singlet of the end atoms 1A_e to 3B_c . The triplet 3B_c then couples^{23,24} with the triplet of the center atom 3B_c to give rise to the 1A state of orthogonal allene. In summary we have

$${}^3B \rightarrow {}^1A_e(P_{1z}P_{3z}) {}^3B_c(P_zP_y) \xrightarrow{l_xS_x} {}^3B_c(P_{1z}P_{3y}) {}^3B_c(P_zP_y) = {}^1A(\pi_z\pi_y) \quad (2)$$

The spin-orbit interaction matrix element referred to above is as follows:

$$\left\langle {}^3B_c[P_{1z}(i) P_{3y}(j) - P_{1z}(j) P_{3y}(i) - P_{1y}(i) P_{3z}(j) + P_{1y}(j) P_{3z}(i)] \frac{1}{2\sqrt{2}}(\alpha_i\alpha_j - \beta_i\beta_j) \left| \frac{1}{2}(\xi_j l_x(i) - \xi_j l_x(j))(S_x(i) - S_x(j)) \right| {}^1A_e[P_{1z}(i) P_{3z}(j) + P_{1z}(j) P_{3z}(i)] \frac{1}{\sqrt{2}}(\alpha_i\beta_j - \beta_i\alpha_j) \right\rangle \quad (3)$$

where the triplet spin ($\alpha_i\alpha_j - \beta_i\beta_j$) of B symmetry is required by the permutationally antisymmetric $S_x(i) - S_x(j)$ operator which is also of B symmetry in the C_2 point group. The "rotated" orbital (P_{3y} or P_{1y}) in eq 2 is accompanied by the concomitantly rotated CH_2 group forming the orthogonal allene. The coupling^{23,24} of the two triplets in eq 1-3 results in the following singlet state

$${}^1A = (1/\sqrt{6})\{|P_{1z}P_{3y}\bar{P}_y\bar{P}_z| - |P_{1y}P_{3z}\bar{P}_y\bar{P}_z| + |\bar{P}_{1z}\bar{P}_{3y}P_yP_z| - |\bar{P}_{1y}\bar{P}_{3z}P_yP_z| - 1/2[|P_{1z}\bar{P}_{3y}P_y\bar{P}_z| + |\bar{P}_{1z}P_{3y}P_y\bar{P}_z| - |P_{1y}\bar{P}_{3z}P_y\bar{P}_z| - |\bar{P}_{1y}P_{3z}P_y\bar{P}_z| + |P_{1z}\bar{P}_{3y}\bar{P}_yP_z| + |\bar{P}_{1z}P_{3y}\bar{P}_yP_z| - |P_{1y}\bar{P}_{3z}\bar{P}_yP_z| - |\bar{P}_{1y}P_{3z}\bar{P}_yP_z|]\} \quad (4)$$

which correlates well to the singlet ground state of orthogonal allene with two perpendicular π bonds in valence-bond notation, viz.

$${}^1A = 1/2[|P_{1z}\bar{P}_zP_{3y}\bar{P}_y| - |P_{1z}\bar{P}_z\bar{P}_yP_{3y}| - |P_{1z}P_zP_{3y}\bar{P}_y| + |P_{1z}P_z\bar{P}_yP_{3y}|] \quad (5a)$$

or

$${}^1A = 1/2[|P_{1y}\bar{P}_yP_{3z}\bar{P}_z| - |P_{1y}\bar{P}_y\bar{P}_zP_{3z}| - |P_{1y}P_yP_{3z}\bar{P}_z| + |P_{1y}P_y\bar{P}_zP_{3z}|] \quad (5b)$$

