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A Theoretical Study of the Role of Valence and Rydberg States in the Photochemistry of Ethylene

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Abstract: A number of proposed reaction paths occurring in the photodecomposition of singlet ethylene are computationally investigated using ab initio MO–CI methods. It is determined that the reactions of twisted singlet excited ethylene to give directly either the lowest singlet state of vinylidene + H_2 or ethylidene are facile pathways having relatively low computed activation energies. The further reaction of singlet ethylidene to give acetylene + H_2 is also found not to be difficult. Finally, excited-state CH bond rupture was found to give excited vinyl radical + H atom. The relative possible roles of the lowest energy $\pi 3s$ and $\pi\pi^*$ singlet states in the photochemistry of ethylene are discussed. A combined overview of ethylene singlet and triplet photochemistry is related to the known thermal chemistry of this material. It is concluded that excited singlet ethylene has direct access to various exit channels which differentiates its properties from those of either triplet ethylene or vibrationally hot ground-state ethylene.

The goal of this article is to theoretically characterize the reactions which have been proposed as the primary photoprocesses in ethylene.

The observed gas and condensed phase photochemistry occurring in the direct photolysis of ethylene shows principally the formation of acetylene and H_2.[1] Based on a number of observations it can be concluded that the primary photoprocesses are monomolecular in both the gas and condensed phases. The most important observation is that both the gas and condensed phase photolysis of C_2H_4–C_2D_4 mixtures mainly yield H_2 and D_2 (97%) and little HD.[1d] However, the photolyses of CD_2CH_2 and *trans*-1,2-dideuteroethylene yield differing mixtures of H_2, D_2, and HD (40/20/40 and 17/10/73, respectively). The molecular elimination mechanisms were originally written as follows:[1d]

$$C_2H_4^* = CH_2C\colon + H_2 \tag{1a}$$

$$CH_2C\colon = HCCH \tag{1b}$$

$$C_2H_4^* = HCCH + H_2 \tag{2}$$

The major problem with this mechanism is that the total gas phase photolysis yield of acetylene is greater than H_2.[1] In addition, a portion of the reaction yields various radical products, the formation of which was subject to pressure quenching and radical trapping.[1] The third portion of the mechanism involves the formation of vinyl radical and energized vinyl radical (reaction 3a,b) and hydrogen atoms. These intermediates yield secondary

$$C_2H_4^* = CH_2{=}\dot{C}H + H \tag{3a}$$

$$C_2H_4^* = CH_2CH^\dagger + H = HCCH + H + H \tag{3b}$$

reactions which are of no concern here. In condensed phase photolyses[1d,h] the formation of vinyl radical is largely suppressed and the molecular mechanisms dominate the radical processes.

The condensed phase photolysis (6.7 eV) of dideuterioethylenes shows isotopic scrambling[1h] in the recovered unreacted ethylenes. The kinetic model proposed by Hirokami and Cvetanovic[1h] involves the relaxation of excited ethylene to ethylidene (reaction 4a) followed by the molecular elimination of H_2 from ethylidene (reaction 4b). This latter reaction is in competition with the retroreaction of singlet ethylidene to yield the ground state of ethylene (reaction 4c). The combination of reactions 4a and 4c would give rise to the observed isotopic scrambling in the recovered ethylene as well as the observed isotopic scrambling reported in the solid-phase 8.4-eV photolysis of CH_2CD_2 in the acetylene products (23% C_2H_2, 37% C_2HD, 40% C_2D_2).[1d]

$$C_2H_4^* = CH_3CH \tag{4a}$$

$$CH_3CH = HCCH + H_2 \tag{4b}$$

$$CH_3CH = C_2H_4 \tag{4c}$$

The triplet-sensitized gas-phase photochemistry[2] of ethylene in some respects resembles the direct photolysis photochemistry. The Hg-sensitized (4.8-eV) reaction yields, at low pressures, only acetylene and H_2. However, this photoreaction is subject to pressure quenching and at intermediate pressures is in competition with both isotopic scrambling and cis–trans isomerization. At lower sensitizer energies[2a,b] (3.5 eV) only isomerization and some scrambling occur. The proposed kinetic models for the triplet photochemistry also involve ethylidene intermediates, the multiplicity of which will be discussed in the conclusion of this paper.

The gas and condensed phase direct photolysis of other olefins is extremely complex and will not be detailed here. The gas phase direct photolysis mostly yields radical type fragmentation reactions ($A^* = M\cdot + N\cdot$)[3] although there is some evidence for molecular processes involving carbene type intermediates in recent work.[4] Kropp[5] has shown a number of examples in which carbene intermediates are present in condensed phase direct photolysis of monoolefins. However, there is no evidence of the existence of vinylidene intermediates in olefinic systems other than ethylene.

The main problem we will address ourselves to in this paper is resolving the theoretical ambiguity of the above reactions as written. None of these reactions really specify the initial and final

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(1) (a) McNesby, J. R.; Okabe, H. *Adv. Photochem.* **1964**, *3*, 228–31. (b) Ausloos, P.; Lias, S. G. "Chemical Spectroscopy and Photochemistry in the Vacuum UV", Sandorfy, C., Ausloos, P. J., Robin, M. B., Eds.; Reidel: Dordrecht, Holland, 1974; pp 478–80. (c) Okabe, H.; McNesby, J. R. *J. Chem. Phys.* **1962**, *36*, 601–4. (d) Gordon, R., Jr.; Ausloos, P. *J. Res. Natl. Bur. Stand.* **1971**, *75a*, 141–6. (e) Potzinger, P.; Glasglow, L. C.; Von Bunau, G. *Z. Naturforsch., A* **1971**, *27A*, 628–38. (f) Hara, H.; Tanaka, I. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 3012–5. (g) Hara, H.; Kodama, K.; Tanaka, I. *Ibid.* **1974**, *47*, 1543–4; **1975**, *48*, 711–2. (h) Hirokami, S.; Cvetanovic, R. J. *J. Phys. Chem.* **1974**, *78*, 1254–61 and references cited therein.

(2) (a) Tsunashima, S.; Hirokami, S.; Sato, S. *Can. J. Chem.* **1968**, *46*, 995–8. (b) Hirokami, S.; Sato, S.; Shin, S. *Ibid.* **1967**, *45*, 3181–6. (c) Terao, T.; Hirokami, S.; Sato, S.; Cvetanovic, R. J. *Ibid.* **1966**, *44*, 2173–80 and references cited therein. (d) Setser, D. W.; Rabinovitch, B. S.; Placzek, D. W. *J. Am. Chem. Soc.* **1963**, *85*, 862–6.

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(4) (a) Inoue, Y.; Takamuku, S.; Sakurai, H. *Chem. Commun.* **1975**, 577–8. (b) Collin, G. J.; Deslauriers, H.; Wieckowski, A. *J. Phys. Chem.* **1981**, *85*, 944–9. (c) Collin, G. J.; Deslauriers, H. *Nouv. J. Chim.* **1981**, *5*, 447–452. The last two articles deal with the gas-phase photochemistry of tri- and tetramethylethylene whose condensed photochemistry is discussed by Kropp (ref 5a,b).

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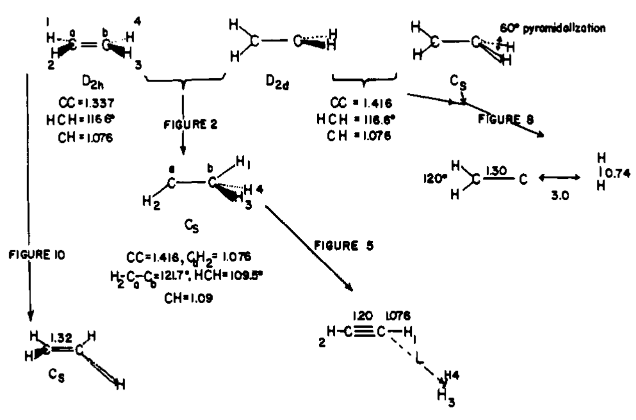


Figure 1. Initial and final geometries for the transformations shown in Figures 2, 5, 8, and 10. *L* is the distance from the carbon atom to the center of the HH bond.

states of the reactant and products. Likewise, there is no clear idea as to which reactions are adiabatic in nature. Therefore, they give no clear idea as to how the electronically excited state(s) evolve and achieve the various proposed exit channels. The main effort of this paper will be correlative in nature. We will use the results of both computations and correlation analysis to clarify some of the aspects of singlet and triplet photochemistry of ethylene.

Theoretical Approach

All the computations reported here used a 4-31G basis set plus a single diffuse 3s (Rydberg) function on each carbon atom ($\alpha = 0.015$).[6] The MO basis set used in the CI treatment was obtained from a Nesbet type[7] non-SCF open-shell solution of the HOMO-LUMO species of unspecified spin.[8] The CI treatment involved the use of 100 singly and doubly excited hand selected configurations without any threshold or symmetry selection procedure. Likewise, no geometry optimization was attempted. The geometry transformations were linear in character for those elements varied. These are detailed in Figure 1 and the figure captions.

