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culated SCF result (15.64 kcal/mol). The nonadditivity correction based on the arctan equation is 3.94 kcal which gives a barrier (15.67 kcal/mol) in somewhat better agreement with Dedieu and Veillard's SCF result (15.64 kcal/mol).

IV. Conclusions

Equation 1 is based on the behavior[5] of ΔE and neglects zero-point energies as well as enthalpy corrections from 0 K. We have found, using data of Aue and Bowers,[8] that eq 1 and 6 work fairly well for $\Delta H°$, and somewhat less well for $\Delta G°$. This is not unreasonable[21] since the progression from $\Delta E \rightarrow \Delta H° \rightarrow \Delta G°$ involves introducing more thermodynamic information at each step. The degree of applicability of eq 1 to $\Delta H°$ or $\Delta G°$ will require further examination. Nonetheless, we find it significant that the same equation (i.e., eq 1) which has been shown[1] to account for *barriers* to group transfer reactions can also account for *well depths* of stable hydrogen-bonded intermediates. The role of multiple minima or maxima in altering the prediction of eq 1 remains an important question,[19] and a more refined theoretical treatment is in progress.

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Ab Initio Studies of (1,2)-Hydrogen Migrations in Open-Shell Hydrocarbons: Vinyl Radical, Ethyl Radical, and Triplet Methylcarbene†

Lawrence B. Harding

Contribution from the Theoretical Chemistry Group, Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439. *Received February 26, 1981*

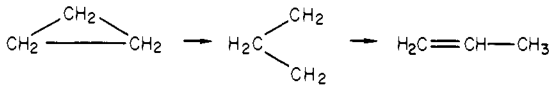
Abstract: Ab initio, POL–CI calculations on the barriers to hydrogen migration in the title compounds are reported. For C_2H_3, C_2H_5, and CH_3CH the predicted barriers are 57, 46, and 53 kcal/mol, respectively. For the first two molecules barriers to C–H bond cleavage are also calculated and found to be lower than the migration barriers. A qualitative analysis of the wave functions indicates that the high migration barriers are due to a geometrical constraint placed on the electronic structure of the transition state. A comparison to hydrogen migration in a closed-shell molecule (vinylidene–acetylene) is also presented.

I. Introduction

It has long been recognized that (1,2)-hydrogen migrations are, at least in principle, viable pathways for rearrangement of alkyl radicals.[1] Many attempts have been made to measure rate constants, activation energies and *A* factors for these rearrangements in order to determine if these reactions play an important role in the chemistry of free radicals.[2-4] To our knowledge however none of these attempts have led to unambiguous results. The primary difficulty here is the extreme complexity of the chemical systems involved. The high reactivity of free radicals leads to a large number of possible reaction pathways, all of which must be considered in any meaningful analysis of the data.[5]

In hydrocarbon combustion chemistry, the importance of (1,4)- and (1,5)-hydrogen migrations in alkyl radicals is well recognized. However, the question of whether or not (1,2) and (1,3) migrations contribute significantly to the flame chemistry of alkyl radicals has not yet been satisfactorily answered. It has generally been assumed though that the rates of these arrangements are too slow to compete with bimolecular reactions under typical flame conditions.[5-7]

A closely related question is whether or not (1,2) migrations occur in biradicals. Here the question is complicated by the existence of two nearly degenerate states, a singlet and a triplet. There is considerable evidence supporting the occurrence of (1,2) migrations in singlet biradicals, particularly in those rearrangements which are extremely exothermic.[8] For example the thermal decomposition of cyclopropane[9] has been shown to require an activation energy only slightly larger than that necessary to break the C–C bond. Assuming the mechanism involves a biradical,



(1)

This would imply that the barrier to (1,2) migration in the biradical is near zero.

For triplet biradicals the evidence for (1,2)-hydrogen migrations is less convincing. This may be due in part to the difficulty of generating triplet biradicals and to the rapidity with which these species cross to singlet surfaces. There are however several combustion reactions which presumably involve triplet biradicals for which (1,2)-hydrogen migrations have been postulated. One

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example here is the reaction of atomic oxygen with ethylene, the proposed mechanism for which is the following[10-14]

$$O(^3P) + C_2H_4 \rightarrow {}^3[\cdot O{-}CH_2{-}CH_2\cdot] \rightarrow {}^3[O{=}CH{-}CH_3] \rightarrow CH_3 + HCO \quad (2)$$

The initial addition forming the biradical is estimated to be ~30 kcal/mol exothermic. Since the observed activation energy is ~1 kcal/mol this mechanism would imply a barrier to migration of less than 31 kcal/mol.

Studies of hydrogen migrations in carbenes are also complicated by the existence of two low-lying states, a singlet and a triplet. A number of different experiments have shown that (1,2)-hydrogen migrations are relatively facile processes for singlet carbenes.[15] Hoffmann[16] has pointed out the key role of the unoccupied p-like orbital of the singlet carbene in these migrations. The case of triplet carbenes appears to be more analogous to that of alkyl radicals. No low-lying unoccupied orbitals are present and experimental evidence for the occurrence of a (1,2) migration in a triplet carbene is at best ambiguous.