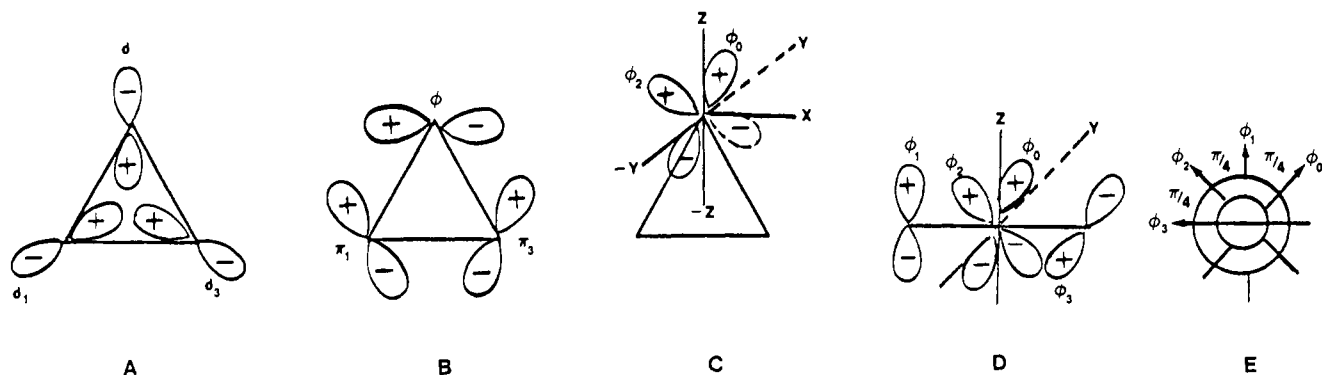


Figure 2. Coordinate system and the definition of the atomic orbitals used in cyclopropylidene (A–C) and in orthogonal allene (D, E). A is an in-plane Hückel system;²¹ B is an in-plane Möbius system.²¹ Together, A and B form the in-plane σ bonds of the Walsh model of cyclopropane. C shows the two orbitals that accommodate the two triplet electrons. ϕ_0 is 45° between y and z and ϕ_2 is 45° between $-y$ and z . D shows the π orbitals of orthogonal allene as a Möbius system.^{21,25} ϕ_1 is along z and ϕ_3 points along $-y$. E shows the end-view projection from the right end.