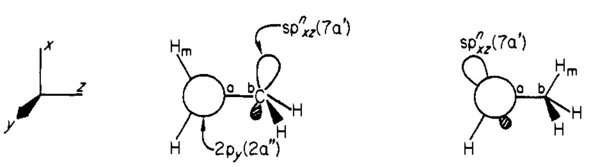
The non-theoretically oriented reader is warned that the calculations presented here are survey in character and not quantitatively reliable. The use of a 4-31G + 3s basis set will not give reliable excited state energies. Likewise, the small CI treatment will only allow for the avoided crossings of same symmetry configurational states and will not yield a significant portion of the valence state correlation energy of ethylene.[9] Finally, the use of a small basis set, small CI, and non-optimization of the reaction pathways will probably overestimate the computed activation energies. While we will show that the energetic results are not generally poor, we urge the reader to view the figures generated more as computational state correlation diagrams than as surface cross sections.

Results and Discussion

We will discuss the computed reaction pathways in the order of reactions 4a,b, 1a, and 3a. We will also discuss computed and some noncomputed adiabatic correlations in order to rationalize the observed computations. Finally, we will give an overall view of the singlet and triplet photochemistry of ethylene and how this relates to some aspects of the thermal chemistry.

A. The Ethylene-Ethylidene Transformation. Previous Observations. Previous computations on the ethylene-ethylidene transformation dealt only with the retroreaction 4c of singlet or triplet ethylidene giving, respectively, singlet ground state or triplet ethylene.[10] The conclusions reached are that the singlet reaction 4c occurs along a nonsymmetric (C_1) pathway with little[10] or no activation energy[11] and that the triplet reaction involves a considerable activation energy (ca. 40-50 kcal/mol).[11-13]

Since previous theoretical approaches were interested only in the ground- or triplet-state reactions, the computational chemists did not concern thermselves with the orbital and state symmetry consequences of the C_s pathway for reactions 4a-c. However, Kropp[5] cites the speculation of Turro and co-workers[14] in which the formation of carbene intermediates could arise from a 1,2-hydrogen or alkyl shift in the twisted excited valence ($\pi\pi^*$) states of monoolefins. Kropp, however, expressed concern that carbene formation occurs in ring-restricted double-bond systems, in which a fully-twisted excited-state configuration is not possible. In addition, Kropp proposed the possibility that at least two singlet excited states, one $\pi\pi^*$ and the other π3s (Rydberg), play a role in condensed-phase monoolefin photochemistry. Thus, the formation of carbene intermediates might also arise from a nearly planar[16] olefin Rydberg state. Turro's speculation[14b] was based on the idea that the twisted excited singlet valence states of ethylene have potentially zwitterionic characters.[16] Therefore, the combined twisted configuration and ionic character of these states (Z_1,Z_2)[16] permit imagining a facile 1,2-migration of the hydrogen atom, H_m, to give ethylidene.



pyramidalized twisted ethylene planar ethylidene

Our own precomputational hypothesis on this reaction was also based on the idea that perhaps the sudden polarization phenomenon occurring in the twisted excited state of ethylene[16] had photochemical manifestations. The 90° twisted conformation of ethylene (D_{2d}) displays the interesting theoretical property in which the V and Z excited states have potentially highly ionic characters if the system is distorted to a geometry which can possess a dipole moment (C_s).[16] The commonly investigated distortion is that of pyramidalization of one of the CH_2 groups while maintaining the orthogonality of the mainly $2p_y(a)$ MO function on atom a with the developing $sp^n_{xz}(b)$ orbital on atom b. With this $D_{2d} \rightarrow C_s$ distortion, the MO sequence[16b] becomes: 1a′, 2a′, 3a′, 4a′, 5a′, 6a′ 1a″, 7a′, 2a″, with $7a' = sp^n_{xz}(b)$ and $2a'' = 2p_y(a)$ being the

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(11) Pople, J. A., private communication. Preliminary results indicate that there may be a small barrier at the SCF level for this singlet ethylidene-ethylene transformation using a large basis set. However, after correlation energy corrections this barrier is essentially zero. The triplet ethylidene-ethylene surface has a considerable barrier (ca. 40 kcal/mol).

(12) Schaefer, H. F., III *Acc. Chem. Res.* **1979**, *12*, 288-96.

(13) The triplet ethylidene-ethylene C_s transformation is orbitally equivalent to the (i) vinylidene-acetylene triplet, (ii) ethyl radical 1,2-shift, and (iii) formaldehyde-hydroxycarbene cation radical transformations. The latter was treated recently by Osamura et al. (Osamura, Y.; Goddard, J. D.; Schaefer, H. F., III; Kim, K. S. *J. Chem. Phys.* **1981**, *74*, 617-21) and shows a barrier in the 40-50-kcal/mol region. We have found similar values for the ethyl radical 1,2-shift and confirm the results of Pople and co-workers (ref 11). Therefore, the semiempirical results reported in ref 10f are probably artifacts of the method used.

(14) (a) Cherry, W.; Chow, M.-F.; Mirbach, M. J.; Mirbach, M. F.; Ramamurthy, V.; Turro, N. J. *Mol. Photochem.* **1977**, *8*, 175-8. (b) Turro, N. J. "Modern Molecular Photochemistry"; Benjamin-Cummings: Menlo Park, 1978; pp 215-8 and 486.

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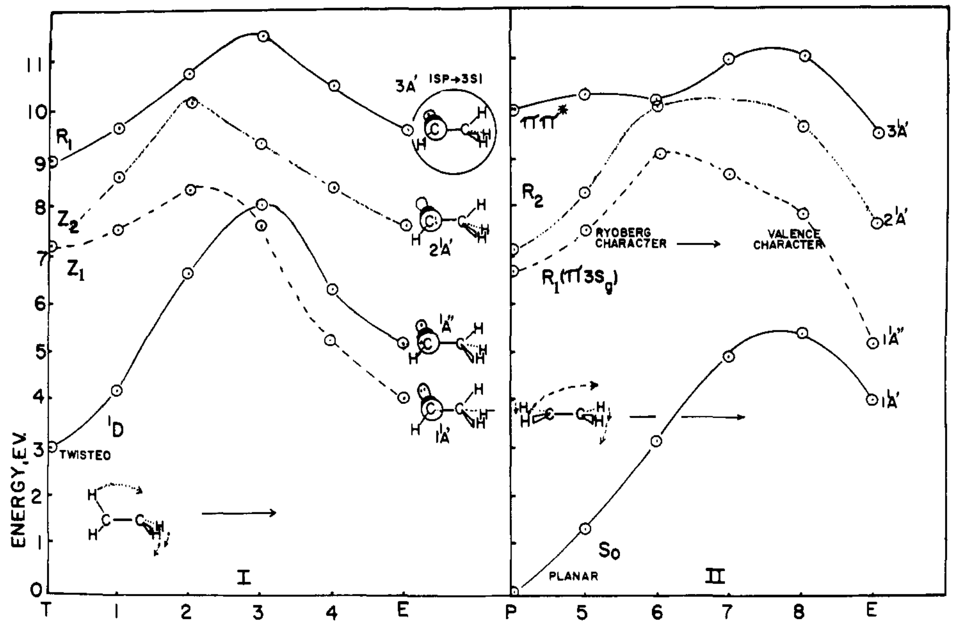

Figure 2. Part I: Transformation of twisted D_{2d} ethylene (T) to C_s ethylidene. Part II: transformation of planar (P) D_{2h} ethylene to C_s ethylidene (E). The scans shown in parts I and II represent least motion circular migrations of the H atom from atom a to atom b. For points 1–8, the intermediate C_a–H and C_b–H distances are (Å), respectively: (part I) 1.29, 2.03; 1.55, 1.84; 1.74, 1.61; 1.92, 1.35: (part II) 1.26, 2.08; 1.45, 1.82; 1.65, 1.74; 1.82, 1.52. D = diradical, Z = zwitterion, R = Rydberg (π3s).

two highly localized MOs. The MO sequence of importance in ethylidene is essentially the same as in C_s ethylene, the only major difference being that 7a′ = $sp^n{}_{x,z}(a)$.