There have been a large number of ab initio calculations reported on the barriers to hydrogen migration in closed-shell molecules.[17] Relatively little however has been reported on open-shell, radical or triplet molecules. One calculation on hydrogen migration in triplet methyl carbene (forming triplet ethylene) has been reported.[18] The barrier in the triplet process was found to be 88 kcal/mol while comparable calculations on the singlet surface led to a barrier of 27 kcal/mol. These calculations are however of more qualitative significance than quantitative value due to the limited size of the basis set and to the neglet of electron correlation. It has been shown, for example, that increasing the basis set size and including correlation effects lowers the barrier on the singlet surface to ~2 kcal/mol.[19] Comparable calculations have not been reported on the triplet state. Similar results have been obtained for the singlet and triplet states of vinylidene[20] and for the formaldehyde radical cation.[21,22]

Very recently, Dunning[24] has reported results on the barrier to migration in the formyl radical. The COH isomer was found to lie 40 kcal/mol above the formyl radical. The calculated barrier for rearrangement of the COH isomer (29 kcal/mol) was found to be 13 kcal/mol above the barrier to formation of CO + H. This molecule is somewhat unusual however in that the COH isomer is predicted to lie 24 kcal/mol above the CO + H limit.

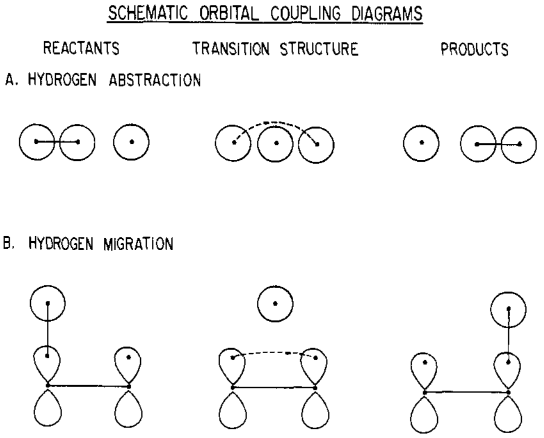

Figure 1. Comparison of valence bond orbital diagrams for the hydrogen abstraction, $H_2 + H \rightarrow H + H_2$, and a (1,2)-hydrogen migration of an alkyl radical. Solid lines connecting orbitals denote singlet coupling while dotted lines denote triplet coupling.

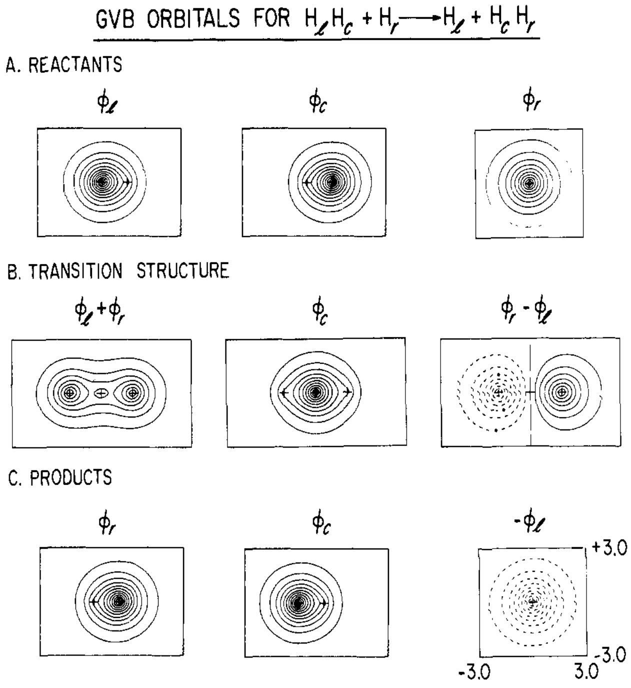

Figure 2. Generalized valence bond orbitals for the reaction $H_2 + H \rightarrow H + H_2$. Positive contours are depicted with solid lines, negative contours with short dashed lines, and nodal planes with long dashed lines. The interval between contours is 0.05 au.

In this paper we present the results of large basis set (polarized double-ζ quality) calculations employing correlated wave functions on migrations 3–5, all of which involve open-shell species. In

$$H_2C{=}\dot{C}H \rightleftarrows H\dot{C}{=}CH_2 \quad (3)$$

$$H_3C{-}\dot{C}H_2 \rightleftarrows H_2\dot{C}{-}CH_3 \quad (4)$$

$$H_3C{-}CH \rightleftarrows H_2\dot{C}{-}\dot{C}H_2 \text{ (triplet)} \quad (5)$$

addition one rearrangement (reaction 6), involving a closed-shell molecule is reported for the purpose of comparing the calculational method used here to previously reported configuration interaction[20] and Møller–Plesset perturbation theory studies.[25]

$$HC{\equiv}CH \rightleftarrows H_2C{=}C{:} \quad (6)$$

The primary goals here are to obtain reliable predictions of the barriers to these rearrangements and to gain insight into the factors that determine the magnitude of these barriers. In section II a qualitative analysis of key electronic structure features involved in hydrogen migrations is presented. In section III the details of the calculation methods used are discussed and in section IV the quantitative results of the calculations are presented and discussed.