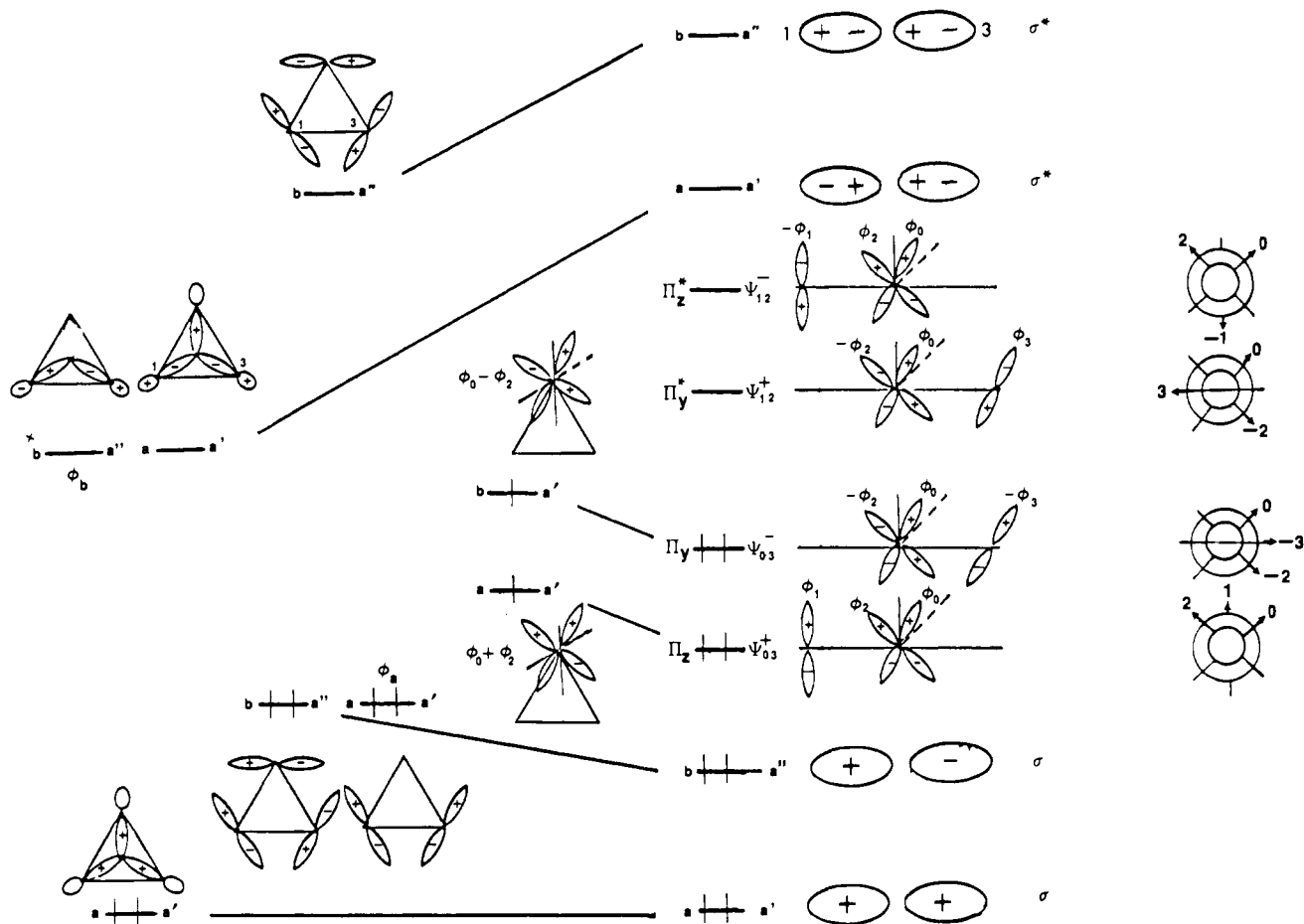


Figure 3. Molecular-orbital picture of triplet cyclopropylidene (left) and singlet orthogonal allene (right). The correlation is not complete without intervention of spin-orbit interaction. Where possible, the orbitals are designated by their symmetry with respect to C_2 (a , b) or with respect to σ^{yz} (a' , a''). The Möbius-orbital representation ψ^\pm of orthogonal allene (ref 27) clearly shows a π^z bond between C-1 and the center carbon atom (recognizing that $\phi_0 + \phi_2 \sim P_z$) and a π^y bond between C-3 and the center carbon atom (recognizing that $\phi_0 - \phi_2 \sim P_y$).

Note that this ground state is 1A with respect to C_2' (axis midway between y and z). Only if eq 5a is added to eq 5b will the resulting symmetrized wave function have 1A symmetry under C_2' .

Equations 1 and 2 with spin-orbit interaction generating perpendicular (P_{1y} or P_{3y}) orbitals are another way of saying that the orthogonal allene 1A state, resulting from monorotatory motion or conrotatory motion accompanying ring opening, will have a high transmission coefficient from the initial 3B state of cyclopropylidene via spin-orbit interaction. In Figure 1, the triplet cyclopropylidene after ring opening can alternatively forgo the nascent π_z bond formation and go to the planar singlet allene. This we think is a less likely path. It does so through $^3\psi(n\pi)$ to $^1\psi(\pi^2)$

conversion by spin-orbit interaction at the center carbon atom. The mechanism and the spin-orbit matrix element are as follows:

$$^3B_2 \rightarrow ^1A_c(P_{1z}P_{3z}) \ ^3B_c(P_zP_y) \xrightarrow{l_x S_x} ^1A_c(P_{1z}P_{3z}) \ ^1A_c(P_yP_y) = ^1A_1 \quad (6)$$

$$\left\langle ^1A_c P_y(i) P_y(j) \frac{1}{\sqrt{2}} (\alpha_i \beta_j - \beta_i \alpha_j) \middle| \frac{1}{2} (\xi_i l_x(i) - \xi_j l_x(j)) (S_x(i) - S_x(j)) \right\rangle ^3B_c [P_y(i) P_z(j) - P_y(j) P_z(i)] \frac{1}{2\sqrt{2}} (\alpha_i \alpha_j - \beta_i \beta_j) \quad (7)$$

