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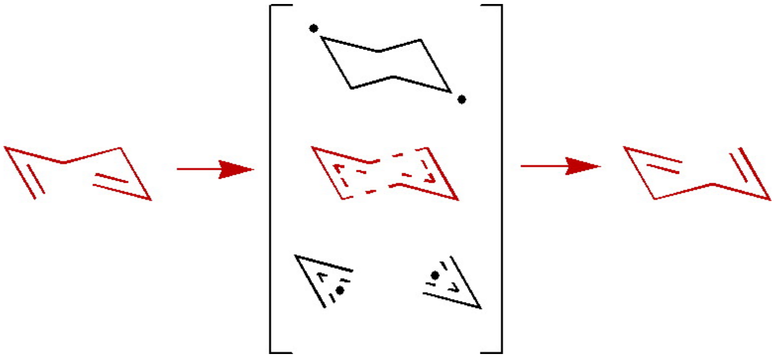

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Balancing Dynamic and Nondynamic Correlation for Diradical and Aromatic Transition States: A Renormalized Coupled-Cluster Study of the Cope Rearrangement of 1,5-Hexadiene

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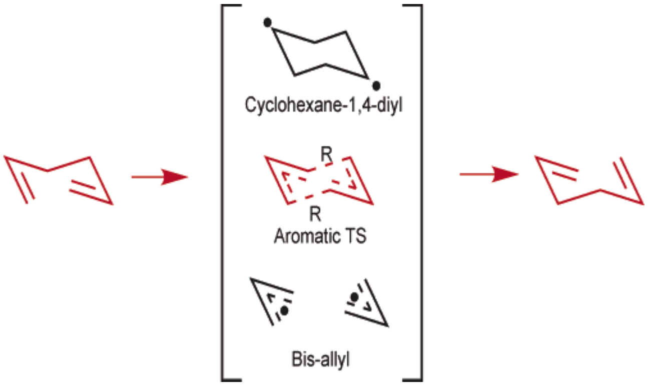
Abstract: Single-reference coupled-cluster calculations employing the completely renormalized CCSD(T) (CR-CCSD(T)) approach have been used to examine the mechanism of the Cope rearrangement of 1,5-hexadiene. In agreement with multireference perturbation theory, the CR-CCSD(T) method favors the concerted mechanism of the Cope rearrangement involving an aromatic transition state. The CCSD(T) approach, which is often regarded as the "gold standard" of electronic structure theory, seems to fail in this case, favoring pathways through diradical structures.

Scheme 1



Introduction

There has been much controversy over the mechanism of the Cope rearrangement of 1,5-hexadiene.[1−5] Since the experimental investigations rule out the dissociative mechanism involving bis-allyl, one is left with the following two alternatives: (i) a concerted σ bond shift involving an aromatic transition state (TS) or (ii) a two-stage process involving a stable 1,4-diyl diradical intermediate (see Scheme 1). As pointed out in ref 1, experimental studies alone may not be conclusive about the mechanism of the Cope rearrangement, and one needs support from theory to solve the problem. Unfortunately, the results of various theoretical studies of the mechanism of the Cope rearrangement are far from being consistent and strongly depend on the method employed in the calculations. Thus, the semiempirical and second-order Møller−Plesset (MP2) calculations result in a concerted pathway through a diradical cyclohexane-1,4-diyl intermediate, whereas the restricted Hartree−Fock (RHF), configuration interaction (CI), and some density functional theory (DFT) calculations support a mechanism involving an aromatic TS.[1] Calculations using the complete-active-space self-consistent-field (CASSCF) method as well as some other DFT methods produce results which make both pathways viable simultaneously.[1−4] Until now, the highest and most reliable level of theory used to examine the mechanism of the Cope rearrangement of 1,5-hexadiene has been multireference perturbation theory.[2−4] Various versions of this theory, including the MROPT2 method of Kozłowski and Davidson[6] and the CASPT2 approach of Roos et al.,[7] predict the existence of a single aromatic TS on the potential energy surface (PES),[2−4] in agreement with the experimental findings favoring the concerted mechanism.[8] Based on the MROPT2 and CASPT2 calculations, the aromatic TS for the Cope rearrangement of 1,5-hexadiene is a chair conformation which lies along a C_{2h} cut of the PES defined by the interallylic distance R (see Scheme 1). The aromatic character of this TS, which represents a minimum energy structure on the C_{2h} cut of the PES shown in Scheme 1, has been supported by Staroverov and Davidson who analyzed the problem using the concept of the density of effectively unpaired electrons.[2,9] Similar conclusions have been reached by

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other calculations.[10] The concerted mechanism of the Cope rearrangement of 1,5-hexadiene has also been supported by the fact that the secondary kinetic isotope effects obtained with DFT for loose TS structures agree much better with experiment[8] than those obtained for tight 1,4-diyl-like intermediates.[11]

Although the analyses provided in the earlier computational work[1−4] are quite convincing, it is very important to reexamine the mechanism of the Cope rearrangement of 1,5-hexadiene at higher levels of theory than previously employed. In particular, it is essential to reexamine the Cope rearrangement of 1,5-hexadiene with methods which provide a highly accurate description of dynamic correlation effects. The significant role of dynamic correlation effects can be seen by comparing the results of the CASSCF-based multireference perturbation theory calculations, including the previously employed MROPT2 and CASPT2 methods, which describe the dynamic and nondynamic correlation effects and which predict a single aromatic TS, with the results of the CASSCF calculations, which only describe the nondynamic correlation effects and which lead to two minima on the C_{2h} cut of the PES, one in the diradical region and another one in the aromatic part of the C_{2h} PES cut (see refs 2−4 and Figure 1).