For twisted C_s ethylene, the ground singlet and lowest triplet states both have essentially the same 7a′2a″ open-shell-orbital occupancies, these being classified as diradical states, $^{1,3}D$, since the electrons are separately associated with atoms a and b. Their molecular symmetries are both A″ in the C_s point group. The V and Z twisted excited states of ethylene present a more complicated conceptual problem in that they are mainly biconfigurational in character, using a two-configuration first-order model.[16b] These states can be reclassified in C_s symmetry as being Z_1 and Z_2 where: $\Psi(Z_1) = c_1Z_a + c_2Z_b$ and $\Psi(Z_1) = c_2Z_a - c_1Z_b$. The functions Z_a and Z_b represent the closed shell occupancies: $[--(2a'')^2]$ and $[--(7a')^2]$, respectively, which in turn nearly represent the classical VB structures: $^-CH_2-^+CH_2$ and $^+CH_2-^-CH_2$, respectively. Thus, Z_a is the structure associated with the anion localized on atom a, the reverse being the case for Z_b. At large pyramidalization angles, $c_1 \rightarrow 1$, $c_2 \rightarrow 0$, and $Z_1 \rightarrow Z_a$ and $Z_2 \rightarrow Z_b$. In C_s symmetry both the Z_1 and Z_2 have the same A′ symmetry.

The predicted order of the states in ethylidene[17] will be: $^3A''(7a'2a''$ occupancy); $1^1A'((7a')^2)$; $1^1A''(7a'2a'')$; and $2^1A'((2a'')^2)$. Therefore, for the C_s reaction pathway of the hydrogen atom H_m migrating from atom a to atom b, the following state-to-state ethylene–ethylidene correlations are obtained: $^1D \rightleftharpoons 1^1A''$, $^3D \rightleftharpoons {}^3A''$, and $(Z_1,Z_2) \rightleftharpoons (1^1A',2^1A')$. These correlations merely tell us that one of the excited states of ethylene must correlate with the lowest singlet state of ethylidene while the ground diradical singlet state of ethylene must correlate with the excited singlet state of ethylidene. This correlatively predicted ground excited state surface crossing will disappear for a nonsymmetric (C_1) H migration: $^1D \rightleftharpoons 1^1A'$, $(Z_1Z_2) \rightleftharpoons (1^1A'',2^1A')$ while the ^3D correlation remains the same. The question as to which Z states correlate with which A states in both the C_s and C_1 transformations will be resolved by the following computations.

Computational Analysis. The computed C_s pathway for reaction 4a is displayed in part I of Figure 2. The nonsymmetrical C_1 transformation is shown in part II of this figure.

We have already cautioned the reader to view the computationally generated reaction pathways presented here as state correlation diagrams. Even so, we will make a direct comparison with previously known experimental and high level theoretically calculated values. The zero reference energy in all figures is that of the computed ground state of planar ethylene. The approximate comparative energies of the various structures and states are: (i) the twisted ground state, ^1D, calcd, 3 eV, (experimental, theoretical, 2.5 eV);[16,18] (ii) planar π3s (Rydberg) singlet state, 6.5 eV (experimental, theoretical, 7.1 eV);[16] (iii) $1^1A'$, ethylidene, 4.0 eV (theoretical, 3.7 eV);[17] (iv) planar ππ* V Z_1 state, 10 eV (experimental, theoretical, 7.4 eV);[16,18] D_{2d} twisted ππ* Z state, 7.1 eV (experimental, theoretical, 5.4–6.1 eV).[16,18] It is only in the case of the planar ππ* that our results are in large error, a result anticipated by the fact that we did not include a diffuse Rydberg contribution of the proper symmetry to mix into the π* orbital.[18] Thus the experimentally small π3s–ππ* energy gap (ca. 0.3 eV) for the Franck–Condon transitions in planar ethylene is computed to be in the order of 3 eV. However, the situation for twisted ethylene is considerably better in that the Z states are computed to be more stable than the Rydberg state as in fact is the case.[18]

An important feature of part I of Figure 1 is that the excited Z_1 state undergoes a resonably low barrier (ca. 1 eV) evolution to give the the correlationally anticipated $1^1A'$ state of ethylidene. Likewise, as anticipated from the above discussed correlations, the ^1D (ground) state of ethylene correlates with the $^1A''$ (excited) state of ethylidene. The Z_2 and twisted Rydberg states show evolution toward the higher excited $2^1A'$ and $3^1A'$ states of ethylidene. The question as to the theoretical nature of the Z_1 surface is resolved in the computation. Initially the surface has Z_a $[^-CH_2-^+CH_2, --(2a'')^2]$ character and the H_m initially appears to be migrating toward a positive carbon atom in analogy with a 1,2 shift in a carbonium ion. However, in the region of the C_s excited state transition state, the wave function has biconfigurational character, $\Psi(Z_1) = c_1[--(7a')^2] + c_2[--(2a'')^2]$. The final portion of the surface leading to the $1^1A'$ state of ethylidene is characterized by $c_1 \rightarrow 1$, $c_2 \rightarrow 0$. Thus, a combination of both the changing nature of the 7a′ MO and the biconfigurational

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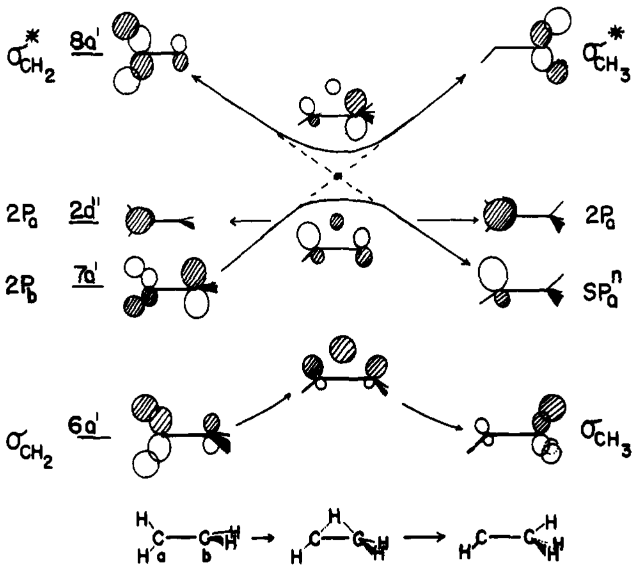

Figure 3. Orbital correlation diagram for the transformation of twisted ethylene to ethylidene, C_s pathway.

nature of the Z_1 wave function in the region of the transition state allows the system to annihilate the actual (C_s) or potentially (in D_{2d}) zwitterionic character of the ethylenic excited state on its evolution to the lowest singlet state of ethylidene.

With respect to the possibility that the lowest Rydberg state of planar ethylene plays a role[5] in the generation of ethylidene, we show part II of Figure 2. The nonoptimized circular passage of the migrating H_m atom to atom b breaks the symmetry of the system and now the $1^1A'$ state of ethylidene directly correlates with the ground state of ethylene while the excited state of ethylene correlates with the $^1A''$ (excited) state of ethylidene. The small activation energy (ca. 1 eV) for the retroreaction 4c is an artifact resulting from a neglect of geometry optimization and other technical factors. The best computed value[11] for this process actually indicates a near zero activation energy as anticipated from earlier computations.[10] The $\pi 3s$ (R_1 = Rydberg) surface rises in energy, undergoes derydbergization[19-22] and eventually evolves to the valence $1^1A''$ state of ethylidene. While this computation seems to argue against an easy involvement of this Rydberg state in the ethylidene forming mechanism there are several factors which indicate that the calculation is deceptive. First, in reality, the planar $^1\pi\pi^*$ and $^1\pi 3s$ states in simple olefins are nearly degenerate and not separated by the 3 eV shown in Figure 2, part II. A more refined calculation will certainly show a more rapid valence–Rydberg mixing and lower barrier than indicated in Figure 2, part II along the C_1 reaction pathway. Secondly, even within the context of the calculations presented here, it is possible to imagine a more optimal H migration which would bring the system onto the C_s reaction coordinate at an earlier stage than shown.

The most important feature of Figure 2 is that there exists the correlationally anticipated ground and excited state surface crossing along the C_s reaction pathway. This crossing will be progressively avoided as the reaction pathway deviates to geometries further and further away from C_s. This crossing or near crossing region provides a funnel area through which electronically excited ethylene can adiabatically or nonadiabatically relax to the ground-state surface. Thus, under collision-free conditions a process can be hypothesized which can be written as: $^1C_2H_4{}^* \rightarrow {}^1C_2H_4{}^\dagger \rightleftharpoons {}^1CH_3CH^\dagger$, indicating that above a certain threshold energy (ca. 4 eV) the ethylene and ethylidene structures are interchanging due to the nearly zero activation energy interconnecting these systems.[11]

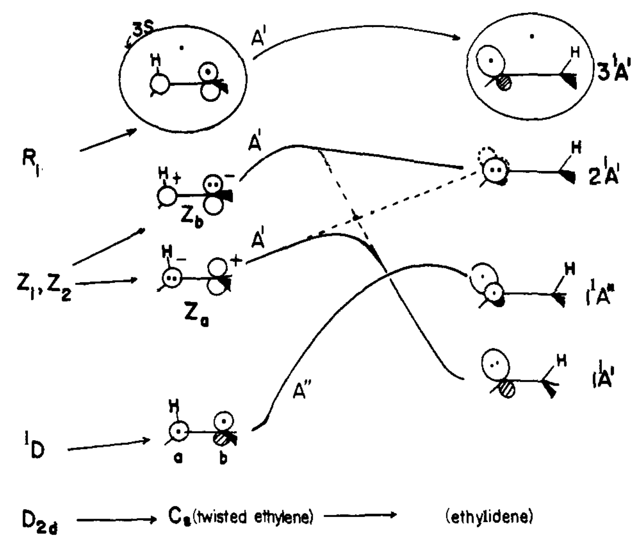

Figure 4. State correlation diagram for the C_s transformation of twisted ethylene to ethylidene.