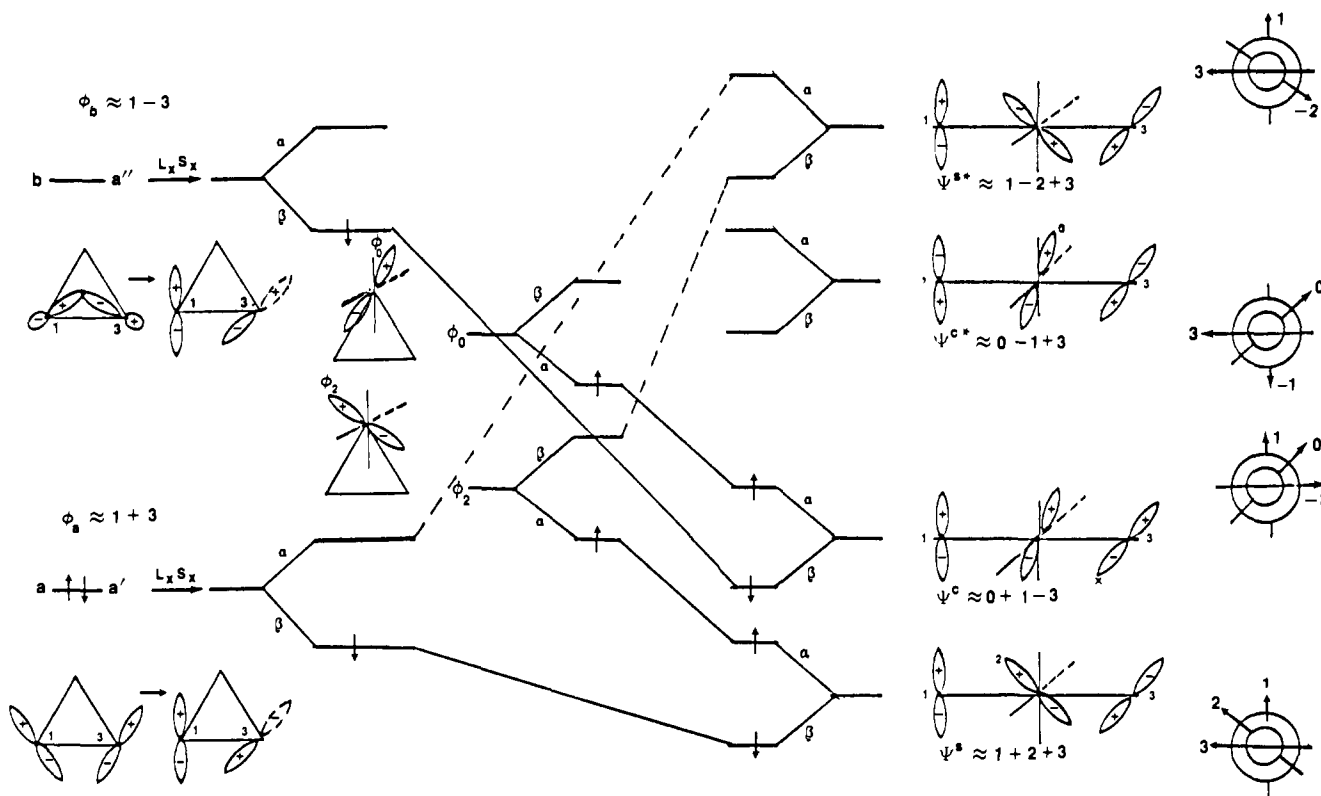


Figure 4. Each individual electron's spin-orbital correlation between triplet cyclopropylidene (left) and singlet orthogonal allene (right) for the four frontier electrons involved. This is after the spin-orbit interaction converts the singlet σ bond (ϕ_a^2) to triplet ($\phi_a \phi_b$), after spin angular momentum coupling of the two triplets, ($\phi_a \phi_b$) and ($\phi_0 \phi_2$), is allowed for, and after configuration interaction is considered (see text and eq 9). The dotted lines (only two out of four shown) indicate correlation to excited configuration of allene (ψ^{*2}) which when mixed into the ground configuration (ψ^2 , by solid lines) will ensure proper dissociation into the constituent orbitals (ϕ_a and ϕ_2) or (ϕ_b and ϕ_0) of cyclopropylidene. Another kind of Möbius-orbital representation (from the linear combination of the degenerate orbitals, ref 27) is used so that the numbering of orbitals gives good indication of orbital following.

We shall now come to the independently conceived molecular-orbital picture, which turns out to support the valence-bond view very well in terms of the symmetries of the states and orbitals. Furthermore, by devising a way to correlate spin-orbit rather than orbital alone, we are able to get MO configuration interaction that ensures correct dissociation of the states into the constituent atomic orbitals. These latter atomic orbitals form the required bonds in the valence-bond theory.

In Figure 2 we use the same coordinate system as the valence-bond treatment of Figure 1. We put the two triplet electrons at the center carbon atoms in $P_z \approx \phi_0 + \phi_2$ and $P_y \approx \phi_0 - \phi_2$ orbitals. The ϕ_0 and ϕ_2 are seen as none other than the two hybrid bond orbitals from the sp^2 ($sP_y P_z$) hybrid at the center carbon atom. The remaining sp^2 hybrid in the plane of the molecules forms one of the three equivalent " σ " orbitals directed toward the center of the triangle in the Walsh model of cyclopropane.²¹ Following Zimmerman²⁵ these three in-plane sp^2 hybrid valence-bond orbitals (which we will call σ , σ_1 , and σ_3) are treated as a Hückel system²⁶ (Figure 2) and the three in-plane orbitals perpendicular to the above (which we will call ϕ , π_1 , and π_3) are treated as the Möbius system.^{25,26} The four π orbitals (ϕ_0 , $\phi_1 = P_{1z}$, ϕ_2 , $\phi_3 = -P_{3y}$) of the orthogonal allene are arranged so that they are 45° apart (Figure 2) and treated as the Möbius system.^{25,27} Since no symmetry is strictly conserved during cyclo-