It is generally acknowledged[12] that dynamic correlation effects are most accurately described by coupled-cluster theory.[13] The problem with single-reference coupled-cluster approaches, including the high-level methods that describe the effects of higher-than-doubly excited clusters, such as CCSD(T)[14] (coupled-cluster method with singles, doubles, and noniterative triples; generally regarded as the state-of-the-art electronic structure method), is that they fail to describe PESs along bond breaking coordinates and systems displaying diradical character. As shown in this study, in the case of the Cope rearrangement of 1,5-hexadiene, the CCSD(T) approach favors the pathway through a diradical structure or produces two nearly isoenergetic minima along the C_{2h} cut of the PES, both significantly shifted toward the 1,4-diyl diradical region, since it artificially lowers the energies of the diradical structures relative to the closed-shell reactant molecule and the aromatic TS. A different kind of high-level coupled-cluster approximation that accounts for singly, doubly, and triply excited clusters, referred to as the completely renormalized CCSD(T) (CR−CCSD(T)) method,[15] which can accurately and effectively deal with PESs involving bond breaking[15] and diradicals,[16] has to be employed in order to determine whether the TS for the Cope rearrangement of 1,5-hexadiene is aromatic or diradical. The CR-CCSD(T) calculations for the Cope rearrangement of 1,5-hexadiene and the comparison of the CR-CCSD(T) results with the results of the CCSD (coupled-cluster singles and doubles), CCSD(T), CASSCF, DFT, and multireference perturbation theory calculations are the main objectives of this study. We also show that the CR-CCSD(T) method provides useful insights into the degree of the diradical character of the Cope rearrangement TS.

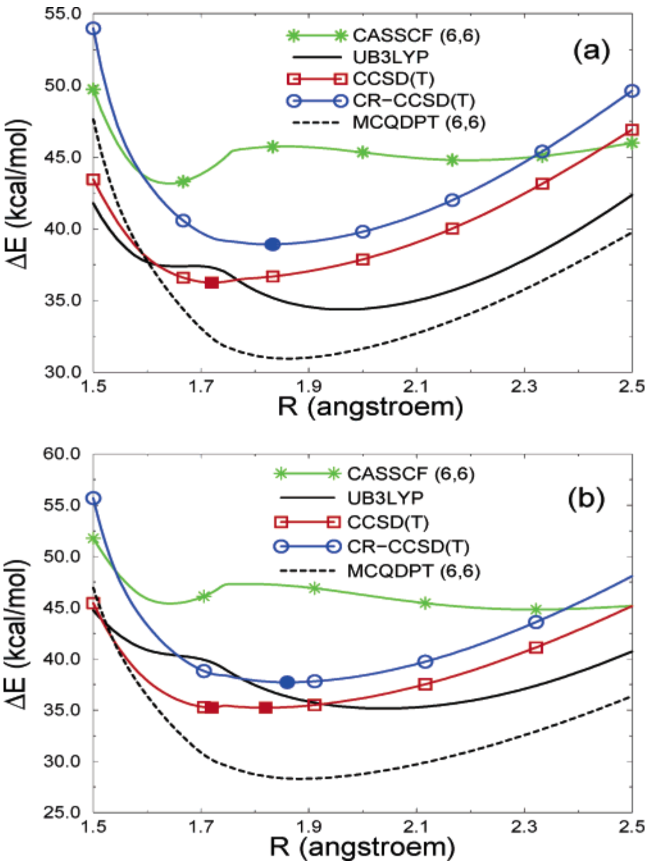

Figure 1. UB3LYP, CASSCF, MCQDPT, CCSD(T), and CR-CCSD(T) energies for the C_{2h} cut of the PES of the Cope rearrangement of 1,5-hexadiene, as obtained with the 6-31G* (a) and 6-311G** (b) basis sets. In every case, ΔE is the energy relative to the 1,5-hexadiene reactant molecule. The points corresponding to the minima on the CCSD(T) and CR-CCSD(T) curves are marked by solid squares and solid circles, respectively. Other symbols at selected geometries are only used to distinguish between different curves, which were all calculated on dense grids of 41 (the 6-31G* basis set) and 37 (the 6-311G** basis set) nuclear geometries along the interallylic coordinate R.

Theory and Computational Details

The CR-CCSD(T) theory is similar to the standard CCSD(T) approach, a perturbative correction due to triply excited determinants is added to the energy obtained from a standard CCSD calculation. Symbolically, the CR-CCSD(T) energy formula can be written as

$$E^{\mathrm{CR-CCSD(T)}} = E^{\mathrm{CCSD}} + N/D \tag{1}$$

where E^{CCSD} is the CCSD energy and the numerator and denominator terms, N and D, respectively, that are used to calculate the correction due to triple excitations are defined elsewhere.[15] The numerator N

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entering eq 1 is similar to the triples correction exploited in CCSD(T). Thus, the main difference between the standard CCSD(T) approach and the CR-CCSD(T) method is the presence of the denominator D in eq 1, which does not enter the standard CCSD(T) energy formula. It is this denominator which allows the CR-CCSD(T) method to improve upon the failing of the standard CCSD(T) approach in the diradical and bond breaking regions of molecular PESs. The amount of diradical character can be gleaned from the magnitude of the denominator D. The larger the value of this denominator relative to the value of D for the corresponding closed-shell structure, the larger the amount of diradical character in the molecular structure in question.

