

The Spatial Extent of the V State of Ethylene and Its Relation to Dynamic Correlation in the Cope Rearrangement

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The classical problem of the extent of Rydberg–valence mixing for the V state of ethylene is re-examined using a large basis set and several different approaches to selecting configurations. The results are interpreted in terms of the general need for dynamic σ – π correlation in π -electron systems. The effect of dynamic correlation on the activation energy of the Cope rearrangement is especially noted.

Introduction

Recent interest has arisen again regarding methods for calculating the spatial extent of the V state of ethylene.^{1–5} We will focus here on the problem in its traditional form.^{6–19} That is, we will consider a vertical transition at the ground state equilibrium geometry and we will measure the spatial extent by the value of $\langle \sum x_i^2 \rangle$ where x is the out-of-plane direction. There is no experimental value for this quantity, but previous theoretical values have varied from a high of about $43 a_0^2$ for the ROHF wave function for this V state to a low of about $16 a_0^2$. The result is very sensitive to the basis set and the method of calculation. By contrast, both the ground state value and the T state value are in the range 11–12 a_0^2 with all reasonable calculations.

In spite of the wide range of values for the spatial extent, most correlated calculations agree on a value of about 8.0 eV for the vertical excitation energy to the V state and 4.6 eV for the T state. The agreement with experiment is good for the T state, but the observed maximum in the vibrationally unresolved absorption spectrum of the V state occurs at 7.65 eV. Peyerimhoff and co-workers^{20–22} have explained why this is not the proper comparison with experiment and 8.0 eV is the generally agreed value.

Many years ago, McMurchie and Davidson¹³ computed a value of 18 a_0^2 for $\langle x^2 \rangle$ for the V state. This was somewhat smaller than other literature values at the time.¹² In doing this, they (a) employed a somewhat larger basis set than had been used previously and (b) chose configurations by classes of excitation instead of by importance sampling as is usual in multireference single and double excitation configuration interaction (MRSDCI). They concluded among other things that single excitations of the σ electrons *relative to the ground state* made an important contribution to the value of $\langle x^2 \rangle$.

Later papers by Buenker et al. obtained values of 19–20 a_0^2 for $\langle x^2 \rangle$ employing larger basis sets and MRSDCI configuration selection.^{15,16} They concluded that inclusion of single excitations of the σ electrons from the ground state configuration in the reference space was not important (less than a 1 a_0^2 effect on $\langle x^2 \rangle$), even though two of the seven configurations with the largest coefficients were of that form. Wiberg² recently obtained 18 a_0^2 for $\langle x^2 \rangle$ using single excitation CI (CIS) and a 6-31 (2⁺,2⁺)G** basis in agreement with the Tamm–Dancoff (an earlier name for the CIS method) value of 18.2 included in the McMurchie and Davidson¹³ paper. They further stated that “McMurchie and Davidson, from their SDCI studies, stated that $\sigma \rightarrow \sigma^*$ configurations are important, but Buenker and Peyer-

imhoff have shown that this was due to the use of an inflexible basis set”. Wiberg provided no further evidence as to the importance of these single excitations in his calculations. Lindh and Roos,⁴ however, in recent large MRSDCI calculations, reported that four of their eight most important configurations were of the form of a single excitation from the ground state, and they included these in their reference space.

All of the older calculations used basis sets that are small by today's standards. Hence, we have re-examined this problem using a much larger basis set and also paying more attention to the methodology of configuration selection. The methodology is very important since recent calculations using size consistent methods^{1–3} seem to agree better with the McMurchie and Davidson¹³ results than do the MRSDCI calculations.^{4,14–16}

The basis set for this paper consisted of 223 contracted Gaussian functions. Most of these are the same as used in previous papers on PES and EMS of ethylene.^{23–25} For PES, the 18s13p Partridge basis²⁶ for C was supplemented with an additional diffuse s and p set and the tightest 12 s and 7 p functions were contracted to 2 s and 1 p. The 10s Partridge basis for H was supplemented with an additional diffuse s, and the tightest 6s functions were contracted into a single function. Additionally, three d and one f polarization functions were added to C, two p and one d polarization functions were added to H, and two p and two d cation Rydberg functions were added on the molecular center. All Cartesian components of d and f were retained. In addition to this PES basis, for the π^* orbital of the neutral ethylene V state ROHF we found we needed two additional diffuse d functions on the molecular center to converge the value of $\langle x^2 \rangle$. They had exponents 0.026 and 0.013.

