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Diels–Alder Dimerization of 1,3-Butadiene: An ab Initio CASSCF Study of the Concerted and Stepwise Mechanisms and Butadiene–Ethylene Revisited

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Abstract: Ab initio CASSCF calculations with the 3-21G basis set have been used to locate transition structures for concerted and stepwise mechanisms of the Diels–Alder and [2 + 2] dimerizations of 1,3-butadiene. The butadiene–ethylene reaction was also studied with six-orbital/six-electron CASSCF calculations and the 3-21G and 6-31G* basis sets. The CASSCF calculations appear to slightly overestimate the stabilities of biradicals relative to concerted mechanisms, based upon comparisons with experimental data and expectations about correlation energies of different species. Energies were also evaluated with QCISD(T)/6-31G* calculations. All the theoretical results taken together lead to the conclusion that the transition structure for the butadiene–ethylene reaction leading to the biradical intermediate is 5 kcal/mol above the concerted synchronous transition structure. The transition states leading to various isomeric diradicals are slightly lower in energy than the concerted transition structures for the butadiene dimerization. The barriers to cleavage and closure of biradicals increase as the radical stability increases. Thus, the cleavage and closure barriers calculated at the CASSCF/3-21G level are 4–5 and 1–2 kcal/mol, respectively, for the biradical formed from two butadienes, as compared to 2 and <1 for the biradical intermediate formed in the butadiene–ethylene reaction. This contrasts to the ethylene dimerization, for which Doubleday *et al.* found no potential energy barrier for the 1,4-butanediyl intermediate to undergo either cleavage or ring closure.

Introduction

After years of controversy about the validity of various theoretical predictions about the mechanisms of the Diels–Alder reaction of butadiene plus ethylene, all results have seemed to converge on the synchronous concerted mechanism.[1] This agrees with available, albeit indirect, experimental data.[1b,d,2] Since the reaction is synchronous and involves an essentially closed-shell transition state, RHF and MCSCF methods give very similar transition states for the favored process. In addition, the MCSCF results predict that there is a biradical mechanism somewhat higher in energy than the concerted mechanism, as described below.

A more stringent test of theory is the mechanism of the Diels–Alder dimerization of 1,3-butadiene.[2] Experimental studies show that this dimerization has an activation energy that is 1–3 kcal/mol lower than that of the butadiene–ethylene reaction.[3,4] The concerted transition state should be affected slightly, whereas the biradical intermediate should be stabilized in the butadiene dimerization as compared to the butadiene–ethylene reaction. Doering and others carried out a thermochemical analysis of the butadiene dimerization[5] and deduced a 1–2 kcal/mol energetic preference for the concerted mechanism over the stepwise biradical mechanism.[5a] For comparison, the energy of concert is deduced as 7 kcal/mol for the Diels–Alder reaction between butadiene and ethylene using similar methods.[6] Experimental measures based on stereochemistry and on the amount of vinylcyclobutane formed indicate a 2–7 kcal/mol preference for the concerted mechanism in the reaction of butadiene with ethylene.[6,7]

Stephenson's experimental studies on the stereochemistry of *cis,cis*-dideuteriobutadiene dimerization, however, showed 10% loss of stereochemistry. This led him to conclude that there is competition between allowed $[4_s + 2_s]$ and forbidden $[4_s + 2_a]$ concerted cycloadditions.[8a] The biradical mechanism might also account for the partial loss of stereochemistry, but Stephenson argued that the ratio of divinylcyclobutane to loss of stereochemistry in vinylcyclohexene was not consistent with this mechanism. However, Klärner and Krawczyk recently found that the reaction actually gives 98% retention of stereochemistry at normal pressure and >99% stereospecificity at 8 kbar of

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pressure, whereas the divinylcyclobutane byproduct is formed nonstereospecifically.[8b] Moreover, the measured pressure effect indicates that the activation volume is more negative for the Diels–Alder dimerizations of butadiene ($\Delta V^{\ddagger} = -26.5$ cm^3/mol) than for the [2 + 2] dimerization of butadiene ($\Delta V^{\ddagger} = -14.4$ cm^3/mol).[8c] This difference was found to be general between concerted and stepwise mechanisms.[8c,d] All these show good evidence for the stereospecific concerted mechanism competing with a small amount of nonconcerted and nonstereospecific reaction for the Diels–Alder reaction.