Correlation Analysis. Our original correlation analysis did not anticipate either an activation energy or changing configurational character along the C_s reaction pathway. Likewise, the derydbergization occurring along the nonsymmetric excited state surface will require some explanation since it is a concept not yet established in the theoretically oriented photochemist's thinking. Figure 3 shows the idealized C_s correlations for the 6a', 7a', 2a'', and hypothetical (in the absence of a Rydberg component) 8a' (virtual) orbitals. In particular, the a' components show a complex interaction due to their allyl-like character of the three principally interacting atomic orbitals involved in the H transfer, these being the 1s on H_m, and the two $sp_{x,z}$ hybridized components on atoms a and b. The 6a'[σ-CH_2(a)] orbital in ethylene correlates through a bonding allyl configuration to yield the 6a'[σ-CH_3(b)] orbital on ethylidene. However, the 7a' orbital of ethylene has a natural nodal and base orbital composition which yields a natural correlation with the σ*[CH_3] orbital on ethylidene. This correlation will experience an avoided crossing with the 8a'[σ*CH_2(a)] orbital. The net result of the interplay of the a' orbitals is that the 7a' orbital will rise before falling in energy. Likewise, since the 7a' orbital is transferring its localized character from atom b to atom a it is anticipated that some conceptual orbital barrier should exist. The 2a'' orbital, however, remains localized on atom a throughout the transformation.

When these orbital behaviors are included in the construction of the state configurations, the before and after avoided crossing behaviors obtained are shown in Figure 4. The $^1D \rightleftharpoons {}^1A''(C_s)$ correlation has an indeterminate barrier controlled by the combined behavior of all the occupied a' orbitals. This correlation shows no avoided crossings and, as computationally observed, the configurational wave function remains essentially monoconfigurational (correlatively treatable at the SCF level) along the entire transformation. The Z_1 surface behavior is more complex. Although the initial portions of the Z_1 surface will have Z_a character because of the dominance of the $[--(2a'')^2]$ configuration, this Z_a configurational state correlates by orbital occupation with the $2^1A'$ state of ethylidene. Likewise, the highly repulsive Z_2 state surface, which is initially Z_b in character, would prefer to evolve to the $1^1A'$ state of ethylidene. Thus the correlations $Z_a \rightleftharpoons 2^1A'$ and $Z_b \rightleftharpoons 1^1A'$ must avoid crossing, giving $Z_1(Z_a) \rightarrow Z_1(Z_a,Z_b) \rightarrow 1^1A'$. In a certain manner the Z_1 surface initially benefits from the low-energy migratory pathway of the H atom to the adjacent carbonium ion but eventually abandons this configuration and

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(19) Mulliken, R. S. *Acc. Chem. Res.* **1976**, *9*, 7-12.

(20) Evleth, E. M.; Kassab, E. "Quantum Theory and Chemical Reactivity", Daudel, R., Pullman, A., Salem, L., Veillard, A., Eds.; Reidel, Dordrecht: Holland, 1980; pp 2 and 261-84.

(21) Evleth, E. M.; Kassab, E. "Computational Theoretical Organic Chemistry", NATO Advance Study Institute; Csizmadia, I. G., Daudel, R., Eds.; Reidel, Dordrecht: Holland, 1981, pp 379-95.

(22) Rydbergization can be viewed as occurring at the orbital or state level. For a full MO viewpoint see ref 19 and: Mulliken, R. S. *Chem. Phys. Lett.* **1977**, *46*, 197-200. However, Rydbergization can be rationalized also within the contect of valence-bond structural diagrams, see ref 21.

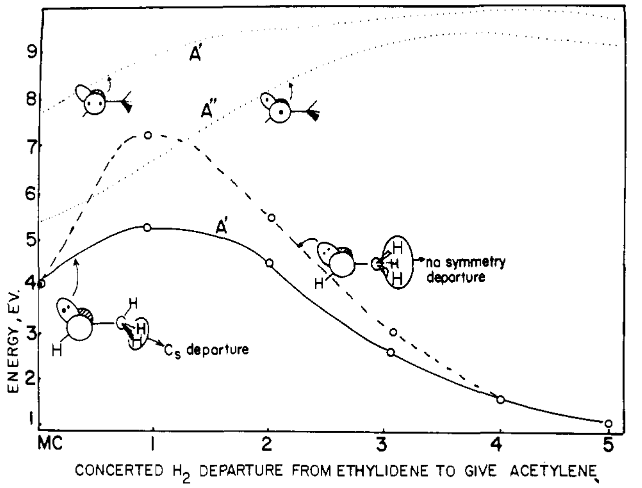

Figure 5. Computed C_s and no symmetry transformations of singlet ethylidene (MC) to acetylene + H_2. Zero energy represents planar ground-state ethylene. Points 1-5 are for L (C-H_2) (see Figure 1) and H-H distances (Å) of, respectively, 1.10, 1.57; 1.58, 1.36; 2.05, 1.16; 2.53, 0.95; and 3.00, 0.74.

takes on the Z_b character necessary to take it to the $1^1A'$ state of ethylidene.

With respect to the general problem of the sudden polarization, it is predicted that on pyramidalization the lowest excited state takes on large Z_b character[16b] while our own calculations favor a Z_a (initially) for another type of C_s distortion (i.e., partial hydrogen migration). These situations arise from the conceptually biconfigurational character of the Z_1 state, $\Psi(Z_1) = c_1Z_a + c_2Z_b$. Therefore the Z_1 state can take on either mainly Z_a or Z_b character depending on what demands are placed upon it on distortion.

Finally, the derydbergization of the lowest excited (π3s) state of ethylene on asymmetric distortion of the system should be a general theoretical phenomenon in other olefinic systems provided that the lowest state is Rydberg in character. Although one might correlatively anticipate a natural Rydberg-state-of-reactant-to-Rydberg-state-of-product correlation under certain symmetry conditions this does not occur.[19-22] In the case treated here the asymmetric distortion allows the 3s orbital to collapse into valence space of the product. Correlatively, what approximately occurs in that the π and 3s open shell orbitals eventually evolve to become the 2a″ and 7a′ orbitals on ethylidene $^1A''$. The 3s MO is not entirely diffuse in character, and the valence orbital components merely become progressively more important along the reaction coordinate, this being the definition of derydbergization. Note, however, if a particular surface undergoes derydbergization on distortion, other surfaces, initially mainly valence in character, may undergo rydbergization. These might be coupled processes and will be of computational importance if the Rydberg state happens to lie below the valence state under consideration. This is apparently the case in most monoolefins.[15]

B. The Ethylidene–Acetylene Transformation. Computational Analysis. The singlet ethylidene-to-acetylene + H_2 reaction pathway 4b for the C_s and C_1 transformations are shown in Figure 5. The C_s transformation is favored and yields a direct evolution from the $1^1A'$ state of ethylidene to the ground states of acetylene ($^1\Sigma_g$) and H_2. A mild activation energy (ca. 1 eV) is predicted for the C_s transformation, the C_1 process being considerably greater. Although our overall computed value for the enthalpy of reaction 4b is about 3 eV, Figure 5 indicates that the enthalpy of the reaction of ground-state ethylene to acetylene + H_2 is about 1 eV. The actual experimental value is about 1.8 eV.[23] Therefore, given the previous estimated value of the enthalpy of formation of ethylidene,[17] the actual enthalpy of reaction 4b is closer to 2 eV. The overall barrier of the reaction of ground-state ethylene to give acetylene + H_2 is about 5 eV (Figure 5). Therefore, there is sufficient excess energy in the direct photolysis of ethylene (the lowest energy experiments are at 6.4 eV)[1] to achieve this exit channel.