The geometry is the same as that in the original McMurchie and Davidson paper.¹³ That is, the C atoms are placed on the z axis at $\pm 1.2639691 a_0$ and the H atoms are in the yz plane with coordinate $(y,z) = (\pm 1.7537465 a_0, \pm 2.3260758 a_0)$. In the following discussion x^2 is in units of a_0^2 and the energy is in hartrees unless otherwise noted.

With this basis, the ground state SCF energy is -78.069485 and the ground state TCSCF energy (including $(\pi)^2$ and $(\pi^*)^2$ configurations) is -78.096938 . This TCSCF energy, within the π -electron approximation, is the correct energy to compare with the ROHF energy for the $^1(\pi,\pi^*)$ V state, -77.801259 , and the $^3(\pi,\pi^*)$ T state, -77.940077 . These ground state energies are about 0.001 hartree lower than those reported by Lindh and Roos⁴ for the basis set they used in the most elaborate CI study on this problem to date. Their basis is not as well converged for the V state ROHF, however, since it gives an energy 0.006 hartree higher and $\langle x^2 \rangle = 28.10$ instead of the ROHF limiting value of 42–44.^{5,13,27} Notice that our basis gives an (ROHF-

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TABLE 1: Expectation Value of $\sum x_i^2$ for V State^a

	TCSCF	V ROHF	T ROHF
¹ ($\pi\pi^*$)	10.9	43.4	11.7
FCI(π)	23.0	36.1	23.8
CIS(π)	30.8	43.4	34.6
CIS	17.8	32.5	19.7
APC	26.3	40.1	27.3
ASSEFAPC	18.8	18.5	18.7
π^* CI-S	21.7	20.5	20.9
MRSDCI (1)		36	14
MRSDCI (2)		29	14

^a The columns are labeled by the calculation from which the molecular orbitals were defined. The rows are labeled by the CI method described more fully in the text. Briefly, ¹($\pi\pi^*$) is a one-configuration wave function, FCI(π) is full CI for two electrons with frozen σ core, CIS is all singles from the SCF ground state configuration, CIS(π) is similar except only π and π^* electrons are excited, APC is full CI for 2 electrons in the $b_{3u}(\pi)$ and $b_{2g}(\pi^*)$ subspaces, ASSEFAPC contains all single excitations from all APC configurations, π^* CI-S includes all single excitations from the CIS(π) configurations. MRSDCI are multireference single and double excitation CI with more than 70 reference functions and 300 000 perturbation selected configurations.

TCSCF) excitation energy of 8.05 eV for the V state, which is close to the expected full CI limit. That something is wrong, however, can be seen from the poor T state excitation energy, 3.78 eV, and the large value for $\langle x^2 \rangle$ of 43.4 for the ROHF V state wave function. Clearly, the closed shell ground state has about 0.8 eV more correlation energy than the open shell T state. The V state has about the same correlation energy as the ground state, but unlike the other states, inclusion of this correlation energy must produce a large qualitative change in the V state wave function.

The nature of this change has been known since the early work of Peyerimhoff and others.⁶⁻¹⁶ Ethylene has ¹(π, π^*) and ¹($\pi, 3d\pi$) configurations that are similar in energy when electron correlation is not included. These mix strongly, producing a ROHF function of high Rydberg character. Electron correlation preferentially lowers the energy of the ¹(π, π^*) component of the wave function so the final correlated wave function has greatly increased valence character compared to the ROHF function. The exact value of $\langle x^2 \rangle$ is thus governed by the extent of the recovery of the electron correlation and hence by the quality of the basis set and the type of wave function employed.