The concerted mechanism was also invoked in the Diels–Alder dimerization of piperylene[9a] and isoprene,[9b] while both concerted and stepwise mechanisms compete in the Diels–Alder dimerization of the more sterically hindered 2,3-dimethylbutadiene,[9c] as revealed by copolymerization competing with the Diels–Alder reactions.

We have applied MCSCF theory to the study of the mechanism of the butadiene dimerization. We have also studied the butadiene–ethylene reaction at a more complete MCSCF level than previously reported. These results represent the current state of the art on calculations of Diels–Alder reaction mechanism and quantify the delicacy of competition between concerted and stepwise processes in this reaction. The results also provide new insights into various processes involved in creation, destruction, and conformational processes of 1,4-diradicals.

Background

Three possible mechanisms have been proposed for the Diels–Alder reactions: a concerted mechanism, a two-step mechanism, and an asynchronous two-stage mechanism.[10] Theoretical attempts to resolve the various mechanisms of Diels–Alder reactions generated a lively debate for years, because semiempirical and ab initio studies often led to opposite conclusions. Semiempirical and ab initio methods using unrestricted Hartree–Fock (UHF) theory predict a stepwise biradical mechanism,[11] while ab initio methods using restricted Hartree–Fock (RHF) theory predict a concerted mechanism.[1,12] Semiempirical RHF calculations give concerted synchronous transition states for the butadiene–ethylene reaction.[1e,11h] Although single-configuration SCF approaches fail to find biradicaloid structures, ab initio RHF calculations give reliable structural, and—after electron correlation corrections—energetic descriptions of the transition structures of allowed pericyclic reactions.[1]

Recently, several pericyclic reactions have been studied by using multiconfiguration SCF (MCSCF) methods that seem to give a properly balanced description of the potential energy surfaces in the regions of reactive and unstable species including both closed-shell concerted transition structures and open-shell biradical intermediates.[13,14] In particular, Bernardi and coworkers reported MCSCF studies on the Diels–Alder reaction of butadiene with ethylene using two sets of complete active space (CASSCF) wave functions derived from four electrons in four orbitals (CAS1) and six electrons in six orbitals (CAS2), respectively.[14] Bernardi's CASSCF calculations with the STO-3G minimal basis set show the concerted mechanism to be less favorable than the stepwise mechanism. They carried out additional CAS1 calculations with the 4-31G basis set but were able to find only two stationary points: one is the transition structure for the concerted mechanism, and the other is a biradical intermediate. When they compared the energy of the fully optimized 4-31G concerted transition structure with the single point energies of other intermediates located with the STO-3G basis set, they concluded that the synchronous concerted path is favored by 2 kcal/mol.[14] These calculations also indicate no apparent barriers for the closure of biradical intermediate to cyclohexene; thus the stepwise mechanism can be described most aptly as a two-stage rather than a two-step pathway, since there is no intermediate.

While our goal was to study the butadiene dimerization, the possible deficiencies of using minimal basis sets or small active spaces in Bernardi's MCSCF calculations prompted us to make further computational efforts on the Diels–Alder reaction of butadiene plus ethylene. We report here our results of CASSCF calculations on both the Diels–Alder dimerization of butadiene and the Diels–Alder reaction of butadiene plus ethylene. These give good estimates of the relative energies of concerted and stepwise mechanisms of these reactions and provide a somewhat more detailed view of the intermediates formed in the stepwise process.