To examine the mechanism of the Cope rearrangement of 1,5-hexadiene, we calculated the C_{2h} cuts of the PES along the coordinate describing the interallylic distance R (cf. Scheme 1). In addition to the CR-CCSD(T) and CCSD(T) approaches and the basic CCSD approximation, and in analogy to the earlier work by Davidson et al., we used the unrestricted DFT (UB3LYP), CASSCF, and second-order multireference perturbation theory methods for comparison purposes. In the latter case, we used the second-order multiconfigurational quasi-degenerate perturbation theory (MCQDPT) of Nakano[17] available in the GAMESS package,[18] which in the single-state calculations performed in this work is equivalent to the multireference MP2 scheme of Hirao.[19] To make sure that our main conclusions are not affected by one particular choice of the basis set, two basis sets were employed in the calculations: the smaller 6-31G* basis[20] and the larger 6-311G** basis.[21] Following ref 2, the geometries defining the C_{2h} cut of the PES were obtained by optimizing the corresponding molecular structures at fixed values of the interallylic distance R, ranging from 1.5 to 4.0 Å, using the UB3LYP functional, as implemented in Gaussian 98.[22] This was done for each of the two basis sets employed in this study. These optimized structures were then used to calculate single-point energies at the CCSD, CCSD(T), CR-CCSD(T), CASSCF, and MCQDPT levels with the same (6-31G* or 6-311G**) basis set as that used in the UB3LYP calculations. Altogether, we considered 41 densely spaced values of R from the range 1.5−4.0 Å for the 6-31G* basis set and 37 densely spaced values of R from the same range for the 6-311G** basis set. All of these geometries are available in the Supporting Information. The ground-state RHF orbitals were used in the CCSD, CCSD(T), and CR-CCSD(T) calculations, which were performed with the coupled-cluster codes[23] available in GAMESS.[18] Following the earlier multireference studies,[2-4] the active space employed in the CASSCF and MCQDPT calculations was obtained by distributing six active electrons among six active orbitals ($7a_\mathrm{g}$, $5a_\mathrm{u}$, $7b_\mathrm{u}$, $8a_\mathrm{g}$, $5b_\mathrm{g}$, $8b_\mathrm{u}$), including four orbitals describing the migrating π bonds and two orbitals describing the migrating σ bond. This choice of active orbitals guarantees that the CASSCF reference function includes the $|\cdots 7a_\mathrm{g}^2 5a_\mathrm{u}^2 7b_\mathrm{u}^2|$, $|\cdots 7a_\mathrm{g}^2 5a_\mathrm{u}^2 8a_\mathrm{g}^2|$, and $|\cdots 7a_\mathrm{g}^2 5b_\mathrm{g}^2 7b_\mathrm{u}^2|$ electron configurations that need to be considered to ensure a balanced description of the aromatic and diradical regions of the PES. As explained, for example, in refs 1 and 2, the closed-shell $|\cdots 7a_\mathrm{g}^2 5a_\mathrm{u}^2 7b_\mathrm{u}^2|$ determinant dominates the wave function in the range of medium interallylic distances R, but it becomes inadequate in the diradical regions corresponding to smaller and larger values of R. At shorter interallylic distances, the molecule becomes a singlet 1,4-diyl with the wave function

$$\Psi_\mathrm{diyl} = |\cdots 7a_\mathrm{g}^2 5a_\mathrm{u}^2 7b_\mathrm{u}^2| - c(7b_\mathrm{u}^2 \rightarrow 8a_\mathrm{g}^2)|\cdots 7a_\mathrm{g}^2 5a_\mathrm{u}^2 8a_\mathrm{g}^2| + \cdots \quad (2)$$

where the coefficient $c(7b_\mathrm{u}^2 \rightarrow 8a_\mathrm{g}^2)$ at the $|\cdots 7a_\mathrm{g}^2 5a_\mathrm{u}^2 8a_\mathrm{g}^2|$ configuration, which can formally be obtained by a $7b_\mathrm{u}^2 \rightarrow 8a_\mathrm{g}^2$ double excitation from the $|\cdots 7a_\mathrm{g}^2 5a_\mathrm{u}^2 7b_\mathrm{u}^2|$ determinant, approaches 1 when R decreases [the analogous doubly excited cluster amplitude $t(7b_\mathrm{u}^2 \rightarrow 8a_\mathrm{g}^2)$ defining the coupled-cluster ansatz for Ψ_diyl approaches −1; this is a consequence of the formula $t(7b_\mathrm{u}^2 \rightarrow 8a_\mathrm{g}^2) = -c(7b_\mathrm{u}^2 \rightarrow 8a_\mathrm{g}^2)$, which results from the fact that the corresponding singly excited cluster amplitude $t(7b_\mathrm{u} \rightarrow 8a_\mathrm{g})$ involving orbitals of different symmetries vanishes]. At larger distances R, the C_{2h} structure becomes a complex of two allyl radicals with a two-configuration diradical wave function

$$\Psi_\mathrm{bis-allyl} = |\cdots 7a_\mathrm{g}^2 5a_\mathrm{u}^2 7b_\mathrm{u}^2| - c(5a_\mathrm{u}^2 \rightarrow 5b_\mathrm{g}^2)|\cdots 7a_\mathrm{g}^2 5b_\mathrm{g}^2 7b_\mathrm{u}^2| + \cdots \quad (3)$$

where the coefficient $c(5a_\mathrm{u}^2 \rightarrow 5b_\mathrm{g}^2)$ at the $|\cdots 7a_\mathrm{g}^2 5b_\mathrm{g}^2 7b_\mathrm{u}^2|$ determinant, which can be obtained by a $5a_\mathrm{u}^2 \rightarrow 5b_\mathrm{g}^2$ double excitation from the $|\cdots 7a_\mathrm{g}^2 5a_\mathrm{u}^2 7b_\mathrm{u}^2|$ configuration, becomes 1 in the limit of infinite R [again, the analogous cluster amplitude $t(5a_\mathrm{u}^2 \rightarrow 5b_\mathrm{g}^2) = -c(5a_\mathrm{u}^2 \rightarrow 5b_\mathrm{g}^2)$ becomes −1 in the same limit]. As shown in this paper, the doubly excited cluster amplitudes $t(7b_\mathrm{u}^2 \rightarrow 8a_\mathrm{g}^2)$ and $t(5a_\mathrm{u}^2 \rightarrow 5b_\mathrm{g}^2)$ obtained in the CCSD calculations, which correspond to coefficients $c(7b_\mathrm{u}^2 \rightarrow 8a_\mathrm{g}^2)$ and $c(5a_\mathrm{u}^2 \rightarrow 5b_\mathrm{g}^2)$ in eqs 2 and 3, respectively, correlate with the magnitude of the denominator D renormalizing the triples correction in the CR-CCSD(T) energy expression, eq 1.