Results

Before considering CI-based methods, it is interesting to look at the CAS-MP2 (OPT2) method.^{28,29} In perturbation methods, one must evaluate properties as energy derivatives. Here, the result is rather remarkable. Even though the ROHF wave function gives 43.4 for $\langle x^2 \rangle$ at zero field, the derivative of the CASMP2 energy (using finite differences for fields $\lambda \sum x_i^2$ with $\lambda = \pm 10^{-4}$ and ROHF functions as the CAS) gives $\delta E / \delta \lambda = \langle x^2 \rangle = 17.8$.

Table 1 summarizes the spatial extent of V state wave functions computed by several methods. Each column of this table was computed starting with a different set of molecular orbitals: the ground state TCSCF orbitals, the V state ROHF orbitals, and the T state ROHF orbitals. The first line of the table simply gives the value of $\langle x^2 \rangle$ for the single configuration approximation to the V state. It shows clearly that the π^* orbital defined by the V state ROHF procedure is much more diffuse than the π^* orbital optimized for either the ground state electron correlation or for the T state.

The second line of the table shows that this is not simply a π orbital problem, however. The FCI(π) result used all

configurations formed by placing the two active electrons from π and π^* in all the virtual orbitals. If the occupied σ orbitals were identical in the three columns, then the entries would be equal. Instead, the V state ROHF orbitals still produce a larger value of $\langle x^2 \rangle$ showing that the σ orbitals for the V state ROHF have relaxed in the presence of the diffuse π^* orbital. Since the true V state π^* orbital is expected to be more like the T state ROHF orbital than like the V state ROHF orbital, the V state ROHF σ orbitals may lock the calculation into a too diffuse final result when limited CI in the σ space is included.

The use of single excitations from the ground state SCF wave function (CIS) has recently been advocated as an effective procedure for computing excited state energies.³⁰ With this basis set, CIS gives 7.68 eV for the V state excitation energy and 3.56 eV for the T state energy. While this is very close to the experimental V state energy (while differing by 0.3 eV from the best calculations), it is still 1.0 eV in error for the T state. The $\langle x^2 \rangle$ value of 17.8 is essentially the same as the value using the same list of configurations with TCSCF orbitals, while use of V state ROHF orbitals with the CIS configuration list gives a much larger $\langle x^2 \rangle$.

Wiberg² implied by his paraphrase of the Buenker et al.^{15,16} conclusion that single excitations from the σ orbitals were not important in this CIS procedure. To test his statement, we have included in Table 1 a line labeled CIS(π) where only single excitations from the π orbitals (relative to the ground state π^2 configuration) were included. Using ground state SCF orbitals gives 30.3 for $\langle x^2 \rangle$ compared to 17.8 when σ excitations are included. Thus, as previously claimed by McMurchie and Davidson,¹³ the single excitations have a large effect in this simple calculation.

The basis set yields 53 a_g , 20 $b_{3u}(\pi)$, 30 b_{2u} , 12 b_{1g} , 43 b_{1u} , 22 $b_{2g}(\pi^*)$, 32 b_{3g} , and 8 a_u molecular orbitals in D_{2h} symmetry with x out of plane and z along the C–C axis. The ground state SCF configuration occupies 1–3 a_g , 1 b_{3u} , 1 b_{2u} , 1–2 b_{1u} , and 1 b_{3g} orbitals. For some calculations that are truncated by the class of excitation (as in the following examples), this basis yields too many configurations. Consequently, we performed some calculations in which the virtual orbitals were transformed to K orbitals³¹ and the MO list was truncated to 34 a_g , 18 b_{2u} , 9 b_{1g} , 26 b_{1u} , 16 b_{3g} , and 6 a_g . No truncation was done in the $b_{3u}(\pi)$ or $b_{2g}(\pi^*)$ symmetries.