II. Elementary Theoretical Considerations

Hydrogen migrations in free radicals are unimolecular variants of free-radical, hydrogen-abstraction reactions. For this reason

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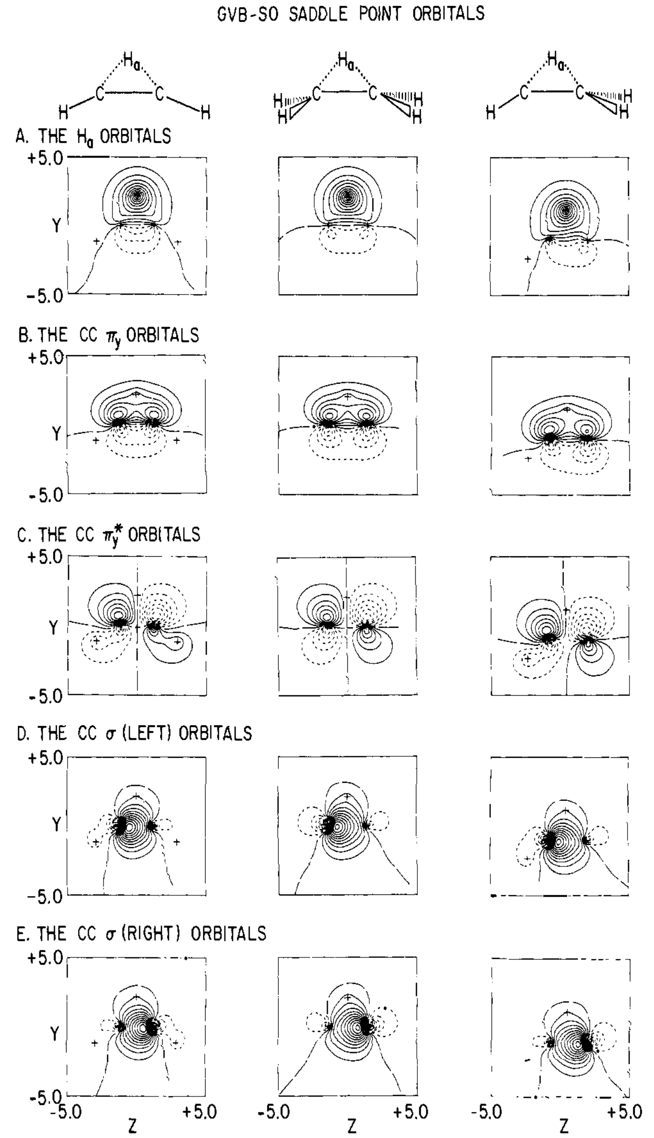

Figure 3. Selected orbitals at the saddle point for (1,2)-hydrogen migration in C_2H_3, C_2H_5, and C_2H_4 (triplet). Plotting conventions are the same as in Figure 2.

it will prove useful to first consider some of the features of hydrogen-abstraction reactions. Take as an example the simplest such reaction,

$$H_2 + H \rightarrow H + H_2 \qquad (7)$$

Qualitatively the electronic structure changes which take place during this reaction may be illustrated schematically as shown in Figure 1. These diagrams show that the electronic structure of the reactants and products is well described as a singlet-coupled bond pair together with a radical center. In the region of the transition structure (TS) however the most accurate localized orbital description of the wave function is one in which the two outer orbitals are triplet coupled while the central orbital is coupled in to form an overall doublet.[26] This permits a net bonding interaction between the central atom and both of the outer atoms at the expense of introducing a repulsive interaction between the two outer atoms.[27]

Self-consistent generalized valence bond (GVB) orbitals for this reaction are shown in Figure 2. Two of these orbitals depict the three center bonding interaction described above. This involves an orbital localized on the central hydrogen and a symmetric combination of orbitals centered on the outer hydrogens. The repulsive interaction mentioned above appears in the GVB calculations as the singlyoccupied orbital, which is an antisymmetric (antibonding) combination of orbitals centered on the outer hydrogens. Note that the triplet-coupled localized orbitals, ϕ_l and ϕ_r, drawn schematically in Figure 1 can be equivalently represented as delocalized orbitals, ϕ_g and ϕ_u, since if

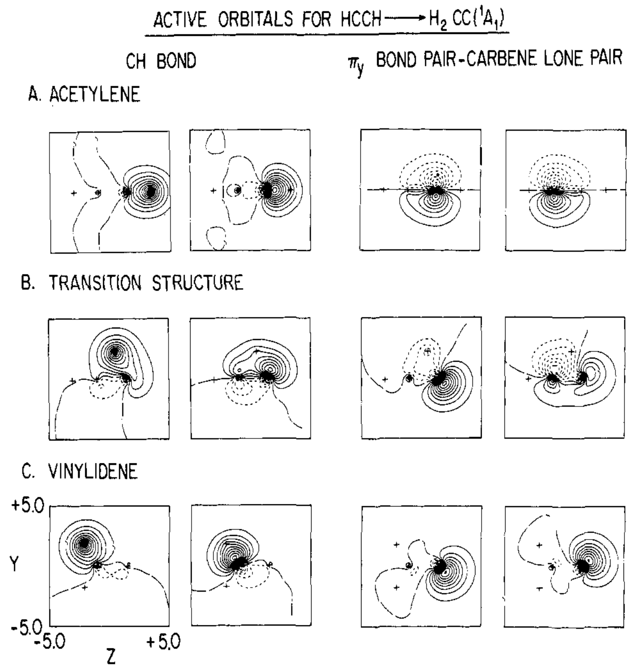

Figure 4. Selected orbitals for the acetylene ($^1\Sigma_g^+$) → vinylidene ($^1A_1$) rearrangement. Plotting conventions are the same as in Figure 2.

$$\phi_g = \frac{1}{\sqrt{2}}(\phi_l + \phi_r)$$

$$\phi_u = \frac{1}{\sqrt{2}}(\phi_l - \phi_r)$$

then it follows that

$$[\phi_g(1)\phi_u(2) - \phi_u(1)\phi_g(2)]\alpha(1)\alpha(2) = [\phi_l(1)\phi_r(2) - \phi_r(1)\phi_l(2)]\alpha(1)\alpha(2)$$

In the H + H_2 reaction the two outer hydrogen atoms are quite far apart in the TS (~2 Å) and therefore the repulsive interaction that results from occupying the antibonding orbital is not large. Consider, however, an intramolecular version of this reaction in which the initial and final radical centers are connected by another bond(s). The schematic orbital diagrams for this are also shown in Figure 1. Now the two orbitals that become triplet coupled in the TS are constrained to be quite close and consequently the resulting repulsive interaction is much larger. In fact, if we ignore the hydrogen for the moment, the coupling of the remaining two orbitals is the same as that found in $^3(\pi \rightarrow \pi^*)$ states. Thus the electronic structure at the migration TS can be qualitatively viewed as bonding a hydrogen atom to the singly-occupied π orbital of a $^3(\pi \rightarrow \pi^*)$ state.