Computational Methods

In this study, the MCSCF[15] wave function consists of a complete active space SCF (CASSCF)[16] wave function obtained by distributing, in all spin consistent ways, the active electrons among the active orbitals. Active electrons are those involved in bonding changes in the course of the reaction. There are six and eight active electrons, respectively, for the butadiene–ethylene reaction and butadiene dimerization. The active orbitals correspond to all the π and π^* orbitals of the reactants. Thus, the active space includes six electrons in six orbitals for the butadiene–ethylene reaction and eight electrons in eight orbitals for the butadiene dimerization.

Our selection of the active space is based upon the chemical intuition that the bonding changes in these reactions involve transfer of π bonds of the reactants to partial σ bonds in transition states and then to σ bonds in the products. The active space selected in our study is also consistent with the assessment of active space[17] based upon the UHF natural orbital populations[18] in the transition structures of these Diels–Alder reactions. Those orbitals with an orbital electron population in the range of 0.02 to 1.98 are included in the active space. In the case of biradical intermediates, inspection of the UHF natural orbital populations indicated a choice of an active space of four electrons and four orbitals for the butadiene–ethylene reaction, because the bonding and antibonding orbitals of the newly formed σ bond are too low and too high in energy, respectively, and are populated with 1.997 and 0.003 electrons, respectively. Nevertheless, we included all orbitals corresponding to the π orbitals of the reactants and used the UHF natural orbitals as an initial guess for the

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MCSCF calculations, in order to maintain a consistent active space for each species studied.

The transition structures for the stepwise pathway and the biradical intermediates were located initially at the UHF level with the 3-21G basis set[19a] and were further optimized at the CASSCF/3-21G level. CASSCF optimizations of the concerted transition structures began with the RHF geometries and RHF orbitals. For the Diels–Alder reaction of butadiene plus ethylene, the transition structures and biradical intermediates were further optimized with the more flexible 6-31G* basis set[19b] at the CASSCF level. All CASSCF geometries were fully optimized with use of Baker's gradient techniques with a UHF Hessian as the initial guess.[20] Both HF and CASSCF calculations were performed with the GAMESS programs developed by Dupuis and co-workers.[21]

The transition structures and biradical intermediates located in this way were proven to be saddle points and energy minima, respectively, by numerical Hessian calculations followed by harmonic vibrational frequency analyses. Each transition structure has one and only one imaginary vibrational frequency, while biradical intermediates have none. Statistical thermodynamic properties and vibrational zero-point energies (ZPE) were computed from the unscaled vibrational frequencies.

The relative energies of various transition structures and the biradical intermediate for the butadiene–ethylene reaction were evaluated further by Pople's QCISD(T) methods[22] with the 6-31G* basis set using the CASSCF/6-31G* geometries, using both UHF and RHF orbitals as reference. These calculations, although based upon single determinant wave functions, including a high level correlation energy correction, were carried out in order to compare the effects of dynamical electron correlation in addition to the non-dynamical corrections which are included in the CASSCF calculations.

Results and Discussion

Several transition structures and biradical intermediates were located for the Diels–Alder reaction of butadiene with ethylene and for the butadiene dimerization. These are shown in Figures 1, 3, and 5. The calculated energies are summarized in Tables I and II and Figures 2 and 4. We begin our discussion with the butadiene–ethylene reaction and compare our results with those reported by Bernardi *et al.* We then describe in detail the Diels–Alder dimerization of butadiene.