Using this truncated MO set, we performed some calculations of the type found by Borden and Davidson³² to be efficacious for planar diradicals with Jahn–Teller singularities. First, we considered “all” π configurations, APC, in which all arrangements of two active electrons among the b_{3u} and b_{2g} symmetries were allowed. This gives less correlation energy than when excitation to all symmetries are included as was done in the FCI(π) calculation. As shown in Table 1 the APC result is a little more diffuse than that from the FCI(π) calculation. Then we performed an ASSEFAPC (all σ single excitations from APC, including excitations from π configurations of the “wrong” symmetry) calculation. This allows for polarization of the σ electrons in the corrected π charge distribution. Remarkably, this procedure gave nearly the same $\langle x^2 \rangle$ of 18.6 ± 0.2 and the same energy independent of the molecular orbital set used. Thus, this procedure allowed the σ space which was polarized differently in each MO set to relax to a common value.

A simpler calculation treating only the π^* electron in this way shows a similar result. Table 1 lists the results, π^* CI, for exciting only the π^* electron into all π^* molecular orbitals and for all single excitations from this set of configurations, π^* CI-S. Again, π^* CI-S is nearly independent of the choice of

molecular orbitals. When only singles for the π electron are included, π^* CI-S(π), the configuration list is the same as APC.

All of the calculations discussed so far involve "complete" spaces of configurations. We also tried to reach these same results using conventional MRSDCI. For this purpose, we iterated on the choice of reference spaces by choosing the most important configurations from one calculation as the reference space for the next. Generally, about 70 reference configurations were chosen and over 300 000 spin- and symmetry-adapted configurations were then selected by perturbation theory for the final CI. The full, untruncated set of MOs was used. Because diagonalization of the CI matrix over the reference space gave a very different wave function, ψ_0^0 , from the actual projection of the final CI wave function onto the reference space, $P\psi$, we tried two different procedures in the perturbation selection. In the first, labeled MRSDCI(1) in the table, ψ_0 for the perturbation selection was taken as the renormalized $P\psi$ from the previous CI calculation. The MRSDCI was then iterated until $\langle P\psi|\psi_0\rangle^2/\langle P\psi|P\psi\rangle$ was nearly unity. In the second procedure, we followed the method used by ourselves and by Peyerimhoff in the past and used ψ_0^0 for the first two roots from the reference space and then selected the doubly excited configurations making the largest contribution to either root. This is sensible in this case because the first two ψ_0^0 do span the space of $P\psi$ fairly well.

The results of the MRSDCI with the full MO set were disappointing in that the value for $\langle x^2 \rangle$ depended on whether the V state ROHF or T state ROHF orbitals were used. This shows that the different σ space polarization in the ROHF could not be overcome with such a small CI. This large basis set generates so many configurations that, even with K orbitals in the virtual space, the convergence is too slow to allow truncation of the CI to only a few hundred thousand configurations. It is unclear whether part of the disagreement in the past literature on this subject was caused by this same problem. McMurchie and Davidson¹³ emphasized "complete" sets from limited classes of configurations and obtained a somewhat smaller (10%) value for $\langle x^2 \rangle$ than Buenker et al.^{15,16} obtained with a better basis set and MRSDCI.

This problem is not easily solved by using a larger MCSCF to define the orbitals. Using up to quadruple excitations from the highest occupied a_g , b_{3g} , b_{3u} , and b_{2g} orbitals into the lowest virtual b_{1u} , b_{2g} , b_{2u} , and b_{3u} orbitals in an MCSCF wave function still gives an average $\langle x^2 \rangle$ of 35.3. This calculation includes the most important σ single excitations, as reported by Buenker et al.^{15,16} and Lindh and Roos.⁴ Starting from this and using frozen iterative natural orbitals to improve the remaining virtual orbitals still gave an $\langle x^2 \rangle$ of 28. This final calculation did give the lowest absolute energy of -78.1962 for the V state among all the calculations discussed here. Most of our MRSDCI calculations give an extrapolated full CI estimate near -78.222 for this basis set, but these extrapolations do not give any estimate for properties other than the energy. Thus, we have to agree with Cave³ that methods that give essentially size-consistent results give an accurate value for this property with less effort than methods that are not size-consistent. All of the MRSDCI calculations that we can do are still truncated too much at the thresholds we can now afford for selection of the configurations. Too many of the configurations required for convergence of this property are not selected as many of them individually give too little correlation energy.