Plots of the GVB orbitals at the TS for reactions 3–5 are shown in Figure 3. We find here, as in the H + H_2 reaction, one pair of orbitals which depict a three center bonding interaction and a third, singly-occupied orbital which is an antibonding combination of orbitals centered at the initial and final radical sites. These latter orbitals closely resemble olefinic π^* orbitals obtained from calculations on $^3(\pi \rightarrow \pi^*)$ states.

For comparison consider a (1,2)-hydrogen migration involving a closed-shell molecule with a low-lying unoccupied orbital such as a singlet carbene or a carbonium ion. As a particular example here we will take vinylidene, an unsaturated singlet carbene. The relevant GVB orbitals for vinylidene, acetylene, and the TS

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connecting them are shown in Figure 4. The pair of orbitals describing the migrating C–H bond remain highly overlapping and strongly singlet coupled throughout this reaction. Similarly the pair of orbitals which are transformed from the in-plane π bond of acetylene to the carbene lone pair of vinylidene also remain strongly singlet coupled throughout the reaction. In fact optimizing the coupling of these four orbitals, as opposed to allowing only the singlet–singlet coupling, lowers the total energy by only 2 kcal/mol. For comparison optimizing the coupling in the vinyl radical TS lowers the energy by 8 kcal/mol, a factor of 4 difference.

III. Calculational Details

Basis Set. In the calculations reported here the carbon basis consisted of the Dunning[28] valence double-ζ contraction of the Huzinaga[29] (9s,5p) set of primitive Gaussians. This was augmented by a single set of d-polarization functions ($\alpha = 0.75$). For the nonmigrating hydrogen atoms, the (4s/2s) contraction scheme[28] was used with a scale factor of 1.2. For the migrating hydrogen atom, a more flexible basis set was employed consisting of an unscaled (5s/3s) contraction[30] with a single set of polarization functions ($\alpha = 1.1236$).[31]

SOGVB Wave Functions. Results of calculations incorporating varying degrees of electron correlation via configuration interaction (CI) are reported here. All of the CI calculations are based on strongly orthogonal generalized valence bond (SOGVB)[32,33] reference wave functions. For the purposes of clarifying the form of these wave functions we will use as an example the hydrogen migration reaction of the ethyl radical. As noted in section II, it is expected that as the molecule moves along the reaction path toward the transition structure (TS), the orbital coupling scheme of the "active" C–H bond and the radical orbitals will change greatly. For this reason it is important to choose a reference wave function in which the coupling scheme of these orbitals is variationally optimized. The simplest such wave function is the SOGVB(1) wave function in which the CH_a bond is correlated. This is a three configuration, MC-SCF, wave function which can be written as follows,

$$\mathcal{A}\{\Phi_{\text{core}}[C_1\phi_a{}^2 + C_2\phi_b{}^2 + C_3(\phi_a{}^1\phi_b{}^1 - \phi_b{}^1\phi_a{}^1)]\phi_r{}^1\chi\}$$

where Φ_{core} = a product of doubly-occupied orbitals, ϕ_a = the CH_a bonding orbital, ϕ_b = the CH_a correlating orbital, ϕ_r = the singly-occupied "radical" orbital, and χ = the general (optimized) spin function. Preliminary calculations indicated that correlation effects involving the carbon–carbon bond pair(s) are also important in determining the barriers to hydrogen migration[40] and for this reason a correlating orbital(s) for this pair(s) was also optimized. The SOGVB wave functions used then were the following,

$$\chi(C_2H_5) = \mathcal{A}\{\Phi_{\text{core}}[C_1\phi_{1a}{}^2 + C_2\phi_{1b}{}^2] \times [C_3\phi_{2a}{}^2 + C_4\phi_{2b}{}^2 + C_5(\phi_{2a}{}^1\phi_{2b}{}^1 - \phi_{2b}{}^1\phi_{2a}{}^1)]\phi_r{}^1\chi\}$$

$$\chi(C_2H_3) = \mathcal{A}\{\Phi_{\text{core}}[C_1\phi_{1a}{}^2 + C_2\phi_{1b}{}^2][C_3\phi_{2a}{}^2 + C_4\phi_{2b}{}^2] \times [C_5\phi_{3a}{}^2 + C_b\phi_{3b}{}^2 + C_7(\phi_{3a}{}^1\phi_{3b}{}^1 - \phi_{3b}{}^1\phi_{3a}{}^1)]\phi_r{}^1\chi\}$$

$$\chi(C_2H_4) = \mathcal{A}\{\Phi_{\text{core}}[C_1\phi_{1a}{}^2 + C_2\phi_{1b}{}^2] \times [C_3\phi_{2a}{}^2 + C_3\phi_{2b}{}^2 + C_5(\phi_{2a}{}^1\phi_{2b}{}^1 - \phi_{2b}{}^1\phi_{2a}{}^1)]\phi_{r_1}{}^1\phi_{r_2}{}^1\chi\}$$

In the C_2H_5 and C_2H_4 wave function the first correlated pair represents the carbon–carbon σ bonds. In C_2H_3 the first two pairs represent the carbon–carbon σ and π bonds.