propylidene to orthogonal allene rearrangement, we rely on the explicit MO phases and pictures to give partial correlation in Figure 3 much in same way as in the orbital-following method of Zimmerman.²¹ However, as a correlation diagram for *triplet* cyclopropylidene to *singlet* orthogonal allene, the picture in Figure 3 is obviously incomplete and inaccurate. To account for spin inversion due to spin-orbit interaction and the subsequent correlation, we detail the changes in Figure 4. We still retain the triplet 3B_c at the center carbon atom of cyclopropylidene, now in ϕ_0 and ϕ_2 orbitals (see eq 1). And we concentrate on the doubly occupied Möbius orbital of a symmetry and the closely nearby empty Hückel orbital of b symmetry. The providence of having this b orbital close by with the correct symmetry is seen later to facilitate the spin-orbit interaction that favors the orthogonal allene. Conversion of the singlet configuration ϕ_a^2 to the triplet $\phi_a \phi_b$ configuration naturally requires either the x or y component of the spin-orbit interaction operator. This is because l_x and l_y

(26) The three Hückel MO's are as follows: the nondegenerate one with energy $E - \alpha = 2\beta_\sigma$, $(1/\sqrt{3})(\sigma + \sigma_1 + \sigma_3)$; the two doubly degenerate ones with $E - \alpha = -\beta_\sigma$, $(1/\sqrt{2})(\sigma_1 - \sigma_3)$ and $(1/\sqrt{6})(2\sigma - \sigma_1 - \sigma_3)$. The three Möbius MO's are as follows: the two doubly degenerate ones with energy $E - \alpha = \beta_\pi$, $(1/\sqrt{6})(2\phi + \pi_1 - \pi_3)$, $(1/\sqrt{2})(\pi_1 + \pi_3)$, and the nondegenerate one with energy $E - \alpha = -2\beta_\pi$, $1/\sqrt{3})(-\phi + \pi_1 - \pi_3)$. β is the overlap between the two neighboring orbitals. The interaction between the two systems is not considered, and it will not alter the qualitative overall molecular orbital symmetry and relative positions.

(27) The four Möbius MO's for the perpendicular allene are as follows: one set of two doubly degenerate orbitals with $E - \alpha = \sqrt{2}\beta_0$, $\psi_{0,3}^b = (1/2)\phi_1 + (1/\sqrt{2})\phi_2 + (1/2)\phi_3$ and $\psi_{0,3}^c = (1/\sqrt{2})\phi_0 + (1/2)\phi_1 - (1/2)\phi_3$, another set of two doubly degenerate orbitals with $E - \alpha = -\sqrt{2}\beta_0$, $\psi_{1,2}^b = (1/2)\phi_1 - (1/\sqrt{2})\phi_2 + (1/2)\phi_3$ and $\psi_{1,2}^c = (1/\sqrt{2})\phi_0 - (1/2)\phi_1 + (1/2)\phi_3$. These may be linearly combined to yield $\psi_{0,3}^{*b} = ((1/\sqrt{2})\phi_0 + \phi_1 + (1/\sqrt{2})\phi_2)/\sqrt{2}$ and $\psi_{0,3}^c = ((1/\sqrt{2})\phi_0 - (1/\sqrt{2})\phi_2 - \phi_3)/\sqrt{2}$, corresponding respectively to bonding π_x and π_y orbitals, and $\psi_{1,2}^{*b} = ((1/\sqrt{2})\phi_0 - (1/\sqrt{2})\phi_2 + \phi_3)/\sqrt{2}$ and $\psi_{1,2}^c = ((1/\sqrt{2})\phi_0 - \phi_1 + (1/\sqrt{2})\phi_2)/\sqrt{2}$ corresponding respectively to antibonding π_y^* and π_x^* orbitals. Note that we differ from Zimmerman's (ref 21) designation of Möbius cyclobutadiene. Our main reason is that the four-member Möbius ring is a truncated eight-member complete Möbius ring. As a truncated ring of four members the "Möbius" cyclobutadiene is not a complete circle and there is a distinct beginning and end. Therefore, the real coefficients cannot be shifted around the four-member truncated, incomplete circle at will. We have to match our coefficients with our orbital choices defining the Möbius system.