The recent work of Lindh and Roos⁴ had some of the same difficulties with MRSDCI convergence. They started with a better guess since they did not include very diffuse basis functions so their $\langle x^2 \rangle$ for the V state ROHF was only 28.1.

This presumably also resulted in a σ core more nearly optimum for the "true" V state π charge distribution. Even with this advantage gained by use of a less complete basis, they were unable to get agreement between SDCI-INO results starting with V state ($18.5 a_0^2$) or T state ($15.5 a_0^2$) ROHF orbitals. Their final MRSDCI energy, -78.124 , is not as low as ours, but this is due to the fact that they did not correlate the carbon 1s electrons. The lower $\langle x^2 \rangle$ reported by them ($16.8 a_0^2$) for their best MRSDCI wave function compared with ours seems partially due to omission of very diffuse functions from the basis set. With the coupled pair functional method, they obtained $15.8 a_0^2$ using either V state INOs or the T state RHF orbitals for the V state calculation.

Discussion

In our recent calculation on the Cope rearrangement,³³ we found that an MCSCF calculation assigned too much diradical character to the wave function. This was traced to placing the ionic configuration too high in energy compared to the diradical. At the transition state, the Cope rearrangement has six loosely bound electrons distributed over six carbon centers, but a six electron/six orbital CASSCF did not give a qualitatively correct result. Because the CAS used the same σ core orbitals for all of the configurations, it did not allow polarization of the core needed to stabilize ionic configurations. This observation stimulated us to return to this classical ethylene example.

The ground state of ethylene in the simple π -electron model (ignoring the complication of the Rydberg 3d orbital) may be written as a linear combination of a diradical configuration

$$\psi_D = |p_A^\alpha p_B^\beta\rangle - |p_A^\beta p_B^\alpha\rangle \quad (1)$$

and an ionic configuration

$$\psi_I = |p_A^\alpha p_A^\beta\rangle + |p_B^\alpha p_B^\beta\rangle \quad (2)$$

involving p orbitals on each carbon center. The excited V state in this approximation is

$$\psi_V = |p_A^\alpha p_A^\beta\rangle - |p_B^\alpha p_B^\beta\rangle \quad (3)$$

while the T state is

$$\psi_T = |p_A^\alpha p_B^\beta\rangle + |p_A^\beta p_B^\alpha\rangle \quad (4)$$

Ignoring normalization (for qualitative purposes) the MOs may be written as

$$\pi = p_A + p_B \quad (5)$$

and

$$\pi^* = p_A - p_B \quad (6)$$

so

$$\begin{aligned} \psi_D &= |\pi^\alpha \pi^\beta\rangle - |\pi^{*\alpha} \pi^{*\beta}\rangle \\ \psi_I &= |\pi^\alpha \pi^\beta\rangle + |\pi^{*\alpha} \pi^{*\beta}\rangle \\ \psi_V &= |\pi^\alpha \pi^{*\beta}\rangle - |\pi^\beta \pi^{*\alpha}\rangle \\ \psi_T &= |\pi^\alpha \pi^{*\beta}\rangle + |\pi^\beta \pi^{*\alpha}\rangle \end{aligned} \quad (7)$$

In all of these configurations the net π charge on each center is

zero so the optimum σ orbitals for both the ionic and diradical configuration will be similar.