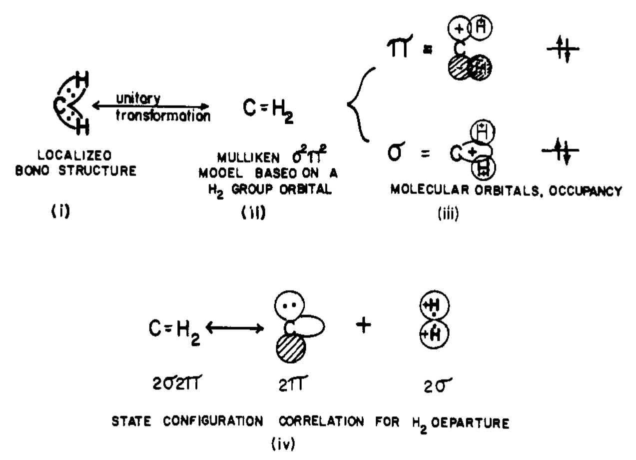

Figure 6. Orbital and state correlations for the departure of H_2 from a CH_2 unit in a $\sigma\pi$ symmetry retaining manner.

Correlation Analysis. Based on previous chemical and theoretical experience the relatively low barrier for the C_s departure of H_2 from ethylidene seems surprising. The concerted departure of H_2 from carbon, oxygen, or nitrogen centers is normally considered a forbidden pathway.[24] However, we will show that this is not the case and important exceptions exist in the work reported here.

The general correlation for a symmetry-retaining depature of H_2 from a CH_2 unit is shown in Figure 6. The localized bond structure (i) can be expressed in $\sigma\pi$ terms as CH_2 (ii), where the MO local symmetry forms of these orbitals are shown in (iii). Departure of H_2 in a $\sigma\pi$-symmetry-retaining manner (iv) produces a direct correlation, $CH_2 \rightleftharpoons C(\pi^2) + H_2(\sigma^2)$, meaning that in the departure the H_2 will attempt to retain the σ electrons and leave the π electrons with the carbon unit. The actual state-to-state correlations in real systems, A=CH_2 or B_2CH_2, will depend on the overall symmetry of the reaction pathway. In the case of the C_{2v} departure of H_2 from CH_4[25] the direct correlation will be $CH_4 \rightleftharpoons CH_2(2^1A_1 = \pi^2) + H_2(\sigma^2)$. However, this direct correlation will avoid crossing with another correlation $CH_4{}^{**}(\sigma^2\sigma^{*2}$, on the CH_2 unit) $\rightleftharpoons CH_2(1^1A_1 = \sigma^2)$. The final real correlation, $CH_4 \rightleftharpoons CH_2(1^1A_1) + H_2$ will be obtained by an avoided crossing computation requiring CI at the C_{2v} transition state. Although this pathway is Woodward–Hoffmann forbidden it computationally occurs with a 27-kcal/mol barrier for the retroreaction, presumably because of the large exothermicity of the overall reaction.[25] In any case, for a C_s reaction pathway there is $\sigma\pi$ mixing, the direct correlation occurs without an avoided crossing, and for certain $CH_2 + H_2$ approaches there is no computed activation energy. However, in the case of either a C_{2v} or C_s nonplanar depature of H_2 from H_2CO the double π degeneracy of the CO unit creates forbidden pathways in each case. Actual calculations show[26] that the system chooses another planar C_s H_2 departure in which the two CH distances are greatly different. In this case the computed activation energy is in the order of 100 kcal/mol.

In some respects the C_s departure of H_2 from singlet 1^1A, ethylidene represents the allowed pathway counterpart of the $H_2CO = CO + H_2$ forbidden pathway. The developing acetylene unit can be viewed as looking for a pair of π_2 electrons which the CH_2 unit can supply by a direct correlation. The electron pair

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[23] JANAF Thermochemical Tables, *Natl. Stand. Ref. Data. Ser., Natl. Bur. Stand.* **1970**, *1*, 37.

[24] Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Verlag Weinheim, 1970; 144. These authors recognized the allowed character for the nonsymmetrical ground-state and symmetrical excited-state pathways.

[25] Bauschlicher, C. A., Jr.; Haber, K.; Schaefer, H. F., III; Bender, C. F. *J. Am. Chem. Soc.* **1977**, *99*, 3610–4.

[26] Goddard, J. D.; Schaefer, H. F., III *J. Chem. Phys.* **1979**, *70*, 5117–34.

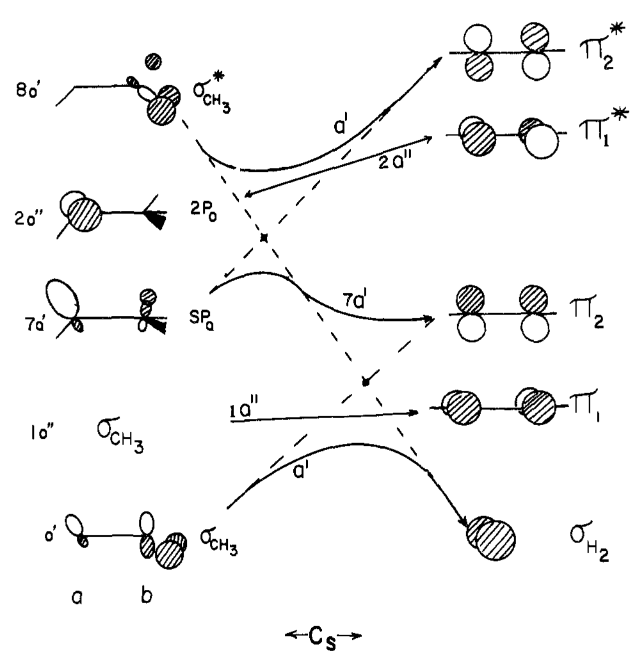

Figure 7. Idealized orbital correlation diagram for the depature (C_s) of H_2 from ethylidene to yield acetylene + H_2.

already on the 7a′ orbital of ethylidene ($1^1A'$) will fill the role of the acetylene π_1 electrons. Thus a direct overall state correlation of $[--(1a'')^2(7a')^2] \rightleftharpoons [--(\pi_1)^2(\pi_2)^2]_{HCCH} + (\sigma^2)_{HH}$ is obtained for the C_s pathway without an avoided crossing. On the other hand, it is the C_1 pathway which is configurationally difficult in that the departure of H_2 in a direction perpendicular to the H–C–C plane will attempt to create a situation in which all four π electrons will attempt to occupy the same inplane π space of acetylene. This situation will be automatically avoided because of the C_1 symmetry of the system, but still represents an unfavorable pathway. What barrier does exist for the C_s pathway can be qualitatively interpreted as arising from the behaviors of the important a′ MOs shown in Figure 7. The nodal and base orbital properties of the 7a′ orbital on ethylidene show a natural correlation with the π_2^* on acetylene, its real correlation with the π_2 orbital being conceptually achieved by an avoided orbital crossing with the 8a′-[$\sigma^*(CH_3)$] MO which has a natural correlation with the σ-bonding space in acetylene and H_2.

C. The Ethylene to Vinylidene Transformation. Computational Analysis. Both the C_{2v} and C_s reaction pathways for the departure of H_2 from the same carbon atom (reaction 1a) of 90° twisted ethylene are shown in Figure 8. The essential features of Figure 8 are that (i) both the ground- and excited-state transformation are forbidden for the C_{2v} twisted ethylene H_2 departure and (ii) there appears to be an easy transformation (C_s) taking the twisted valence excited state of ethylene directly to the ground state of vinylidene.

With regard to the overall correlation between reactant and product states, the ground and excited states of vinylidene have been recently estimated.[27,28] With respect to the ground state of vinylidene, $^1A_1$ (computed enthalpy of 3.8 eV for $C_2H_4 = CH_2C + H_2$),[11] the excited states of vinylidene are:[27] $^3B_2$ (2.0 eV), $^3A_2$ (3.2 eV), $^1A_2$ (3.5 eV), and $^1B_2$ (4.6 eV). Shown on the right-hand portion of Figure 8 are our computed states at an H_2–vinylidene separation of 3 Å. Our overall enthalpy at this distance is about 4.5 eV and both the order and energies of the vinylidene states are in fair agreement with the higher level computation.[27]

The C_{2v} twisted ethylene reaction paths for either the ground or triplet diradical, $^{1,3}D$, have high computed barriers and eventually evolve to the $^{1,3}A_2$ excited states of vinylidene. While the Z_1 excited state of ethylene does correlate with the ground 1^1A_1 state of vinylidene + H_2, it does so by a high energy pathway. The C_s twisted ethylene reaction pathway is computed in which the H_2 departure starts from a pyramidalized carbon atom b. The Z_1 state surface, which initially has anionic character at the carbon center losing the H_2 pair, smoothly evolves along an A′ surface to yield the 1^1A_1 vinylidene + H_2 ground states with a low computed activation energy (ca. 1 eV). However, the twisted ground state, ^1D, still correlates with the vinylidene excited state, $^1A_2$, along an A″ reaction pathway. The importance of this C_s pathway is found in the ground- and excited-state surface crossing. As in the case of the C_s pathway in the ethylene–ethylidene surface, this intersection constitutes a funnel region through which direct ground–excited state relaxation can take place.