Results and Discussion

Figure 1 shows the C_{2h} cuts of the PES for the UB3LYP, CASSCF, MCQDPT, CCSD(T), and CR-CCSD(T) methods used in this study. As can be seen in Figure 1a (and as shown earlier, for example, in ref 2), the C_{2h} cuts of the PES resulting from the CASSCF and UB3LYP calculations with the 6-31G* basis set show two minima. The CASSCF calculations produce a deep minimum in the diradical region of the C_{2h} cut near the value of $R = 1.64$ Å and a shallow minimum in the aromatic region of the C_{2h} cut around $R = 2.2$ Å, corresponding to the aromatic TS. The energy difference between the two minima is approximately 1.6 kcal/mol. The UB3LYP calculations give a shallow minimum in the diradical portion of the surface at $R = 1.65$ Å and a deep minimum in the aromatic region of the PES at $R = 1.97$ Å. Thus, the CASSCF/6-31G* method favors the stepwise mechanism for the reaction involving a diradical intermediate due to its lower energy, while the UB3LYP/6-31G* method favors the concerted mechanism involving the aromatic TS, which is lower in energy than the other minimum on the UB3LYP curve shown in Figure 1a. The use of the larger 6-311G** basis set affects the results of the CASSCF and UB3LYP calculations, but none of the resulting two curves seems correct. As shown in Figure 1b, the CASSCF/6-311G** curve still has two minima, one in the diradical region at $R = 1.64$ Å and another one shifted toward the bis-allyl region around $R = 2.35$ Å. Compared to the 6-31G* basis set, the

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energy difference between the two minima is smaller (only 0.6 kcal/mol) and the minimum at $R = 1.64$ Å is slightly higher in energy, but the overall shape of the CASSCF curve is incorrect. The U3BLYP/6-311G** curve has only one well-pronounced minimum in the aromatic region of the PES at $R = 2.04$ Å, but there remains a significant change in the curvature in the diradical region, which is reminiscent of the secondary shallow minimum on the UB3LYP/6-31G* curve at $R = 1.65$ Å.

As shown in Figure 1, the more advanced, high-level MCQDPT, CCSD(T), and CR-CCSD(T) methods change the results of the CASSCF and UB3LYP calculations quite dramatically. What is perhaps even more important, there are significant differences between the MCQDPT and CR-CCSD(T) results on one hand and the results of the CCSD(T) calculations on the other hand. Although, for the 6-31G* basis set, all three methods produce only a single minimum on the C_{2h} cut of the PES, the minima on the MCQDPT and CR-CCSD(T) curves are in the aromatic region, at $R = 1.86$ Å and $R = 1.83$ Å, respectively, whereas the minimum on the CCSD(T) curve, at $R = 1.72$ Å, is significantly shifted to the diradical region, contradicting the earlier multireference perturbation theory calculations[2-4] and our MCQDPT and CR-CCSD(T) results (cf. Figure 1a). The situation is even more interesting when the larger 6-311G** basis set is employed (see Figure 1b). The MCQDPT and CR-CCSD(T) curves are still very similar to each other. In particular, the MCQDPT and CR-CCSD(T) curves both have a single well-pronounced minimum in the aromatic region, at $R = 1.88$ Å in the MCQDPT case and at $R = 1.86$ Å in the CR-CCSD(T) case. However, the CCSD(T) curve is now entirely different. The diradical minimum at $R = 1.72$ Å is still present on the CCSD(T)/6-311G** curve, but there is also another minimum at $R = 1.82$ Å. Although the new minimum at $R = 1.82$ Å is slightly lower in energy than that at $R = 1.72$ Å, both minima are nearly isoenergetic (the energy difference between both minima is less than 0.03 kcal/mol) and separated by a tiny 0.2 kcal/mol barrier. Thus, the CCSD(T) approach makes the diradical region of the PES corresponding to tighter 1,4-diyl-like structures a lot more accessible than the MCQDPT and CR-CCSD(T) approaches. Neither of the two minima on the CCSD(T) curve are located in close proximity to the minimum on the MCQDPT curve when the 6-311G** basis set is employed. As in the 6-31G* case, the R values characterizing the MCQDPT and CR-CCSD(T) minima along the C_{2h} cut of the PES, obtained with the 6-311G** basis set, are virtually identical. We can conclude that the CCSD(T) method seems to favor the diradical mechanism for the Cope rearrangement of 1,5-hexadiene or makes the reaction pathways through tighter 1,4-diyl-like structures more accessible compared to the MCQDPT and CR-CCSD(T) approaches. At the same time, despite its formally single-reference character, the CR-CCSD(T) approach of ref 15 eliminates the problems of CCSD(T), producing a single minimum on the C_{2h} cut of the PES in close proximity to the minimum in the aromatic region obtained with MCQDPT and other multireference perturbation theory techniques.[2-4] These general findings seem to be independent of the basis set employed in the calculations. The fact that the standard CCSD(T) method favors the diradical mechanism for the Cope rearrangement of 1,5-hexadiene or that it makes the 1,4-diyl-like structures more accessible compared to the MCQDPT and CR-CCSD(T) approaches is a consequence of the failure of the CCSD(T) approach in the diradical region resulting from the unphysically large negative triples corrections to the CCSD energies produced by CCSD(T).