This is very different from the situation if CH_2^+ and CH_2^- were computed separately since then there would be a large σ polarization. To obtain the same energy for a symmetrical $\text{CH}_2^+ \text{CH}_2^-$ ion pair supermolecule as for the sum of the ions calculated separately, it is necessary to introduce a polarized σ core Σ^\pm , so

$$\psi_V = |\Sigma_A^- \Sigma_B^+ p_A^\alpha p_A^\beta\rangle - |\Sigma_A^+ \Sigma_B^- p_B^\alpha p_B^\beta\rangle \quad (8)$$

To the first approximation, $\Sigma^+ + \Sigma^- = 2\Sigma^D$ where Σ^D is the unpolarized diradical σ core, and $\Sigma^\pm - \Sigma^D = \pm \text{SE}$ where SE is a sum of single excitations describing core polarization. Hence, the difference between (8) and (3) is approximately

$$\Delta\psi_V = |\text{SE } p_A^\alpha p_A^\beta\rangle + |\text{SE } p_B^\alpha p_B^\beta\rangle \quad (9)$$

When expressed in MO form, this becomes

$$\Delta\psi_V = |\text{SE}(\pi^\alpha \pi^\beta + \pi^{*\alpha} \pi^{*\beta})\rangle \quad (10)$$

Hence the σ polarization of the V state is expected to be predominantly described by single excitations of σ electrons relative to the $(\pi)^2$ and $(\pi^*)^2$ leading configurations of the ground state. Buenker et al.^{15,16} found two σ single excitations from $(\pi)^2$ and one from $(\pi^*)^2$ among the top 7 configurations of the V state. Similarly, Lindh and Roos⁴ reported four σ single excitations from $(\pi)^2$ and one from $(\pi^*)^2$ among the top eight configurations. Malmqvist and Roos³⁴ have also noted this need for dynamic polarization of the Σ core and have introduced an approximate model for treating it. Their model gives improved energies, but they did not report $\langle x^2 \rangle$.

Similarly the ψ_I contribution is actually underestimated by the TCSCF calculation. It would have an increased coefficient (resulting in a decreased coefficient for the $(\pi^*)^2$ configuration) if polarized Σ cores specific to each π configuration were used. That is ψ_I could better be written as

$$\psi_I = |\Sigma_A^- \Sigma_B^+ p_A^\alpha p_A^\beta\rangle + |\Sigma_A^+ \Sigma_B^- p_B^\alpha p_B^\beta\rangle \quad (11)$$

The same approximation as before yields

$$\Delta\psi_I = |\text{SE } p_A^\alpha p_A^\beta\rangle - |\text{SE } p_B^\alpha p_B^\beta\rangle \quad (12)$$

for the difference of (11) and (2). In MO form, this becomes

$$\Delta\psi_I = |\text{SE}(\pi^\alpha \pi^{*\beta} - \pi^\beta \pi^{*\alpha})\rangle \quad (13)$$

so the leading dynamic σ polarization consists of single excitations of the sigma core relative to the V state configuration. It was configurations similar to this last type that were needed to obtain correct results for the Cope rearrangement³³ and were missing from the 6 electron/6 orbital MCSCF. They can be expected to be needed, generally, for any symmetrical diradical³² such as $\text{X} \cdots \text{X}$ with a stretched bond. They also should have a large effect on the location of the avoided crossing of diatomic potential curves such as $\text{Na}^+ \text{Cl}^-$ and $\text{Na}^+ \text{Cl}^-$.

For ethylene, the consequence of placing the ionic V state configuration too high in energy is dramatic because of the presence of the Rydberg $3d\pi_g$ configuration at nearly the same energy. In a way, this mixing makes the energy artificially good because the single configuration energy of the V state evaluated with T state orbitals is 10 eV above the TCSCF energy of the ground state (11.6 eV using TCSCF orbitals). If the optimum Σ core for the V state configuration and the Rydberg configuration were the same, the correlation problem would probably be simply solved by a full CI involving only two electrons.

Because the optimum Σ cores are different, it is very difficult to obtain a correct balance between these two configurations in a CI calculation.