Table I. The Vinylidene–Acetylene Rearrangement. Comparison of Calculated Barriers and Energy Differences (kcal/mol)

calculational method	barrier	$E(H_2CC) - E(HCCH)$
RHF/6-31G*	16.4	34.2
RMP4(SDQ)/6-31G*	8.1	41.9
RHF/DZ+P	14.7	33.5
SCEP/DZ+P	8.6	40.0
SOGVB/DZ+P	21.6	31.0
POL-CI/DZ+P	5.0	41.7
POL-CI(S+D)/DZ+P	6.2	39.5

CI Wave Functions. The SOGVB wave functions discussed in the previous section include important correlation effects and provide a conceptually simple description of the migration processes. However in order to obtain accurate relative energies it is necessary to take into account many-body effects neglected in the simple SOGVB wave function. Here, this is accomplished through the use of configuration interaction (CI) wave functions based on the SOGVB orbitals and reference configurations. The CI calculations reported here are of the POL-CI[34] variety in which double excitations from each of the three SOGVB(1) configurations are allowed with the restriction that at most one electron be excited into the virtual orbitals. For the molecules H_3C_2, H_5C_2, and H_4C_2 this procedure leads to 8781, 9519, and 15046 symmetry-selected spin eigenfunctions, respectively. For the H_4C_2 calculations it was necessary to use the B_k approximation with the reference set selected using the A_k scheme (applied to the three SOGVB(1) configurations) with a cumulative energy threshold of 0.010 hartree.[35,36] For the H_4C_2 saddle point this calculation was repeated with a cumulative threshold of 0.001 hartree. The difference in total energies between the two calculations was 0.0008 hartree or 0.5 kcal/mol.

In addition a second set of calculations were performed which included higher order correlation effects involving the two electrons of the CH_a bond and the unpaired electron(s). This was accomplished by adding to the POL-CI configuration list all those configurations generated by allowing double excitations into the full virtual space. The resulting wave functions will be referred to as POL-CI + ACTIVE(2). For the vinyl radical this procedure adds approximately 2000 spin eigenfunctions to the list. The rationale here is that during the course of these reactions only these three orbitals are undergoing dramatic changes and therefore it is expected that the most important changes in correlation energy will come from terms involving these orbitals.

Geometry Optimizations. Partial geometry optimizations at the SOGVB level were carried out for all of the species. For the minimum energy structures two assumptions were made; the C–H bonds were taken to be 1.09 Å and all trivalent carbons were assumed to be planar with 120° bond angles. For the TS optimizations it was assumed that the reaction coordinate is well represented by the C–M–H_a angle, where M is the midpoint of the carbon–carbon bond. The energy was then maximized with respect to this one parameter and minimized with respect to the other parameters. Again the C–H bonds not involved in the migration were frozen at 1.09 Å. For reaction 3 the TS was

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(40) The reason for this is that at the saddle points, the orbitals involved in the migrations resemble π and π^* orbitals. Analysis of the CI wave functions indicates that many-body effects between these electrons and the $CC\sigma$ (and π) bond pairs are more important than the corresponding effects involving the CH_a bonds of the reactants or products.

Table II. Calculated Barriers to Hydrogen Migration (kcal/mol)[a]

method	H_2CCH	H_3CCH_2	H_3CCH ($^3A''$)
SOGVB	65.3	52.7	60.0
POL-CI	55.5	45.5	51.6
POL-CI + ACTIVE (2)	57.0	46.4	53.3

[a] The total SOGVB energies at the saddle points for C_2H_3, C_2H_5, and C_2H_4 are −77.33942, −78.54788, and −77.90209 hartrees, respectively. The POL-CI energies are −77.441984, −78.62420, and −77.98631 hartrees, respectively. The POL-CI + ACTIVE (2) energies are −77.45221, −78.63605, and −77.99643 hartrees, respectively.

initially assumed to be planar. However, at the optimum planar structure, nonplanar distortions were examined and were found to raise the energy. It was therefore concluded that the optimum TS for this reaction is of C_{2v} symmetry. In reaction 4 the TS was constrained to be C_{2v} (consistent with the UHF calculations of Hase)[37] and in reaction 5 it was assumed that a plane of symmetry is maintained throughout the migration.

For the vinylidene–acetylene rearrangement, the geometries used were those reported by Dykstra and Schaefer.[20a]

Computer Codes. The Raffenetti BIGGMOLI, ORDER and TRAOMO programs were used to evaluate, sort, and transform the molecular integrals. The Bobrowicz SOGVB and CITWO programs were used to obtain the SOGVB and CI wave functions. The CI configuration lists were generated using the CIGEN program written by B. D. Olafsen.

IV. Results and Discussion

Acetylene–Vinylidene Rearrangement. The acetylene–vinylidene rearrangement has been extensively examined by Dykstra and Schaefer,[20a] using self-consistent electron-pair theory (SCEP), and by Pople et al.,[25] using the spin-restricted form of the Møller–Plesset perturbation theory (RMPn). In both cases polarized double-ζ basis sets were used, comparable in quality to that used here. A comparison of the calculated barriers and energy differences is made in Table I. The agreement on the barrier height is quite good, with the results ranging from 5.0 kcal/mol for POL–CI to 8.6 kcal/mol for DZ + P − SCEP. Similarly the predicted vinylidene–acetylene energy differences in the various correlated calculations are found to agree to within ~2 kcal/mol.