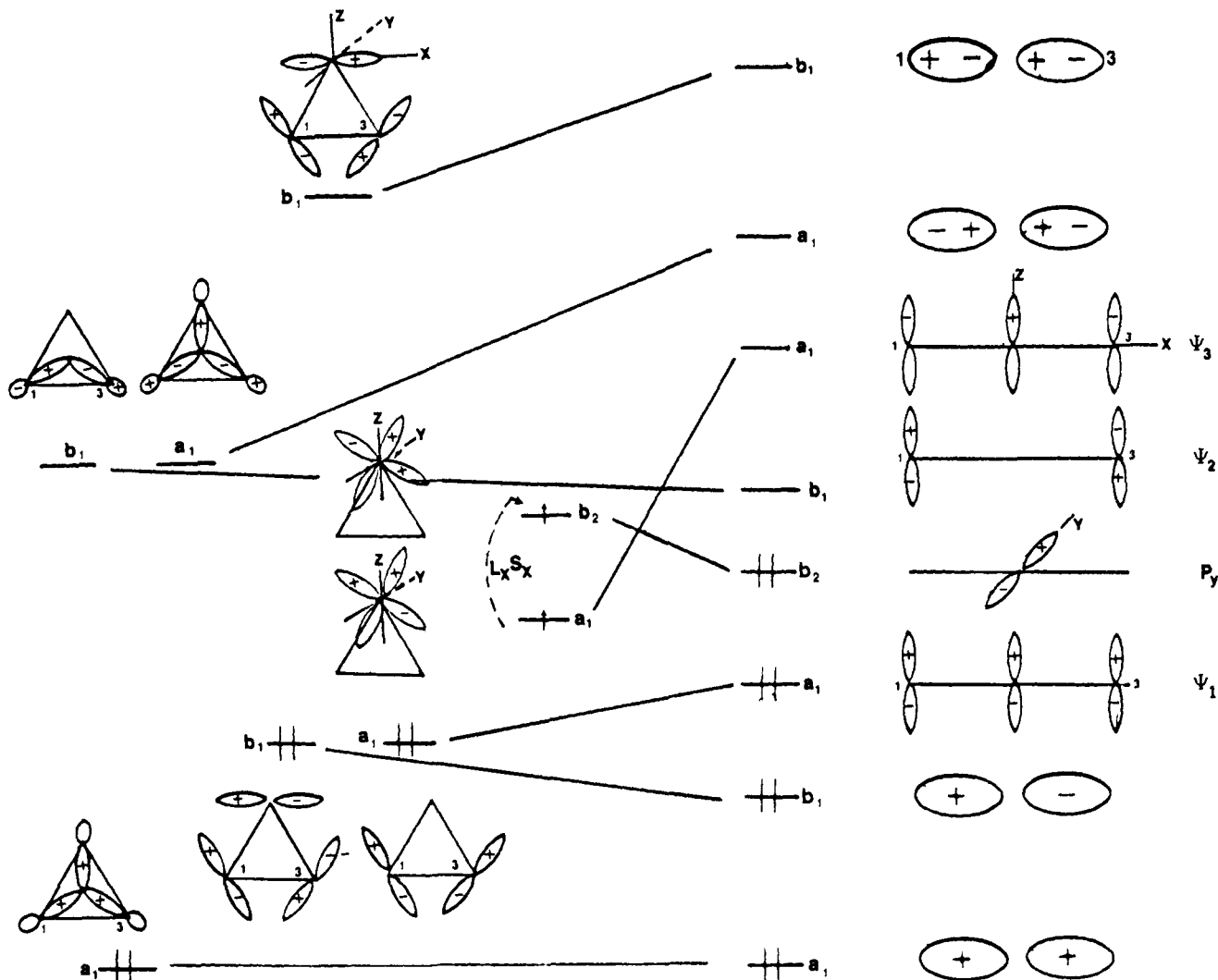
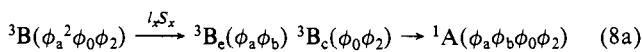


Figure 5. MO symmetry correlation for conversion of triplet cyclopropylidene to singlet planar allene. C_{2v} point group symmetry is conserved.