Additional Details for the Cope Rearrangement. In the absence of substituents, the Cope rearrangement begins and ends with the 1,5 hexadiene molecule in a nonplanar cisoid local minimum with C_2 symmetry. During the reaction, six electrons distributed in six atomic orbitals change their spin coupling pattern in much the same way as the change in bonding pattern between the two Kekule structures of benzene. In the MO single Slater determinant model, there are two filled "a" symmetry orbitals and one filled "b" symmetry orbital at the beginning and end of the reaction. Further, if the reaction proceeds along a path crossing through a C_{2h} shape, the orbital configuration can change smoothly from $a^2a^2b^2$ to $(a')^2(a'')^2(b')^2$ and back to $a^2a^2b^2$ so the reaction is allowed by the Woodward–Hoffmann rules. The experimental barrier, $\Delta H^\ddagger(298)$, of 33.5 kcal/mol is fairly high, however.³⁵ Consequently, Dewar has questioned whether this single-determinant MO picture adequately describes the transition state.³⁶

Since all discussions^{33,36–42} agree that the rearrangement passes through a C_{2h} structure we will focus here on the electronic structure and energy of this structure. At long C_1-C_6 (and C_3-C_4) distances, the molecule separates into two allyl molecules with an energy 52 kcal/mol above the diene and with a two configuration biradical wave function

$$c_1(a')^2(b')^2(a'')^2 - c_2(a')^2(b')^2(b'')^2 \quad (14)$$

describing a pair of allyl radicals in their ground 2A_2 states. At a C_1-C_6 distance close to a normal C–C single bond length, the wave function describes two C–C single bonds between centers 1–6 and 3–4 with the remaining two electrons on centers 2 and 5 forming a biradical pair.

$$c_1(a')^2(a'')^2(b')^2 - c_2(a')^2(a'')^2(a')^2 \quad (15)$$

While the first configuration connects smoothly to these limits, the second configuration changes character.

The CASSCF wave function has the flexibility to smoothly connect all of these variations in the wave function. With a 6-31G* basis set, the CASSCF calculation finds a diyl stable intermediate with a short (1.641 Å) 1–6 bond length and an "aromatic" transition state with a long (2.189 Å) bond length. At the diyl structure, c_2/c_1 is about 0.63, while at the aromatic transition state, $(a')^2(a'')^2(a')^2$ is no longer the second most important configuration ($c_2/c_1 = 0.17$) because $(a')^2(b')^2(b'')^2$ has a slightly larger coefficient of $c_2/c_1 = 0.18$. Between the diyl and the transition state, there is a small barrier in the C_{2h} bond stretching at a 1–6 distance of 1.9 Å. At this point, the second configuration in eq 15 has $c_2/c_1 = 0.28$ and the second configuration in eq 14 has $c_2/c_1 = 0.11$.

As would be expected from the discussion given above for ethylene, these biradical wave functions underestimate the contribution from ionic electron distributions. Lack of correlation with the passive electrons effectively places the calculated ionic structures too high in energy, and inclusion of this correlation by CASMP2 methods qualitatively changes the wave function and the shape of the PES along this C_{2h} cut. The second configuration, which removes ionic character from the leading configuration, becomes much less important at the diyl bond length. The barrier in the C_{2h} PES disappears, and the wave function becomes more like a single determinant at all distances. Consequently, the final PES has a single stationary point near 1.85 Å corresponding to a transition state for the Cope reaction. At this distance, c_2/c_1 in eq 15 is equal to 0.14

TABLE 2: Bond Lengths and Activation Energies for Cope Rearrangement^a

method	C ₁ –C ₆ (Å)	ΔE [‡] (kcal/mol)	ref
ROHF/ROHF ^b	2.046	56.6	43
CASSCF	1.641	45.8	39
	2.189	47.7	39
6e [−] CI/CASSCF	1.641	43.0	39
	2.189	44.5	39
CASPT2N ^c	1.745	31.2	40
CASMP2 ^c	1.85	30.7	33
MP2	1.783	28.4	37
ROHF/MP2		61.4	
MP4(SDTQ)/MP2		32.7	
QCISD(T)/MP2		35.3	
QCISD	1.871	42.0	
ROHF/QCISD		57.9	
MP2/QCISD		28.8	
MP3/QCISD		40.1	
MP4(SDQ)/QCISD		41.8	
MP4(SDTQ)/QCISD		34.1	
QCISD(T)/QCISD		36.7	
CCD	1.873	41.8	
ROHF/CCD		57.9	
MP2/CCD		28.8	
MP3/CCD		40.1	
MP4(SDTQ)/CCD		34.1	
CCSD/CCD		42.0	
CCSD(T)/CCD		36.7	
UHF/CCD		44.9	
PUHF/CCD		7.9	
UMP2/CCD		54.9	
PUMP2/CCD		19.7	
UMP3/CCD		55.3	
PUMP3/CCD		23.3	
UMP4(SDTQ)/CCD		53.0	
MP4(SDTQ)	1.794	33.8	37
QCISD(T)	1.769	35.8	37
BLYP	2.034	29.7	42
Becke 3LYP	1.971	34.2	42