Table 1. Activation Energies, $\Delta E^{\ddagger}$, and Interallylic Distances of the Transition States, $R^{\ddagger}$, for the Cope Rearrangement of 1,5-Hexadiene[a]

	6-31G*		6-311G**	
method	$R^{\ddagger}$ (Å)	$\Delta E^{\ddagger}$ (kcal/mol)	$R^{\ddagger}$ (Å)	$\Delta E^{\ddagger}$ (kcal/mol)
CCSD	1.87	42.19	1.89	41.07
CCSD(T)	1.72	36.24	1.72	35.27
			1.82	35.24
CR-CCSD(T)	1.83	38.91	1.86	37.73
CR-CCSD(T)/$D = 1.0$[b]	1.73	37.13	1.72	36.23
			1.83	36.07
CR-CCSD(T)/$D = 1.4$[c]	1.81	38.79	1.85	37.54
MCQDPT	1.86	30.95	1.88	28.31
experiment[d]	$\Delta E^{\ddagger} = 35.0$ kcal/mol			

[a] $R^{\ddagger}$ is defined as the value of the interallylic distance R corresponding to the minimum on the C_{2h} PES cut (note that each of the CCSD(T) and CR-CCSD(T)/$D = 1.0$ curves obtained with the 6-311G** basis set has two minima). $\Delta E^{\ddagger}$ is the energy at $R = R^{\ddagger}$ relative to the reactant molecule. [b] The CR-CCSD(T) approach in which the true, geometry-dependent denominator D in eq 1 is replaced by a fixed value of $D = 1.0$. [c] The CR-CCSD(T) approach in which the true, geometry-dependent denominator D in eq 1 is replaced by a fixed value of $D = 1.4$. [d] The experimentally derived result reported in ref 1.

Interestingly enough, if we just looked at the electronic activation energies $\Delta E^{\ddagger}$, corresponding to the minima on the potential curves shown in Figure 1, we might get a false impression that the CCSD(T) approach provides the most accurate description. As shown in Table 1, the CCSD(T) values of $\Delta E^{\ddagger}$ for the 6-31G* and 6-311G** basis sets of 36.2 and 35.2 kcal/mol, respectively, seem to be very close to the experimentally derived $\Delta E^{\ddagger}$ value of 35.0 kcal/mol reported in ref 1. We must be careful though. This very good agreement between the CCSD(T) and experimentally derived $\Delta E^{\ddagger}$ values is, most likely, a result of the fortuitous cancellation of errors, since the TSs corresponding to the CCSD(T) values of $\Delta E^{\ddagger}$ are tight structures shifted toward the 1,4-diyl region of the PES, contradicting the accepted interpretation of the mechanism of the Cope rearrangement of 1,5-hexadiene as a concerted process involving an aromatic TS. In fact, based on the results in Table 1, we may expect that, for basis sets larger than 6-311G**, the CCSD(T) values of $\Delta E^{\ddagger}$ become smaller than the experimentally derived value of 35.0 kcal/mol. This should be contrasted with the CR-CCSD(T) approach, which produces activation energies of 38.9 and 37.7 kcal/mol for the 6-31G* and 6-311G** basis sets, respectively, that are above the experimentally derived $\Delta E^{\ddagger}$ value and that correspond to aromatic TSs. Based on the results in Table 1, we expect that the $\Delta E^{\ddagger}$ values obtained with the CR-CCSD(T) method and basis sets larger than 6-311G** will continue to approach the experimental value of 35.0 kcal/mol from above (unfortunately, we cannot afford such calculations at this time). It should also be noted that the MCQDPT method gives activation barriers that are considerably below the experimentally derived value of $\Delta E^{\ddagger}$, which might be a consequence of the inability of the multireference perturbation theory methods to provide a well balanced description of the TS and reactant structures.

It is interesting to examine the role of the denominator D entering the CR-CCSD(T) formula, eq 1, which renormalizes the triples correction N, in improving the CCSD(T) results and

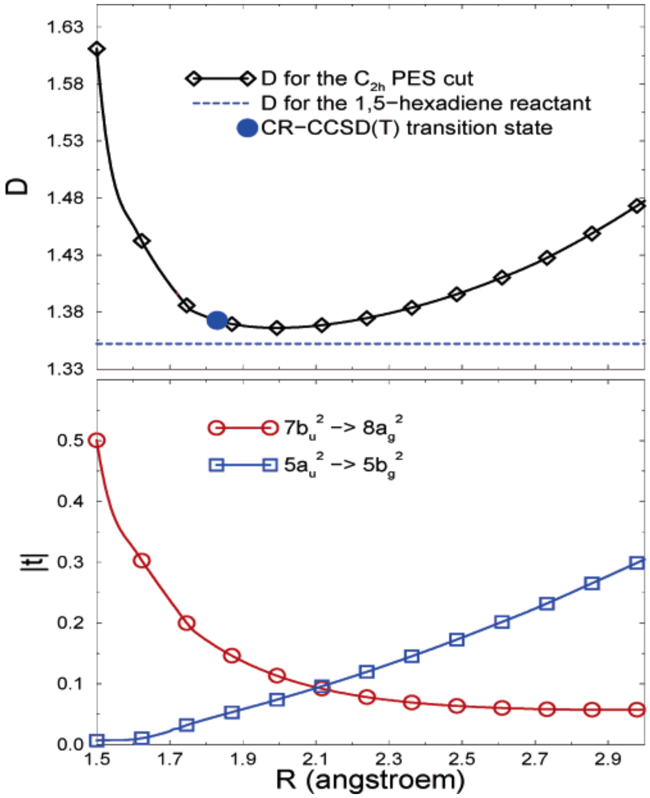

Figure 2. CR-CCSD(T) denominator *D* (top panel) and the absolute values of the doubly excited cluster amplitudes *t* obtained in the CCSD calculations corresponding to the $7b_u^2 \rightarrow 8a_g^2$ and $5a_u^2 \rightarrow 5b_g^2$ excitations (bottom panel), obtained with the 6-31G* basis set, as a function of the interallylic distance *R*.

the relationship between the magnitude of *D* and the $t(7b_u^2 \rightarrow 8a_g^2)$ and $t(5a_u^2 \rightarrow 5b_g^2)$ cluster amplitudes that measure the significance of the $|\cdots 7a_g^2 5a_u^2 8a_g^2|$ and $|\cdots 7a_g^2 5b_g^2 7b_u^2|$ configurations in the wave function (see Figure 2). Since the behavior of this denominator and its relationship with the $t(7b_u^2 \rightarrow 8a_g^2)$ and $t(5a_u^2 \rightarrow 5b_g^2)$ cluster amplitudes almost do not depend on the basis set employed in the calculations, we focus on the results obtained with the 6-31G* basis set.