belong to b symmetry of the C_2 point group. Among these only l_x is seen to "rotate" P_{1z} and P_{3z} leading to the twisted (out of the yz plane) orbitals for the end atoms required for the orthogonal allene. This twisting of two end orbitals to be mutually orthogonal in a relative sense (e.g., P_{1z} vs. P_{3y}) can be achieved by conrotatory or monorotatory motion during ring opening. If we represent the orthogonal allene by the ψ^c and ψ^s set of Möbius orbitals,^{22,27} they are seen to correlate perfectly to the spin-orbitally favored twisted "triplet" orbitals $\phi_a\phi_b$. The result coming from the coupling of ${}^3B_c(\phi_a\phi_b)$ and ${}^3B_c(\phi_0\phi_2)$ will again give rise to a singlet 1A (besides a triplet and a quintet) orthogonal allene as follows (compare eq 2):



where the 3B_c came from the following spin-orbit interaction:

$$\left\langle {}^3B_c[\phi_a(i)\phi_b(j) - \phi_a(j)\phi_b(i)] \frac{1}{2\sqrt{2}}(\alpha_i\alpha_j - \beta_i\beta_j) \middle| \frac{1}{2}(\xi_i l_x(i) - \xi_j l_x(j))(S_x(i) - S_x(j)) \middle| {}^1A_c\phi_a(i)\phi_b(j) \frac{1}{\sqrt{2}}(\alpha_i\beta_j - \beta_i\alpha_j) \right\rangle \quad (8b)$$

This also guarantees correct state-to-state correlation via spin-orbit interaction.

The 1A wave function is of a form similar to that in eq 4 with $\phi_a\phi_b\phi_0\phi_2$ taking the place of $P_{1z}P_{3y}P_yP_z$ (and of $P_{1y}P_{3z}P_yP_z$). In the correlation we have taken a departure from the conventional orbit-to-orbit correlation in that (1) we have added the spin so that it is now spin-orbital-to-spin-orbital correlation and (2) we

have added MO configuration interaction. The configuration interaction is conceived as follows. The twisted (out-of-plane) Möbius orbital $\phi_a \cong (\phi_1 + \phi_3)/\sqrt{2}$ can now combine with ϕ_2 in a bonding fashion giving rise to $\psi_{0,3}^s = (\phi_1/2 + \phi_2/\sqrt{2} + \phi_3/2) = \psi^s \cong \phi_a + \phi_2$ or in an antibonding fashion giving rise to $\psi_{1,2}^s = \phi_1/2 - \phi_2/\sqrt{2} + \phi_3/2 = \psi^{s*} \cong \phi_a - \phi_2$. The configuration mixing of the resulting singlet orthogonal allene that will guarantee correct dissociation into ϕ_2 and ϕ_a is, symbolically, not counting the exact weighting of the orbitals

$$\frac{1}{2} [|\psi^s\bar{\psi}^s| - |\psi^{s*}\bar{\psi}^{s*}|] \cong \frac{1}{2\sqrt{2}} [(\phi_a(1) + \phi_2(1)) \times (\phi_a(2) + \phi_2(2)) - (\phi_a(1) - \phi_2(1))(\phi_a(2) - \phi_2(2))] \frac{1}{\sqrt{2}}(\alpha_1\beta_2 - \beta_1\alpha_2) \rightarrow \frac{1}{\sqrt{2}}[\phi_a(1)\phi_2(2) + \phi_a(2)\phi_2(1)] \frac{1}{\sqrt{2}}(\alpha_1\beta_2 - \beta_1\alpha_2) \quad (9)$$

This is much in the same way that mixing of the bonding σ_g^2 with antibonding σ_u^2 gives the two hydrogen atoms of opposite spins in the Heitler-London valence-bond theory for singlet H_2 in ${}^1\Sigma_g^+$ state. This is our basis for spin-orbital correlation whereby we can take ϕ_a orbital of one spin to correlate to the bonding orbital ψ^s and ϕ_a with the opposite spin to correlate to the antibonding orbital ψ^{s*} . The numbering of the orbitals also shows correct orbital following during the rearrangement.