^a C_{2h} symmetry constrained optimized bond lengths and energies compared to 1,5-hexadiene C₂ symmetry constrained using the 6-31G* basis set. ^b GAUSSIAN notation for energy method/geometry method. ^c Least energy along CASSCF C_{2h} path.

in the CASMP2 wave function. There is little qualitative resemblance between the CASMP2 and CASSCF results.

Because the final CASMP2 wave function is more nearly a single determinant than the CASSCF function, one might suppose that methods derived for electron correlation in a closed shell system would apply. Table 2 shows that this is not true. For a fixed 6-31G* basis, a variety of results are obtained by such methods for the optimum 1–6 bond length in C_{2h} constrained structures and for the energy difference from 1,5-hexadiene computed with the same method. The single determinant transition state energy is about 57 kcal/mol above that of 1,5-hexadiene with a 1–6 distance of 2.05 Å. MP2 lowers the energy to 28 kcal/mol but predicts a stable intermediate at a 1–6 distance of 1.783 Å. MP3 gives an energy of about 40 kcal/mol, and MP4(SDQ) gives 42 kcal/mol. Inclusion of triple excitations reduces the MP4 result to 34 kcal/mol. This large effect from triple excitations is not unexpected in view of the ethylene discussion since it represents (among other effects) polarization of the passive electrons in the second configuration. Other than the fact that the MP4 activation energy happens to be close to the experimental activation energy, there is no hint of convergence in these MP_n energies. In fact, at the C_{2h} stationary point, the contributions to the total energy are ΔE(MP2) = −814 mhartrees, ΔE(MP3) = −34 mhartrees, and ΔE(MP4) = −51 mhartrees. Thus, the fourth order term in the infinite series exceeds the third order term and there is no justification for truncating the series at this point.

While coupled cluster with double excitations (CCD) and “quadratic CI” (QCISD) give nearly identical results, the perturbation estimate of the effect of triple excitations indicates that neither of these methods is converged. Triple excitations reduce the 1–6 bond length by 0.1 Å and the energy barrier by 6 kcal/mol in these methods. Hence, none of these single reference based methods for including electron correlation can demonstrate convergence to a numerically stable result, although the MP4, CCSD(T), and QCISD(T) total energies are all within 1 mhartree of each other at the C_{2h} stationary point and within 4 mhartrees at the diene minimum.

For a simple system like H₂ with a greatly stretched bond, a broken symmetry UHF calculation gives the correct energy (although the wave function is qualitatively wrong). Hence, a perturbation calculation starting from the UHF energy is often advocated for biradicals. At the CCD transition state structure, the SCF wave function for 1,5-hexadiene, like H₂, is unstable to breaking the spin symmetry and the UHF energy is 12 kcal/mol lower in energy than RHF with <S²> = 0.80. As shown in Table 2, the UMP_n series (UMP2 = 45, UMP3 = 55, and UMP4 = 53 kcal/mol) appears to be converging to a quite different result from the MP_n activation energy with much less oscillation. The spin projected energies, however, are wildly different (PUHF = 8, PUMP2 = 20, and PUMP3 = 23 kcal/mol) from the results of any other method with this basis set.

These results illustrate that establishing the full CI limit for this basis set, in the absence of experimental data, is a difficult numerical challenge. Single reference methods that are correct only to fourth order do not demonstrate convergence to the desired precision.

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