Two points should be noted here. First, both the RMP4 and the POL–CI calculations include configurations that are more than a double excitation away from the dominant configuration. The SCEP calculations do not. In the POL–CI calculations, the effect of these high-order excitations can be determined by deleting them from the configuration list, denoted POL–CI(S+D) in Table I. We find that these configurations decrease the barrier height by 1.2 kcal/mol and increase the acetylene–vinylidene energy difference by 2.2 kcal/mol.

The second point is that the small disagreements in the relative energies are not necessarily due to differences in the methods used since the basis set differences are apparently significant. For example, with RHF wave functions the 6-31G* basis gives a barrier 1.7 kcal/mol above that reported by Dykstra.[20a] Thus the excellent agreement between the RMP4 and the SCEP barriers with these two basis sets must be somewhat fortuitous. The basis used in the POL–CI calculations is slightly more flexible than either of the other basis sets, since it employs a (5s/3s) contraction on the hydrogen whereas a (4s/2s) is used in both the RMP and the SCEP calculations. This may account for some of the 2 kcal/mol difference between the POL–CI(S+D) and both the SCEP and RMP4 results.

Migration Barriers. The calculated barriers to migration are summarized in Table II. Note that for reactions 3 and 4 the overall migrations are thermoneutral (reactants and products are indistinguishable) while reaction 5, in the direction written, is 0.2 kcal/mol endothermic in the SOGVB calculations and 2.3 and 1.7 kcal/mol exothermic in the POL–CI and POL–CI + ACTIVE(2) calculations respectively.

Table III. Calculated Barriers (E_b) and Dissociation Energies (D_e) for CH Bond Cleavage (kcal/mol)

	H_2CCH		H_3CCH_2	
method	D_e	E_b	D_e	E_b
SOGVB	41.1	50.9	33.5	41.8
POL–CI	36.7	42.1	32.9	37.4
POL–CI + ACTIVE (2)	39.9	44.2	37.7	41.4

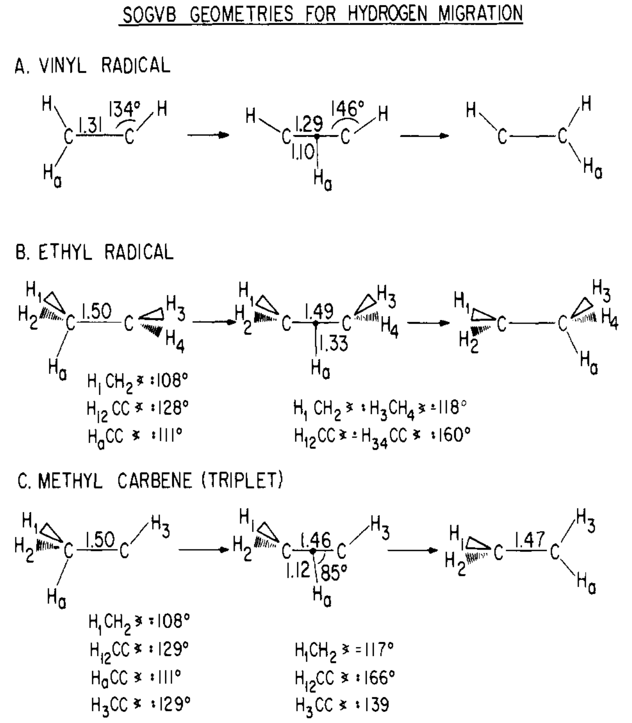


Figure 5. Calculated SOGVB geometries for the reactants, saddle points, and products in the (1,2)-hydrogen migrations of C_2H_3, C_2H_5, and C_2H_4 (triplet).

The calculated barriers are all quite large ranging from 46 kcal/mol for the ethyl radical to 57 kcal/mol for the vinyl radical. The size of these barriers indicates that these reactions should not be important in room-temperature radical chemistry. However, in order to determine whether or not such migrations will occur at higher temperatures it is necessary to consider possible competing reactions. The most obvious candidate for a competing unimolecular reaction is the elimination of atomic hydrogen. For the vinyl and ethyl radicals the barriers to C–H bond cleavage have also been calculated, using the same methods, and the results are summarized in Table III. We see that in all three calculations for both reactions, the barriers to CH bond cleavage are significantly less than those for migration.

These predictions are in fair agreement with a recent experimental study[4] of the relative rates for hydrogen migration vs. dissociation in the ethyl radical in which it was concluded that the activation energies for the two processes are identical (41 ± 4 kcal/mol). Kaplan,[5] however, has recently criticized the interpretation of these experiments, suggesting that the hydrogen migration rate is unobservably slow (presumably due to a higher activation energy). This latter conclusion is more consistent with the theoretical results, although the expected accuracy here is not sufficient to rule out the possibility that the barrier to migration in the ethyl radical may be equal to or even slightly below the CH cleavage barrier.

At this point it is appropriate to compare briefly the results of the two sets of CI calculations in order to establish the effect of the higher order "active" correlations included in the POL–CI + ACTIVE(2) calculations. From Table II we see that the differences between the migration barriers predicted in the two CI's are all quite small (<2 kcal/mol). In Table III though we see that the added configurations increase the C–H bond energies by 3–5 kcal/mol and the barriers to cleavage by 2–4 kcal/mol. Apparently then as long as the hydrogen atom is fairly closely bound to the hydrocarbon fragment (as in the radicals and the migration TS) these higher order correlations nearly cancel. When the hydrogen atom is far removed from the hydrocarbon (as in the dissociated fragments or the TS leading to dissociation) these correlations are, not surprisingly, less important. Consequently inclusion of the higher order "active" correlation effects increases the bond energies and barriers to dissociation while it has little effect on the migration barriers.