The value of the denominator *D* for $R = 1.83$ Å, which is the *R* value for which the CR-CCSD(T)/6-31G* method produces a minimum on the C_{2h} cut of the PES, is 1.37. This is not much different than the value of *D* of 1.35 obtained for the closed-shell 1,5-hexadiene reactant. The value of *D* for $R = 1.72$ Å, which is the *R* value at which the CCSD(T)/6-31G* curve shown in Figure 1a has a minimum, is 1.40. This increase in the value of *D* at the minimum obtained with CCSD(T) relative to the closed-shell reactant molecule and relative to the CR-CCSD(T) result is related to the increase in the amount of the diradical (1,4-diyl) character of the TS in the CCSD(T) calculations compared to CR-CCSD(T). Indeed, the absolute value of the $t(7b_u^2 \rightarrow 8a_g^2)$ cluster amplitude, which determines the degree of the 1,4-diyl character of the wave function (cf. eq 2), obtained in the CCSD/6-31G* calculations, increases from 0.16 at $R = 1.83$ Å (the CR-CCSD(T) minimum) to 0.22 at $R = 1.72$ Å (the CCSD(T) minimum). Similar or even bigger increases in the values of *D* and $|t(7b_u^2 \rightarrow 8a_g^2)|$ are observed when we calculate them at the *R* values corresponding to diradical minima on the UB3LYP/6-31G* and CASSCF/6-31G* curves. At the same time, the values of *D* calculated at the aromatic minima on the UB3LYP and CASSCF curves are almost identical to those obtained for the closed-shell reactant molecule. For example, for the diradical minimum on the UB3LYP/6-31G* curve shown in Figure 1a, occurring at $R = 1.65$ Å, the value of *D* is 1.43, which is a significant increase compared to $D = 1.35$ obtained for the reactant. The absolute value of the $t(7b_u^2 \rightarrow 8a_g^2)$ cluster amplitude at $R = 1.65$ Å of 0.28 is also quite large. This should be contrasted with the aromatic minimum on the same UB3LYP/6-31G* curve at $R = 1.97$ Å, where $D = 1.37$ and the value of $|t(7b_u^2 \rightarrow 8a_g^2)|$ is only 0.12 (since this is an aromatic region, the absolute value of the $t(5a_u^2 \rightarrow 5b_g^2)$ cluster amplitude, which measures the degree of the bis-allyl character of the wave function, is also relatively small; at $R = 1.97$ Å, $|t(5a_u^2 \rightarrow 5b_g^2)| = 0.07$).

All of these changes in *D* and the corresponding changes in the cluster amplitudes $t(7b_u^2 \rightarrow 8a_g^2)$ and $t(5a_u^2 \rightarrow 5b_g^2)$ can be seen in Figure 2, where the value of the denominator *D* resulting from the CR-CCSD(T)/6-31G* calculations and the absolute values of $t(7b_u^2 \rightarrow 8a_g^2)$ and $t(5a_u^2 \rightarrow 5b_g^2)$ obtained with the underlying CCSD/6-31G* approach are plotted as a function of the interallylic distance *R*. As shown in Figure 2, the values of *D* become very large as we go deeper and deeper into the diradical region of tight 1,4-diyl structures ($R \leq 1.7$ Å), they pass through a minimum in the aromatic region ($R \approx 2.0$ Å), and they increase again in the dissociative region involving two separated allyl structures ($R > 3.0$ Å), in agreement with the behavior of the denominator *D* observed in the earlier studies of bond breaking.[15] There is a clear correlation between the magnitude of the denominator *D* on one hand and the absolute values of cluster amplitudes $t(7b_u^2 \rightarrow 8a_g^2)$ and $t(5a_u^2 \rightarrow 5b_g^2)$ on the other hand. For the 6-31G* basis set, the $t(7b_u^2 \rightarrow 8a_g^2)$ amplitude, which determines the importance of the $|\cdots 7a_g^2 5a_u^2 8a_g^2|$ configuration (cf. eq 2), increases in absolute value from 0.05 at $R = 4.0$ Å (the bis-allyl region) and 0.11 at $R = 2.0$ Å (the aromatic region) to 0.50 at $R = 1.5$ Å (the diradical 1,4-diyl region). Similarly, the absolute value of $t(5a_u^2 \rightarrow 5b_g^2)$, which determines the significance of the $|\cdots 7a_g^2 5b_g^2 7b_u^2|$ configuration (cf. eq 3), increases from 0.01 at $R = 1.5$ Å (the diradical 1,4-diyl region) and 0.08 at $R = 2.0$ Å (the aromatic region) to 0.59 at $R = 4.0$ Å (the bis-allyl region). The $|\cdots 7a_g^2 5a_u^2 8a_g^2|$ and $|\cdots 7a_g^2 5b_g^2 7b_u^2|$ configurations become equally important at $R \approx 2.1$ Å, which is an aromatic region. In this region, the curves representing the dependence of $t(7b_u^2 \rightarrow 8a_g^2)$ and $t(5a_u^2 \rightarrow 5b_g^2)$ on *R* cross and $t(7b_u^2 \rightarrow 8a_g^2) = t(5a_u^2 \rightarrow 5b_g^2) \approx -0.09$. The point of equal significance of the $|\cdots 7a_g^2 5a_u^2 8a_g^2|$ and $|\cdots 7a_g^2 5b_g^2 7b_u^2|$ configurations ($R \approx 2.1$ Å) is very close to the point where the denominator *D* reaches the minimum value of 1.37 ($R \approx 2.0$ Å). As we go toward the diradical regions of the PES (tight 1,4-diyl structures at shorter distances *R* and dissociative bis-allyl structures at larger values of *R*), one of the $t(7b_u^2 \rightarrow 8a_g^2)$ or $t(5a_u^2 \rightarrow 5b_g^2)$ amplitudes increases in absolute value causing the denominator *D* to grow. This property of the denominator *D*, which is a consequence of the definition of *D* in terms of cluster amplitudes obtained with the CCSD approach,[15] helps to bring important chemistry into the CR-CCSD(T) calculations. When the wave function gains a significant diradical character and the absolute value of $t(7b_u^2 \rightarrow 8a_g^2)$ or $t(5a_u^2 \rightarrow 5b_g^2)$ increases, causing the standard CCSD(T) approximation to fail by producing the unphysically large negative triples corrections, the denominator *D* increases its