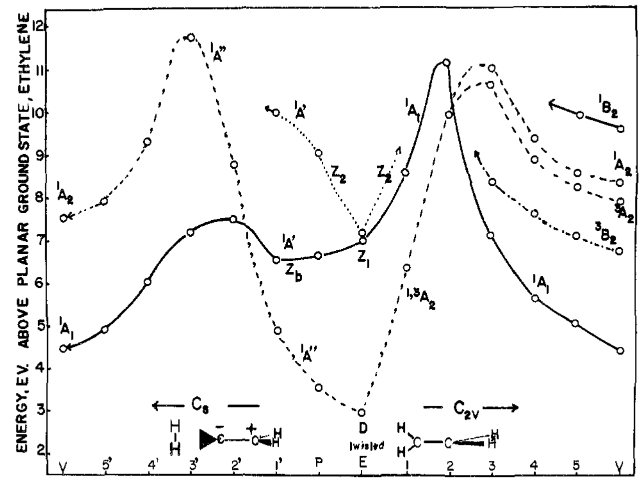

Figure 8. Computed C_{2v} and C_s transformations of twisted ethylene (E) (P = twisted + 60° pyramidalized) to vinylidene (V) + H_2. Z_1 and Z_2 are the two zwitterionic excited states of twisted ethylene. The Z_1 becomes largely Z_b (anion on pyramidalized carbon) on distortion. Geometrical points 1,1′ to 5,5′ have L and H–H distances (Å) (see Figure 1) of, respectively, 0.96, 1.68; 1.37, 1.49; 1.79, 1.30; 2.21, 1.11; 2.62, 0.93; and 3.04, 0.74 at the vinylidene limit.

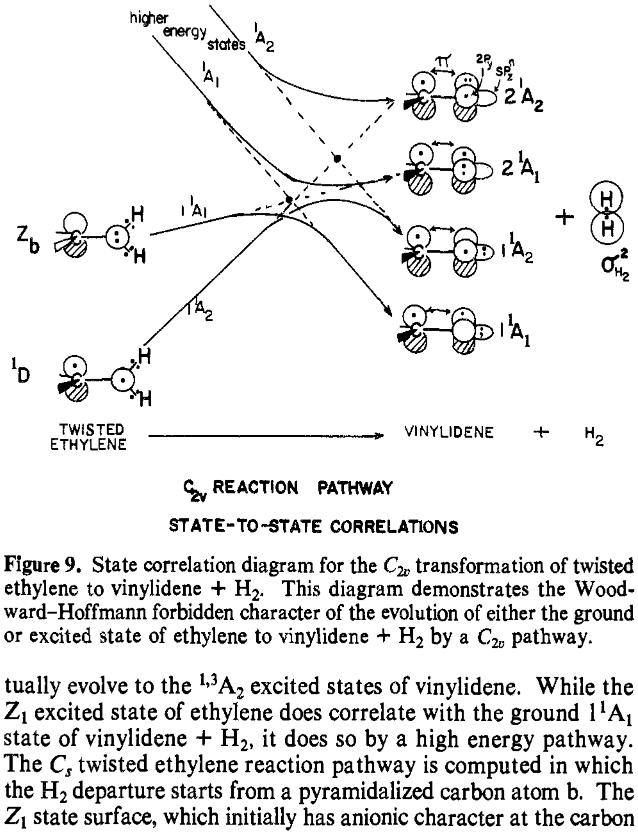

Figure 9. State correlation diagram for the C_{2v} transformation of twisted ethylene to vinylidene + H_2. This diagram demonstrates the Woodward–Hoffmann forbidden character of the evolution of either the ground or excited state of ethylene to vinylidene + H_2 by a C_{2v} pathway.

Correlation Analysis. The high barriers computed for the C_{2v} reaction pathway result from the forbidden character of the transformation. Simple CH_2 excited-state pyramidalization reduces the excited-state $Z_1 \rightarrow 1^1A_1$ barrier from about 6 to 1 eV, while the ground-state barrier remains high. The reason for the difficulty of the H_2 departure from twisted ethylene is seen from

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(27) Davis, J. H.; Goddard, W. A., III,; Harding, L. B. *J. Am. Chem. Soc.* **1977**, *99*, 2919–25.

(28) (a) Krishnan, R.; Frisch, M. J.; Pople, J. A.; Schleyer, P.v. R. *Chem. Phys. Lett.* **1981**, *79*, 408–411. (b) Osamura, Y.; Schaeffer, H. F., III *Ibid.* **1981**, *79*, 412–5. (c) Osamura, Y.; Schaeffer, H. F., III; Gray, S. K.; Miller, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 1904–7.

examining the state correlation diagram (Figure 9). As shown by the orbital populations for the state-to-state correlation, the Z_b state has a natural occupancy correlating it with the 2^1A_1 state of vinylidene since the departure of H_2 will leave an electron pair in the π orbital of the vinylidene and none in the $sp^n{}_z$ (b) σ orbital. This natural occupancy correlation will cross with a higher excited ethylene $\rightleftharpoons$ 1^1A_1 vinylidene + H_2 correlation. An attempt to use an Z_a excited state of ethylene for this correlation will place four electrons in the π space of vinylidene which is a worse situation than that encountered with the Z_b state correlation. The situation is similar for the ^1D correlation where an avoided crossing is also encountered.

The C_s twisted excited state reaction pathway shows some of the same theoretical behavior as found in the H_2 departure from ethylidene. This reaction pathway mixes the orbitals containing the electron pairs shown for the 1^1A_1 and 2^1A_1 states of vinylidene. This permits the doubly filled $2p_y$(b) orbital of the Z_b state of ethylene to evolve in the manner: $2p_y(b) \rightarrow s(2p_y(b)(2p_z(b)) \rightarrow sp^n{}_z(b)$ as the H_2 pyramidalizes, departs, and finally evolves to the C: configuration present in the 1^1A_1 state of vinylidene. Thus, for the $Z_b \rightarrow 1^1A_1$ reaction the A′ C_s surface will not show an avoided crossing behavior. However, the $1^1A''$ surface will retain its forbidden character since the departure of an H_2 unit will still attempt to deposit two electrons into the π space of vinylidene producing the same direct $^1D \rightleftharpoons 2^1A_2$ correlation as found in the C_{2v} pathway shown in Figure 9.

With respect to the uncomputed C_{2v} H_2 departure from planar ethylene, the following correlations can be shown to occur: $S_0 \rightleftharpoons 1^1A_1$ (forbidden, by an avoided crossing); $S^*(\pi\pi^*) \rightleftharpoons 2^1A_1$; and $S^{*\prime}(\pi 3s) \rightleftharpoons 1^1B_1$. The latter two excited states were not treated theoretically in previous work[27] and presumably represent very high energy species. Therefore the excited-state surfaces are probably highly bound for this departure. The $S_0 \rightleftharpoons 1^1A_1$ correlation is conceptually identical with that previously discussed in the $CH_4 \rightleftharpoons CH_2(^1A_1) + H_2$ correlation. Although an avoided crossing situation will be encountered the barrier for the retroreaction $CH_2{=}C{:} + H_2 \rightarrow C_2H_4$ planar process should be similar to that encountered in the $CH_2 + H_2$ C_{2v} reaction (27 kcal/mol).[25] This would place the threshold energy for the formation of vinylidene + H_2 from acetylene by a C_{2v} planar pathway at about 5.0 eV 3.8 + 1.2). This value would probably be lower if a C_s planar or nonplanar H_2 departure is selected. Even at the 5 eV figure, singly excited ethylene has enough excess energy to achieve this exit channel if the molecule can relax to the ground state.

D. The Ethylene to Vinyl Radical Transformation. Computational Analysis. Figure 10 shows the C_s CH bond rupture pathways for planar ethylene going to vinyl radical + H atom. Unlike the other transformations discussed above, this fragmentation yields radical pairs. This type of calculation requires either an MCSCF single[29] or double replacement type computation[30] or GVB-CI method,[27] or, as used here, a non-SCF generation of the basis MOs used in a conventional CI treatment. The use of non-SCFMOs negates the Brillouin theorem[30] and permits direct CI mixing of filled and single-occupancy open-shell configurations. In the case of the rupture of a simple σ bond, the ground state wave function takes on mainly mixed closed–open shell character of the type $c_1(\sigma^2) + c_2(^1\sigma\sigma^*)$ so that as the bond breaks $c_1 \rightarrow 0$ and $c_2 \rightarrow 1$, if we are dealing with heteronuclear systems, A:B. If A is more electronegative than B, $\sigma \rightarrow A\cdot$ and $\sigma^* \rightarrow B\cdot$ and the $^1\sigma\sigma^*$ configuration will represent, in proper determinental form, the wave function of the radical pair, A·, ·B. At large A–B separations the energies of the triplet and singlet biradicals, $^{1,3}D_{\sigma\sigma}$, will be degenerate.