The above MO pictures as illustrated in Figure 3 and 4 are in complete agreement with the valence-bond treatment of Figure

1 and lend additional support to the feasibility of triplet cyclopropylidene to singlet orthogonal allene conversion by spin-orbit interaction. As mentioned in the valence-bond treatment, triplet cyclopropylidene to singlet planar allene is also possible. The molecular-orbital correlations for this are much simpler and are given in Figure 5. It essentially involves the pairing up of the two triplet electrons at the center carbon atom by spin-orbit coupling. We believe this path is less likely because the singlet planar allene has higher energy. The triplet-to-singlet conversion is quite facile in other orthogonal π systems, for example, in the reaction of $O(^3P)$ with singlet carbon suboxide (C_3O_2) to give three singlet carbon monoxides²⁸ and the reaction of $O(^3P)$ with singlet allene to give singlet ethylene and singlet carbon monoxide.²⁹ I believe³⁰ that these arise from the same kind of spin-orbit interaction in perpendicular π systems and should be of interest in the reactions of cumulenes in general. It is suggested that ex-

perimentalists and theoreticians may want to look more into such triplet-singlet inversion possibilities. In a recent (1977) simplex-INDO study of energy contours, Dillon and Underwood¹⁰ had allowed that in the region "in which the triplet state is calculated to be more stable than the singlet of the same geometry ... it may reasonably undergo intersystem crossing to the singlet.... We submit that, even if ab initio numerical computations show that the potential surfaces of triplet and singlet cross, a mechanism must still be found to account for the nonvanishing spin-orbit conversion matrix element and for qualitative understanding of the process. In this work we have attempted to find such a mechanism.

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Registry No. Cyclopropylidene, 2143-70-6; allene, 463-49-0.

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Hydrogen-Evolving Semiconductor Photocathodes. Nature of the Junction and Function of the Platinum Group Metal Catalyst

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Abstract: Noble metal incorporation in the surface of p-type semiconductor photocathodes to catalyze hydrogen evolution leads to efficient solar to chemical conversion if a set of energetic and kinetic criteria are satisfied: (1) the semiconductor-catalyst junction barrier height must be equal to or greater than that of the semiconductor H^+/H_2 junction; (2) the recombination velocity of photogenerated electrons at the semiconductor-catalyst interface must be low; (3) the overpotential for hydrogen evolution at solar cell current densities (~ 30 mA/cm²) must be minor. Because of substantial differences in the vacuum work functions of Pt, Rh, Ru, and the (redox potential of the) H^+/H_2 couple, the barrier heights for junctions of each of the four systems with p-InP ought to vary widely. Yet experiments show that all p-InP(M)/ H^+/H_2 junctions, where M = Pt, Rh, Ru, or no metal, have essentially the same ~ 0.7 -V gain in onset potential for hydrogen evolution relative to Pt/ H^+/H_2 . We attribute the similarity to the known lowering of metal work functions upon hydrogen alloying. Such alloying increases the barrier height and thereby the gain in onset potential over that anticipated from the vacuum work functions. The barrier height, measured as the limiting value of onset potential gain at high irradiance, approaches in all cases the Fermi level difference of p-InP and H^+/H_2 (0.9 ± 0.2 eV). That Fermi level pinning by interfacial states is not the cause of the similar barriers is evident from the reversible decrease in onset potential with hydrogen depletion and by a unity diode perfection factor of the p-InP(Rh)/ H^+/H_2 photocathode, which indicates no measurable interfacial recombination of photogenerated carriers. In agreement, the quantum efficiency of carrier collection (hydrogen evolution) nears unity. The criterion of low overpotential is met by the expected electrocatalytic effect of the noble metals, manifested in a $\geq 10^4$ increase in fill factor. Introduction of the metal into the semiconductor surface allows a p-InP(Rh)/3 M HCl photocathode to sustain 0.25 A/cm² at 0.4 V positive of an identically operating Pt electrode. As expected for a semiconductor/ H_2 junction, the onset potential shifts by 62 mV per pH unit, quite close to the theoretical Nernst factor, over the entire pH range. To sustain over the long term the 12% solar power conversion efficiency earlier reported and defined, operation at potentials suitable to produce both hydrogen saturation of the catalyst and the thin surface oxide film (where exposed) is necessary. In cells with strong acids this is met in the region +0.4 to +0.55 V vs. SHE overlapping the maximum solar to hydrogen conversion point, typically at +0.45 V. Thus, with adequately pure solutions, efficiency and stability can be compatible.

Introduction

The generation of fuels or chemicals by coupling photon-induced carrier separation at a semiconductor-liquid junction and an electrolytic reaction into a single integrated system is one of the most interesting prospects for photoelectrochemistry. Many recent publications discuss the chemistry, electrochemistry, and physics of semiconductor photoanodes in which platinum group metals catalyze photoelectrolytic processes.¹⁻²⁶ Others describe photo-

cathodes on which protons are reduced to hydrogen.²⁷⁻³⁶ In this class, p-InP catalyzed by noble metals has proved to have par-

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