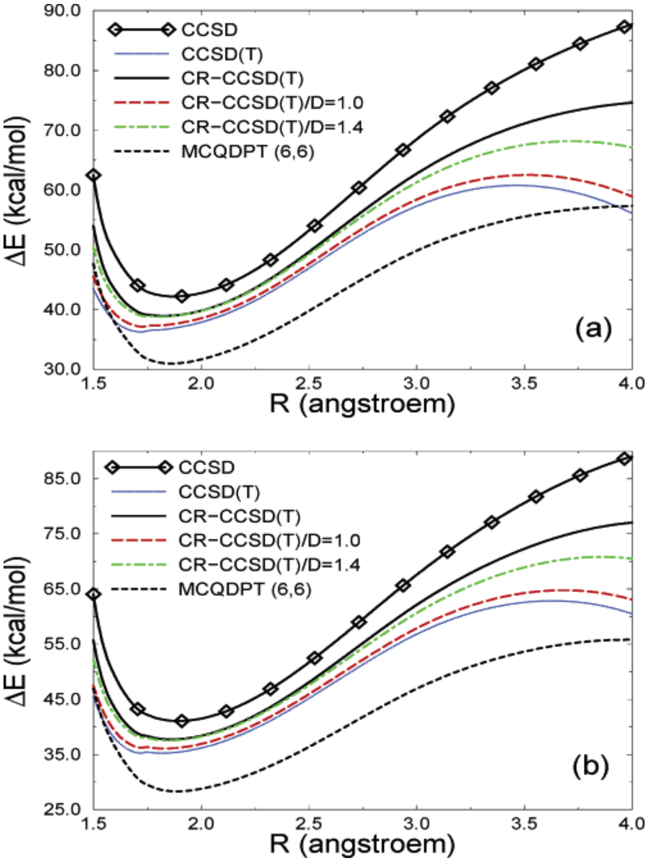

Figure 3. A comparison of the CCSD(T), CR-CCSD(T), and MCQDPT energies, relative to the reactant molecule, for the C_{2h} cut of the PES of the Cope rearrangement of 1,5-hexadiene with the corresponding CCSD, CR-CCSD(T)/$D = 1.0$, and CR-CCSD(T)/$D = 1.4$ curves (the latter two curves were obtained by setting D in eq 1 at 1.0 and 1.4, respectively). (a) The results of the calculations with the 6-31G* basis set. (b) The results of the calculations with the 6-311G** basis set. Open symbols (◇) at the selected geometries on the CCSD curve are only used to distinguish between the CCSD and CR-CCSD(T) curves, which are both represented by solid lines.

value, damping the triples correction N and bringing the triples correction to the CCSD energy to a more reasonable value.

Since the CR-CCSD(T) approach provides a correct description of the C_{2h} cut of the PES by scaling down the triples correction N, one may wonder if the CCSD method itself, which can formally be obtained by replacing the denominator D in eq 1 by ∞, provides the correct description too. Moreover, since the value of the denominator D in the wide range of R distances between 1.7 and 2.5 Å is approximately 1.4, varying by 0.03 or less (for the 6-31G* basis set, D varies between 1.37 and 1.40, while, for the 6-311G** basis set, D varies between 1.40 and 1.43 in this region), one may also wonder if it is sufficient to use a fixed value of D, such as $D = 1.4$, to obtain a qualitatively correct description of the TS region of the PES. The results of such analyses are shown in Figure 3, where we compare the CCSD(T), CR-CCSD(T), and MCQDPT energies relative to the reactant, as functions of R in the entire $R = 1.5-4.0$ Å region explored in this work, with the corresponding CCSD, CR-CCSD(T)/$D = 1.0$, and CR-CCSD(T)/$D = 1.4$ curves. The latter two curves are obtained by artificially setting the denominator D, defining the CR-CCSD(T) method (cf. eq 1), at 1.0 and 1.4, respectively. As one can see, the CCSD method, in which triples corrections are ignored, provides a qualitatively, but not quantitatively, correct shape of the C_{2h} cut of the PES. The minima on the CCSD curves obtained with the 6-31G* and 6-311G** basis sets occur at $R = 1.87$ Å and $R = 1.89$ Å, respectively, in very good agreement with the MCQDPT and CR-CCSD(T) values, but the resulting activation energies $\Delta E^{\ddagger}$ of 42.2 and 41.1 kcal/mol, respectively, are considerably higher than the corresponding CR-CCSD(T) values or the experimentally derived $\Delta E^{\ddagger}$ (see Table 1). Moreover, the CCSD energies become too high in the dissociative bis-allyl region. If we, for example, calculate the energy differences $E(R = 4.0\ \text{Å}) - E(R = R^{\ddagger})$ ($R^{\ddagger}$ is the value of R at the minimum along the C_{2h} PES cut) using the CCSD data, we obtain 45.5 and 48.0 kcal/mol for the 6-31G* and 6-311G** basis sets, respectively. The CR-CCSD(T) and MCQDPT approaches give significantly lower values of these differences (35.7 and 26.4 kcal/mol, respectively, for the 6-31G* basis set, and 39.3 and 27.5 kcal/mol, respectively, for the 6-311G** basis set). This clearly shows that one needs to incorporate the effects of triple excitations in coupled-cluster calculations to obtain a more quantitative description of the C_{2h} cut of the PES. Unfortunately, as already discussed, the incorporation of these effects through the standard CCSD(T) method yields incorrect curves. Figure 3 shows that the CCSD(T) approach fails not only in the region of small and intermediate R values but also in the dissociative bis-allyl region, providing an unphysical hump on the PES around $R = 3.5$ Å (not present on the MCQDPT and CR-CCSD(T) curves). The CR-CCSD(T) approach eliminates the failure of the CCSD(T) method in the diradical 1,4-diyl and bis-allyl regions by scaling down the triples corrections with the denominator D entering eq 1. Indeed, as shown in Figure 3, if we set the denominator D in eq 1 at 1.0, the resulting curves become virtually identical to the corresponding CCSD(T) curves (they are not exactly identical, since the numerator N in eq 1 is similar, but not identical, to the triples correction of CCSD(T); the expression for N used in the CR-CCSD(T) theory provides a somewhat more complete description of the triples correction to the CCSD energy through the use of the generalized moments of CCSD equations[15]).