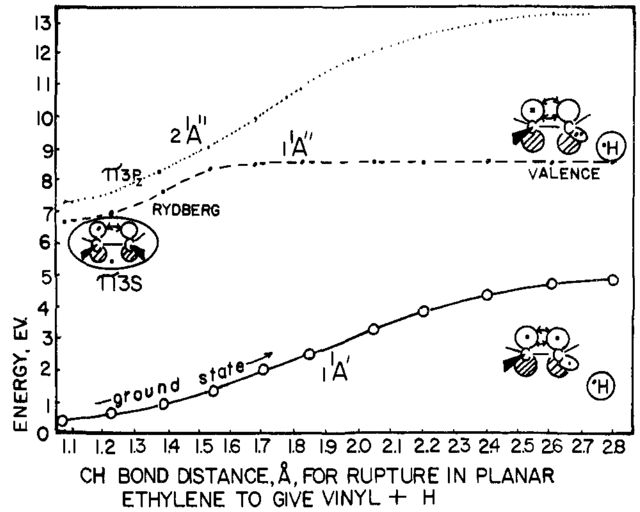

Figure 10. Departure of an H atom from planar ethylene. This computation was initiated at a C–C distance of 1.416 Å; the zero reference energy is that of ethylene in its ground-state geometry (Figure 1). The structure formulas represent the approximate bonding character of the π3s Rydberg state of ethylene (see ref 3a, 13, and 18) and the ground and first excited valence states of vinyl radical.

As seen from Figure 10, the computation of the ground-state $^1A'$ bond-rupture surface in ethylene yields a ground-state vinyl radical + H with a computed enthalpy of about 4.5 eV (experimental ca. 4.4 eV).[31-33] The lowest planar excited state surface ($1^1A''$) initially has a π3s Rydberg electronic configuration but terminates at the diradical limit as a valence excited state of the vinyl radical ($\sigma^2\pi$) + H atom. This configuration is achieved by a $\pi \rightarrow \sigma$ excitation of the ground-state vinyl radical ($\sigma\pi^2$), where the σ orbital is essentially localized at the radical center. The π3s state derydbergization[20] correlatively arises because the 3s orbital is actually intravalent in character[34] having the approximate form $c_13s + c_21s$ (H, departing) or σ^* (CH) at intermediate distances. At large CH distances, $|c_2| \rightarrow 1$, and this orbital localizes on the departing H atom. This can also be viewed as if the 3s Rydberg orbital undergoes an avoided crossing (type D)[35] with a repulsive σ^* (CH) orbital, the overall evolution being 3s $\rightarrow \sigma^*$ (CH) $\rightarrow$ 1s (H, departing).

Our computation of the $1^1A''$ excited state surface shows a 2 eV endothermicity for the CH excited state bond rupture. The threshold for this process is between 8 and 9 eV and electronically excited vinyl radicals would be generated. Finally, Figure 10 shows a $2^1A''$ surface having $\pi 3s_1$ ($=\pi 3p_z$ by symmetry) character. There is no computed $2^1A'$ surface lying between these two A″ surfaces, indicating no role for a $^1\pi\pi^*$ state in the planar excited-state bond-rupture process.

Correlation Analysis. Since reaction 3a is classified as a topicity 2-bond rupture[36] it was anticipated by correlation rules that there would be no direct excited ethylene to ground state radical pair correlation. These must be: $S_0 \rightleftharpoons {}^1D_{v,h}$ and whatever $S_1^* \rightleftharpoons {}^1D_{v,h}^*$, where v = vinyl and h = hydrogen. While we only treated planar ethylene in Figure 10, it is anticipated that these correlations will remain from the twisted configuration (i.e., $^{1,3}D_e \rightleftharpoons {}^{1,3}D_{v,h}$, e = ethylene). Likewise, it can be shown that singlet ethylidene, $1^1A'$, $CH_3CH \rightleftharpoons CH_2{=}CH(1^2A')$ + H along a C_1 pathway. These above correlations merely say that the ground state of vinyl radical + H is correlatively accessible with either the ground states

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(29) Dacre, P. D.; Watts, C. J.; Williams, G. R. J.; McWeeny, R. *Mol. Phys.* **1975**, *30*, 1203–11.

(30) Wahl, A. C.; Das, G. "Methods of Electronic Structure Theory", Schaeffer, H. F., III, Ed.; Plenum Press: New York, 1977; pp 3 and 51–78.

(31) Reference 27 places the CH bond in ethylene at about 101–110 kcal/mol. In a private communication with Professor Th. Just the threshold energy for the vinyl radical generation in the thermal chemistry of ethylene is estimated (ref 32) from previous experimental data (ref 33) as being in the 101–102 kcal/mol region. However, the system is still under detailed investigation and this figure can be used as being probably very close to whatever final figure is determined.

(32) Just, Th.; Troe, J. *J. Phys. Chem.* **1980**, *84*, 3068–72.

(33) Just, Th.; Roth, P.; Damm, R. *Sym. (Int.) Combust.*, [*Proc.*] **1977**, *16*, 961–9.

(34) Robin, M. A., "Higher Excited States in Polyatomic Molecules"; Academic Press, New York, 1974.

(35) Salem, L.; LeForestier, C.; Segal, G.; Wetmore, R. *J. Am. Chem. Soc.* **1975**, *97*, 479–87.

(36) Dauben, W. G.; Salem, L.; Turro, N. J. *Acc. Chem. Res.* **1975**, *8*, 41–54.

of ethylene or ethylidene singlet. However, there is no direct excited singlet ethylene–ground state vinyl radical + H correlation.

E. Correlation Analysis of Some Uncomputed Reaction Paths. Reaction 1b, the transformation of 1^1A_1 vinylidene to acetylene, has been treated a number of times and has now been shown to have essentially a zero energy activation energy (2.2 kcal/mol).[28a] Correlatively, this is seen to be an easy transformation by examinign the approximate electronic structure of 1^1A_1 vinylidene (Figure 9). The 1,2-H shift from atom a to atom b should encounter little orbital resistance since the H atom is approaching a conceptually empty $2p_y(b)$ orbital, similar to the situation encountered in a 1,2-shift in a carbonium ion.

Reaction 2, the proposed 1,2-departure of H_2 from ethylene to give acetylene directly,[37] is a symmetry-forbidden ground-state process. The correlation $C_2H_4 \rightleftharpoons HCCH + H_2$ nevertheless occurs, interrelating the ground states of ethylene and acetylene + H_2 by a presumably high-energy pathway. The approximately estimated barrier for this transformation, 81 kcal/mol,[38] seems intuitively low in comparison with the three above proposed exit channels. Even if this value is not correct it still seems likely that this exit channel is lower in energy than singlet excitation energies employed in ethylene photolyses. However, this channel is only adiabatically accessible from the ground state of ethylene. The excited-state symmetry-allowed correlation, $C_2H_4^* \rightleftharpoons HCCH^* + H_2$ seems relatively unimportant since it will be endothermic under most experimental conditions.[1e] However, although the direct process, ${}^1C_2H_4^* = HCCH + H_2$, is adiabatically forbidden, the four-centered character of the transformation has the theoretical potential of having a funnel region in the vicinity of the HOMO–LUMO crossing point through which a nonadiabatic relaxation can occur ($S^{**} \rightarrow S_0$).[9,39]

So far, we have excluded from consideration the C–C bond rupture correlations which could be important at higher energy excitations.[1d,e] These are: $C_2H_4(S_0,{}^1D) \rightleftharpoons CH_2({}^3B_1) + CH_2({}^3B_1)$ and $C_2H_4^*(C_s,Z_b) \rightleftharpoons CH_2({}^1A_1) + CH_2({}^1A_1)$.[16e,40]

F. Conclusions and a Final Overview of Ethylene Photochemistry. The above computations and correlation analysis now permit us to be more specific about the possible adiabatic and nonadiabatic characters of reactions 1–4. First, the formations of both vinylidene and ethylidene ground singlet states can occur directly from an excited $\pi\pi^*$ twisted state of ethylene. Likewise, the π3s Rydberg state could play a role in ethylidene formation. A combined examination of Figures 2 and 5, as well as the left-hand portion of Figure 8, shows that the $\pi\pi^*$ singlet state has direct access to both the $CH_2{=}C{:} + H_2$ and $HCCH + H_2$ translational continua. However, the existence of two ground-excited-state crossing regions along these same reaction coordinates permits electronically excited ethylene to pass directly to the ground-state surface. Under collision-free conditions, this passage would generate vibrationally hot ground-state ethylene having sufficient energy to potentially achieve all of the four exit channels proposed in reactions 1–4, except 3b which will be wavelength dependent. Therefore, the appearance of ethylidene or vinylidene intermediates is not diagnostic of a direct excited ground state adiabatic process. On the other hand, the appearance of vinyl radical is theoretical evidence for either a process occurring through a hot ground-state ethylene or a nonadiabatic direct relaxation, $C_2H_4^* \rightarrow CH_2CH + H$. It is the presence of these two processes which differentiates the *threshold* photochemistry of ethylene from that occurring in other small molecules (e.g., NH_3, H_2O, alkanes)[19] where only one process occurs even though other channels are thermodynamically available.