The effect of zero-point energies on the results discussed above should be considered. The main question here is whether or not ZPE will affect the relative heights of the barriers for migration and cleavage. Qualitatively, since the migration saddle points are predicted to be quite tight while the cleavage saddle points are predicted to be relatively loose (vide infra), we expect ZPE to decrease the barriers to cleavage relative to those to migration. For the cleavage reaction of vinyl radical, a normal mode analysis was carried out which indicates that ZPE decreases this barrier by 7.4 kcal/mol. Comparable calculations have not been carried out on the migration TS. However, from the results of Osamura et al.[21] on the isoelectronic rearrangement of H_2CO^+, we expect ZPE to decrease this barrier by ~5 kcal/mol. The net effect then of including ZPE is to raise the migration barriers by a few kcal/mol relative to the cleavage barriers.

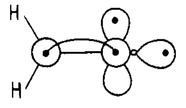
Finally we note that the calculated barrier to migration in the vinyl radical, 57 kcal/mol, is significantly less than that obtained for the vinyl anion, 74 kcal/mol, by Dykstra et al.[39] This is in line with the qualitative arguments of section II since in the anion the highly antibonding π^*-like orbital will necessarily be doubly occupied rather than singly occupied as in the radical. This trend was in fact predicted 20 years ago by Zimmerman.[23]

Saddle-Point Geometries. The calculated geometries are summarized in Figure 5. Two features of the TS geometries should be noted. First the distance from the midpoint of the carbon–carbon bond to the migrating hydrogen is quite short (1.1–1.3 Å) indicating that this hydrogen is still quite tightly bound at least in a local sense. Hase et al.[37] have already noted this result for the ethyl radical and have shown that the tightness of the migration TS leads to a fairly low *A* factor for migration (compared to CH bond cleavage).

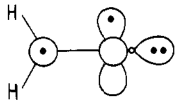
A second interesting feature of the calculated geometries is that the saddle point, carbon–carbon bond lengths are all shorter than those of either the reactants or products. This might at first seem surprising in light of the C–C antibonding nature of the singly-occupied orbital at the saddle point. Consider though a comparison between these saddle-point bond lengths and those of the species in which the migrating hydrogen has been removed completely. For the vinyl radical, the saddle-point bond length is 1.29 Å; if we remove the hydrogen we have acetylene which has a calculated C–C bond length of 1.20 Å (0.09 Å shorter). Similarly for the ethyl radical the TS bond length is 1.49 Å while for ethylene the value is 1.35 Å. For methylcarbene the comparison is saddle point 1.46 Å, vinyl radical 1.31 Å. The effect then of bringing up the hydrogen atom and its electron is to increase the C–C bond lengths by 0.09–0.15 Å. The reason that there is a net decrease on going from reactants (or products) to the saddle points is due to the three center bonding interaction discussed in section II. Indeed, from Figure 3 we see that in each case, one of the TS orbitals resembles a C–C π-bonding orbital, occupation of which should shorten the bond length.

One signficant difference between the results here and those of Conrad and Schaefer[20b] on triplet vinylidene should be noted. For the $^3B_2$ state of vinylidene it was found that allowing the TS to become nonplanar led to a decrease of ~20 kcal/mol in the barrier height. It was also found that the C–C bond length of the nonplanar TS was much longer than that of the planar structure. Of the reactions considered here the one most closely related to triplet vinylidene is the vinyl radical. As was noted in section III, nonplanar structures were examined in this reaction and found to be higher in energy.

The key difference between these two molecules is that in vinylidene there is a second low-lying triplet state, $^3A_2$, less than 1 eV above the $^3B_2$ state.[20,38] Schematic diagrams for these two states are given below. The electronic structure of the $^3B_2$ state is similar to that of a saturated triplet carbene. The structure of the $^3A_2$ state however is more analogous to that of a *singlet* carbene. Note in particular that the carbene-like center of the $^3A_2$ state has a doubly-occupied lone pair and an unoccupied p–π orbital. Given this orbital structure, three qualitative conclusions can be drawn immediately:



$^3B_2$



$^3A_2$

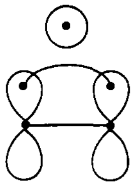
(1) The $^3A_2$ state should possess a low barrier to hydrogen migration analogous to that of other single carbenes.

(2) The TS for this migration should be highly nonplanar since the migrating C–H bond will be stabilized by delocalization into the empty p–π orbital.

(3) The C–C bond length of the $^3A_2$ state should be longer than that of the $^3B_2$ state since it is a double bond in the $^3B_2$ state while it is only a single bond in the $^3A_2$ state. This longer bond length can be expected to persist in the TS for migration.

For nonplanar geometries the $^3B_2$ and $^3A_2$ states can interact and thus an avoided crossing will occur leading to the observed nonplanar TS for migration from the $^3B_2$ state. These conclusions, based on the assumption of an avoided crossing between the $^3B_2$ and $^3A_2$ states, are all consistent with the results reported by Conrad and Schaefer.