As mentioned earlier, $D \approx 1.4$ over a wide range of R values, so that it is also interesting to see what happens if we replace the geometry-dependent denominator D defining the true CR-CCSD(T) method by a fixed $D = 1.4$ value. The resulting curves shown in Figure 3 are almost identical to the corresponding CR-CCSD(T) curves up to $R \approx 2.5$ Å. In particular, the activation energies $\Delta E^{\ddagger}$ resulting from the CR-CCSD(T)/$D = 1.4$ and true CR-CCSD(T) computations, which are calculated as the energies relative to the reactant at the respective minima along the C_{2h} cuts of the PES (that are all located in the $R < 2.5$ Å region), are in perfect agreement with each other (see Table 1). Unfortunately, the agreement between the CR-CCSD(T) energies and their counterparts obtained with D fixed at 1.4 remains good only up to $R \approx 2.5$ Å. For $R > 2.5$ Å, the CR-CCSD(T)/$D = 1.4$ and true CR-CCSD(T) curves are entirely different. The fixed, geometry-independent denominator $D = 1.4$ cannot eliminate the failure of the standard CCSD(T) approach in the dissociative bis-allyl region. As shown in Figure 3, we begin to see the emergence of the unphysical, CCSD(T)-like, humps on the CR-CCSD(T)/$D = 1.4$ curves in the region of larger R values, which are not seen in the corresponding CR-CCSD(T) and multireference perturbation theory calculations. This shows that one has to scale the triples correction in a geometry-dependent manner to obtain a correct description of the PES. One might contemplate various empirical ways of rescaling the triples correction of CCSD(T) to improve the results in the diradical and dissociative regions of the PES, but the CR-CCSD(T) approach provides us with a rigorous ab initio recipe of how to do it by relating the denominator *D* entering eq 1 to the singly and doubly excited cluster amplitudes obtained in the CCSD calculations.[15] Since cluster amplitudes vary with nuclear geometry, correctly sensing the presence of diradical regions of the PES (cf. Figure 2), the resulting denominator *D* defining the CR-CCSD(T) approach provides the desired improvements in the CCSD(T) results.

Although the above observations require further analysis, the correlation between the leading cluster amplitudes defining the diradical character of the wave function and the denominator *D* obtained in the CR-CCSD(T) calculations, combined with the changes in the value of *D* relative to the corresponding closed-shell reactant(s), may prove useful in examining the degree of the diradical character in the TS under investigation (particularly, when the degree of the diradical character is large enough to cause significant changes in the values of *D*). For example, a comparison of the values of the denominator *D* obtained in this work with the effective number of unpaired electrons *n* reported in ref 9, used by the authors of ref 9 to argue the aromatic character of the TS for the Cope rearrangement of 1,5-hexadiene, shows that both quantities follow similar overall patterns. As shown in the Supporting Information to ref 9 (see, also, Table 1 in ref 9), the values of *n* obtained in multireference CI calculations employing the 6-31G* basis set monotonically decrease from 2.85 at $R = 1.54$ Å to 1.55 in the $R \approx 2.0$ Å region and then increase to 3.26 at $R = 4.0$ Å. The values of the denominator *D*, obtained with the same basis set in this work, decrease from 1.49 at $R = 1.55$ Å to 1.37 at $R = 2.0$ Å, to increase again to 1.78 at $R = 4.0$ Å. Thus, there seems to be a similarity in the behavior of the denominator *D*, which renormalizes the triples correction to the CCSD energy in the CR-CCSD(T) calculations, and the dependence of the effective number of unpaired electrons *n* on the interallylic distance *R* discussed in ref 9.

Conclusions

In summary, we demonstrated that, unlike the standard CCSD(T) approach, the recently developed single-reference CR-CCSD(T) method favors the concerted mechanism of the Cope rearrangement of 1,5-hexadiene, in agreement with the earlier multireference perturbation theory calculations[2−4] and experimental[8] and theoretical[11] studies of the secondary kinetic isotope effects. In addition to the highly accurate treatment of electron correlation that the CR-CCSD(T) approach offers, the advantage of the CR-CCSD(T) method over multireference techniques is the ease-of-use that does not require selecting active orbitals on a molecule-by-molecule basis. We have also demonstrated that the denominator *D* resulting from the CR-CCSD(T) calculations correlates with the degree of diradical character of the system of interest.

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Supporting Information Available: The U3BLYP, CASSCF, MCQDPT, CCSD, CCSD(T), and CR-CCSD(T) energies along the C_{2h} cut of the PES shown in Figure 1 and the corresponding energies of the 1,5-hexadiene reactant (the 6-31G* and 6-311G** basis sets), the stationary points on the U3BLYP PES (the 6-31G* and 6-311G** basis sets), and the values of the denominator *D* and cluster amplitudes $t(7b_u^2 \rightarrow 8a_g^2)$ and $t(5a_u^2 \rightarrow 5b_g^2)$ along the interallylic distance *R* (the 6-31G* basis set). This material is available free of charge via the Internet at http://pubs.acs.org.

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