With regard to the interpretation of the observed deuterium distribution in the hydrogen and acetylene products one is unable to quantitatively assign the relative importance of reactions 1, 2, and 4 in the molecular H_2 elimination. It should be noted that while there is no great wavelength effect on the deuterium distribution in the photolysis products[1d] there is a gradually increasing portion of the reaction which passes by the vinyl radical route at higher excitation energies in the gas phase. This relative lack of selectivity can be interpreted as arising either from a system in which the nonvibrationally equilibrated "intermediate" is very hot or that the system has direct access to various translational continua which are achieved before relaxation generates vibrationally-excited ground-state ethylene. The essential question could revolve around the issue of whether the nuclei are moving in the potential field of the ground state or excited state at the product-forming stages of the reaction. However, both the vinylidene and ethylidene pathway calculations show an ambiguity in the definition of what is either the ground or excited state along certain portions of the potential surfaces. This ambiguity is further extended when one moves away from the Born–Oppenheimer approximation and hypothesizes that the nuclear potential field is varying in time and is conceptually a superpositioning of the fields of a number of Born–Oppenheimer states. Our interpretation of the lack of wavelength selectivity of the deuterium distribution in the H_2 and HCCH products as well as the lack of product quenching in the condensed phase photolysis is that we are dealing with a nearly predissociative process occurring at an early stage after excitation. We would prefer to describe this stage as being more excited-state-like than ground-state-like because of its earliness (a variation of the Hammond postulate). Finally, the mere fact of a lack of excitation wavelength sensitivity indicates that the spectroscopic state excited is not determining the reaction course and that all states are coupled with the same translational continua. These observations lead to an interpretation in which it would be best not to describe the product-forming processes as arising from a conceptually hot ground-state molecule.

With regard to the known high-temperature thermal decomposition of ethylene, this system is still under study by Just, Troe, and co-workers.[32,33] Thermally, this system can be analyzed within the context of a two-channel system, (i) $C_2H_4 = HCCH + H_2$ and (ii) $C_2H_4 = CH_2CH + H$, in which the observed kinetic activation energies must be corrected to obtain the threshold energies for these reactions.[32,33] The computed threshold energies are in the order of 100 kcal/mol each.[41] However, this analysis does not permit establishing whether the molecular elimination of H_2 occurs through a vinylidene or ethylidene intermediate. Although our own calculations are not sufficiently precise for assessing the favored pathway, preliminary higher level computations by Pople and co-workers indicate that the vinylidene route is the lowest energy pathway.[11] However, even if one assumes that the direct photolysis of ethylene generates nonequilibrated but vibrationally hot ground-state ethylene, the energy of such a species (150–200 kcal/mol) would create a relative lack of selectivity as to which exit channels were selected if their respective threshold energies are in the 100–120-kcal/mol region. Therefore, what actually occurs in the thermal chemistry of ethylene is only of relative importance in interpreting the direct photolysis results.

Finally, some comment can be made on the observed gas-phase triplet-sensitized photochemistry of ethylene.[2] While obviously vibrationally-excited triplet ethylene is initially formed, the observed low-pressure formation of HCCH + H_2 must occur through a singlet exit channel.[1e,2] The observed pressure quenching of both acetylene formation[2d] and the deuterium scrambling in the recovered ethylene has been rationalized with a two-state kinetic scheme in which triplet ethylene, E*, relaxes to an intermediate, E**. E* yields only cis–trans isomerization while E** yields both isomerization and scrambling as well as being a precursor for HCCH formation. While E** has at times been hypothesizes as being triplet ethylidene, there are several factors which speak

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(37) The symmetry rules for a four-centered reaction are discussed in ref 24.

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(41) Just and Troe estimate (ref 31–33) the threshold energy for thermal molecular elimination of H_2 at several kcal/mol below that for vinyl formation. The system is still under study in the fall-off region to better establish this number.

against this assignment. First, the best theoretical values for the activation energy for the triplet ethylidene–ethylene transformation are in the order of 40–50 kcal/mol. Theoretically, triplet ethylene generated from aromatic sensitizers (80–85 kcal/mol)[2] would only have 15–20 kcal/mol excess vibrational energy which is insufficient to yield the fast reaction rates observed for the E* = E** process (10^7–10^8 s^{-1}). A simpler interpretation is to assume that E** is singlet ethylene–ethylidene, which above about 80 kcal/mol are in dynamic structural exchange. The measured rates for the E* = E** processes, at least using low-energy sensitizers, are those for intersystem crossing in ethylene, their values being in the order estimated by the trajectory calculations of Warshel and Karplus.[42,43] In this respect, the observed triplet gas-phase photochemistry of ethylene is occurring through a vibrationally hot and equilibrated ground-state species. While it would also be a simplication to assume that direct photolysis generates essentially the same species having considerably more vibrational energy, our computations indicate that there are direct excited-state–product-state exit channels which make the singlet photochemistry conceptually more complicated than either the triplet-sensitized photochemistry or the thermal chemistry.

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Kinetics of Outer-Sphere Electron Transfers between Metal Complexes in Solutions and Polymeric Films on Modified Electrodes

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Abstract: Rotated Pt disk electrodes coated with polymeric films of poly-Ru(VB)$_3{}^{2+}$ (where VB is 4-vinyl-4′-methyl-2,2′-bipyridine) electrocatalytically mediate oxidations of the complexes [Ru(bpy)$_3$]$^{2+}$, [Ru(bpy)$_2$(4,4′-bpy)$_2$]$^{2+}$, [Ru(bpy)$_2$(py)(CH$_3$CN)]$^{2+}$, [Ru(bpy)$_2$(CH$_3$CN)$_2$]$^{2+}$, and [Ru(bpy)$_2$(pyrazine)$_2$]$^{2+}$ and reduction of the complex [Fe(bpy)$_3$]$^{3+}$, even though these reactions are thermodynamically unfavored with equilibrium constants as small as 5×10^{-6}. Similarly, electrodes coated with poly-Fe(VB)$_3{}^{2+}$ drive the electron transfer mediated oxidations of [Fe(bpy)$_3$]$^{2+}$ and [Fe(VB)$_3$]$^{2+}$ and the reduction of [Fe(4,4′-Me$_2$-2,2′-bpy)$_3$]$^{3+}$. The rates $k_{crs}\Gamma$ of these electron-transfer cross-reactions as measured using reciprocal $1/i_{lim}$ vs. $1/\omega^{1/2}$ plots are independent of poly-Ru(VB)$_3{}^{2+}$ film thickness from $\Gamma_T = 10^{-9}$ to 10^{-8} mol,/cm^2; the electron-exchange reactions involve only the outermost monolayer(s) of poly-Ru(VB)$_3{}^{2+}$ sites in the film. $k_{crs}\Gamma$ varies systematically with the reaction K_{eq}' (i.e., the difference $\Delta E°$ in formal potentials of catalyst and substrate complexes), $k_{crs}\Gamma$ being least when K_{eq}' is least. A plot of log $k_{crs}\Gamma$ vs. $\Delta E°(1 + \chi\Delta E°)$ is linear with slope predicted by the Marcus relation for electron-transfer cross-reactions. The results demonstrate outer-sphere character for the electron-transfer reaction at the polymer/solution interface.

Electrocatalysis of electrochemical reactions by surfaces to which electron transfer mediator catalysts are attached has been of considerable recent interest.[1,2] Quantitative measurements of the rates of these reactions have started to appear,[1b,e–g,o,p,2] and ideas of how to interpret them in terms of quantity of attached mediator catalyst are emerging.[1b,e,p,3–5] However, the available kinetic data remain quite limited. The reactions catalyzed, with a single exception,[2] have been driven at electrode potentials which are still relatively far from the reversible reaction substrate values. The relationship between reaction substrate structure and catalytic rate has been only briefly explored.[1b] And to date there are no data which examine the relationship between the free energy of the electron transfer mediated reaction and its rate on a modified electrode surface.

We describe here electron exchanges between metal complexes and modified electrodes where the electrocatalyzed reaction is thermodynamically unfavorable,[7] including one where the reaction equilibrium constant K_{eq}' is as small as 5×10^{-6}. The reactions are electron-exchange cross-reactions between dissolved ruthenium

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(7) The sole previous example[2] of (nonphotolytic) thermodynamically unfavorable electrocatalysis had a K_{eq}' of only 0.2.

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