An Alternative Pathway for Migration. In the calculations presented above we have considered a relatively tight TS for migration with a singly-occupied orbital of C–C, π^*-like character. For the vinyl and ethyl radicals the overall symmetry of this state is $^2B_2$. Since the $^2B_2$ barriers are quite large, an alternative, one in which the singly-occupied orbital is of a_1 symmetry, should be considered. The electronic structure of this state may be schematically represented as follows. Comparison to the diagrams in Figure 1 reveals that the difference between the $^2B_2$ and $^2A_1$ states is that in the $^2B_2$ state the in-plane, π-like orbitals are triplet coupled while in the $^2A_1$ state these orbitals are singlet coupled. Thus in the $^2A_1$ state we have eliminated the repulsive interaction between the two carbon centered orbitals at the expense of introducing a repulsive interaction between the hydrogen atom and the π-like orbitals.



For the vinyl radical a search was made for a TS of $^2A_1$ symmetry, however it was found that variation of the distance between the migrating hydrogen and the CC bond midpoint leads to a purely repulsive potential curve. More extensive calculations would undoubtedly find a weak van der Waals minimum at large separation, however this saddle point (if it is a saddle point) will be located further out than the TS for CH bond cleavage. Therefore the energetic requirements for migration on the $^2A_1$ surface should be the same as that for CH bond cleavage followed by reattachment.

V. Conclusions

The primary conclusion to be drawn from the calculations presented here is that in simple alkyl radicals and triplet carbenes the lowest energy pathway for (1,2)-hydrogen migration will in most cases be CH bond cleavage followed by reattachment. It is the case that migration saddle-point structures exist in which the migrating hydrogen remains tightly bound, however the energies of these structures are predicted to be significantly above the barriers to CH bond cleavage.

The electronic structure at these migration saddle points is analogous to that found in hydrogen-abstraction reactions. Furthermore the cause of the high barriers can be traced to a geometric constraint placed on the electronic wave function which forces two triplet coupled orbitals to be proximate.

The Central Bond Length in Hexaphenylethane and Hexakis(2,6-di-*tert*-butyl-4-biphenylyl)ethane

Eiji Osawa,*[1a] Yoshiaki Onuki, and Kurt Mislow*[1b]

Contribution from the Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan, and the Department of Chemistry, Princeton University, Princeton, New Jersey 08544. *Received April 13, 1981*

Abstract: In corroboration of previous work,[4] full relaxation calculations on the D_3 and S_6 conformers of hexaphenylethane (**1**) by several empirical force field (EFF) schemes (MMI, MMPI, MM2), as well as by the MNDO SCF MO method, show that the D_3 form is 2–5 kcal mol^{-1} more stable than the S_6 conformer, and that the central C–C bond length has a value of 1.60–1.64 (EFF) or 1.68 (MNDO) Å. EFF calculations (MMPI, MM2) on hexakis(2,6-di-*tert*-butyl-4-biphenylyl)ethane (**2**) show that the bonding parameters in the hexaphenylethane portion of this structure differ in no significant way from the corresponding parameters in **1**. We thus conclude that either the central bond length of 1.47 (2) Å reported[8] in a recent X-ray study of **2** is grossly in error, or a novel shrinkage effect is operative in **2**, and by implication in **1**, which is not taken account of in the parametrization of any of the above computational schemes. The chemical implications of the discrepancy between the observed and calculated central C–C bond length are sufficiently important to call for a confirmation of the X-ray structure. The D_3 conformer of **2** is calculated to be more stable than the S_6 form by 4–6 kcal mol^{-1}; given the enormous size of this molecule ($C_{122}H_{150}$), such a conformational energy difference is quite small, and the observation[8] of molecular S_6 symmetry can be readily ascribed to a crystal packing effect.

Hexaphenylethane (**1**), a molecule of historic importance[2] and a focal point of chemical interest since Gomberg's initial investigation of "triphenylmethyl" at the turn of the century,[3] has thus far resisted all attempts at synthesis. We recently reported[4] a computational study of this elusive molecule, using full relaxation empirical force field (EFF) calculations.[5] A search of the potential energy hypersurface too low-lying minima, one corresponding to a D_3 structure composed of two essentially eclipsed homochiral trityl propellers, and the other to a S_6 structure composed of two staggered heterochiral propellers. The D_3 form was computed to be the more stable by 2.55 kcal mol^{-1}, a conclusion which was qualitatively confirmed by a hybrid EFF–EHMO calculation.[6] That both forms were under substantial internal strain was manifest from the marked deviations of some of the calculated structural parameters from standard values. Most strikingly, the central C–C bond lengths calculated for the D_3 and S_6 forms, 1.639 and 1.636 Å, were abnormally long compared to the standard value of 1.53 Å,[7] evidently as the result of a severe nonbonded repulsion between the two trityl moieties (*front strain*).

Against this background, the subsequent announcement[8] by Stein, Winter, and Rieker of the synthesis and X-ray structure of the first, and so far only, unbridged hexaarylethane, hexakis(2,6-di-*tert*-butyl-4-biphenylyl)ethane (**2**), was an event of singular import,[9] not least because much emphasis was placed on the allegation that our predictions[4] were badly off the mark. First, the finding of an S_6 conformation for **2** was considered contradictory to our prediction of D_3 symmetry for the ground state of **1**; second, **2**, was reported to have the surprisingly short central C–C bond length of 1.47 (2) Å and a C_{ethane}–C_{phenyl} bond length (average value) of 1.65 (3) Å, in marked contrast to the values of 1.636 and 1.576 Å calculated[4] for S_6-**1**. The authors suggested[8] that the presence of the *tert*-butyl groups in **2** might be responsible for these large discrepancies between their findings and our predictions.

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