Butadiene–Ethylene Reaction. The concerted transition structure **2** of the butadiene–ethylene reaction is, as expected,[1] very much like those reported at various levels of theory; there is little change from the 3-21G basis set to the 6-31G* basis set at the CASSCF level. Unlike Bernardi's CAS1/4-31G calculations, we were able to locate both a transition structure **3** and a biradical intermediate **4** for the stepwise pathway. The forming σ-bond in **3** and newly formed σ-bond in **4** calculated at the CASSCF/3-21G level are 0.1 Å shorter than the corresponding lengths obtained at the CAS1/STO-3G level. Numerical Hessian calculations and harmonic vibrational frequency analyses show that **3** is an authentic transition structure and **4** is an intermediate. On the other hand, we were unable to find either an asynchronous transition structure or a biradical minimum when the methylene radical center in **3** or **4** is rotated syn–gauche to the allyl moiety. That is, when the two radical centers are near each other, the only stationary points found are **2** and cyclohexene. A transition structure search at the CASSCF level starting with the UHF syn–gauche transition structure collapsed to the concerted synchronous transition structure **2**; MCSCF optimizations starting from the UHF biradical in the syn–gauche conformation led to the boat cyclohexene. This result indicates that there is a very small potential energy barrier, if any, for the closure of biradical intermediate when the radical centers are in a conformation where interaction is possible. There is no asynchronous concerted transition state except as a vibrationally excited synchronous transition state. The only stepwise mechanism of the parent Diels–Alder reaction involves formation of **4** in the rate-determining step which is followed by rotation involving a second barrier of 2–3 kcal/mol accompanied by collapse with no further barrier to cyclohexene. Although we have not investigated this portion of the potential surface in detail, the fact that **1** is a minimum and the well-known values of rotational varriers in hydrocarbons lead to this conclusion.

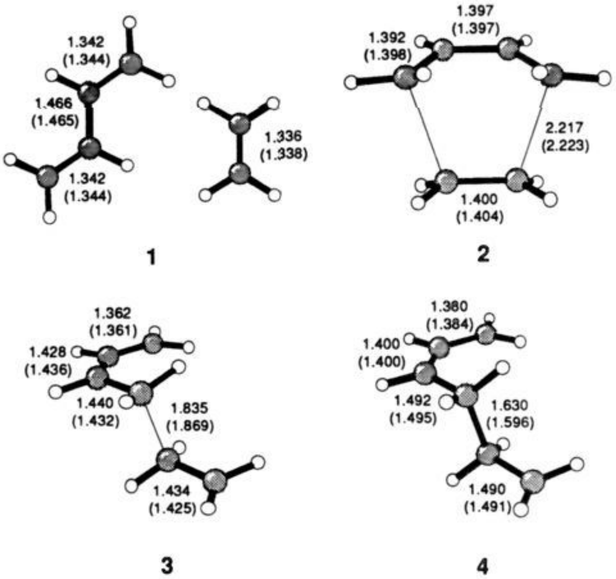

Figure 1. CASSCF/3-21G (CASSCF/6-31G*) reactants, transition structures, and biradical intermediate of the Diels–Alder reaction of butadiene with ethylene. Bond lengths are in angströms.

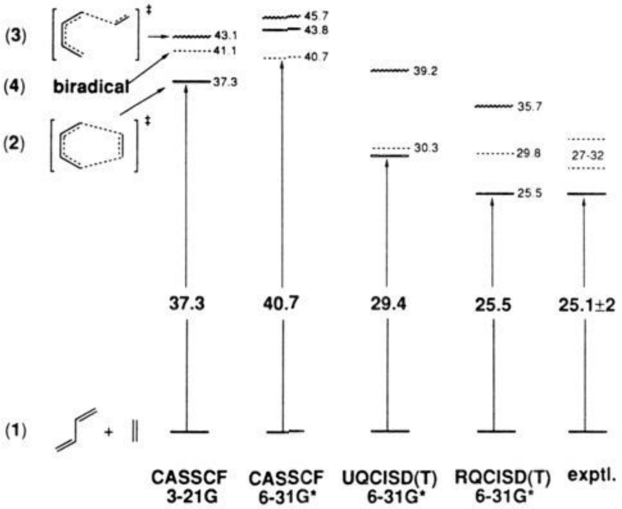

Figure 2. Relative energies (kcal/mol) of reactants, transition structures, and diradical intermediates for the Diels–Alder reaction of butadiene and ethylene.

A small barrier of 2 kcal/mol is found for the cleavage of biradical intermediate **4** via σ-bond breaking involving transition structure **3**. In the simpler butan-1,4-diyl system,[23] there is no potential energy barrier for the dissociation of the butanediyl biradical to two ethylenes.[23c] The biradical **4** is slightly stabilized by allylic resonance.[24,25]

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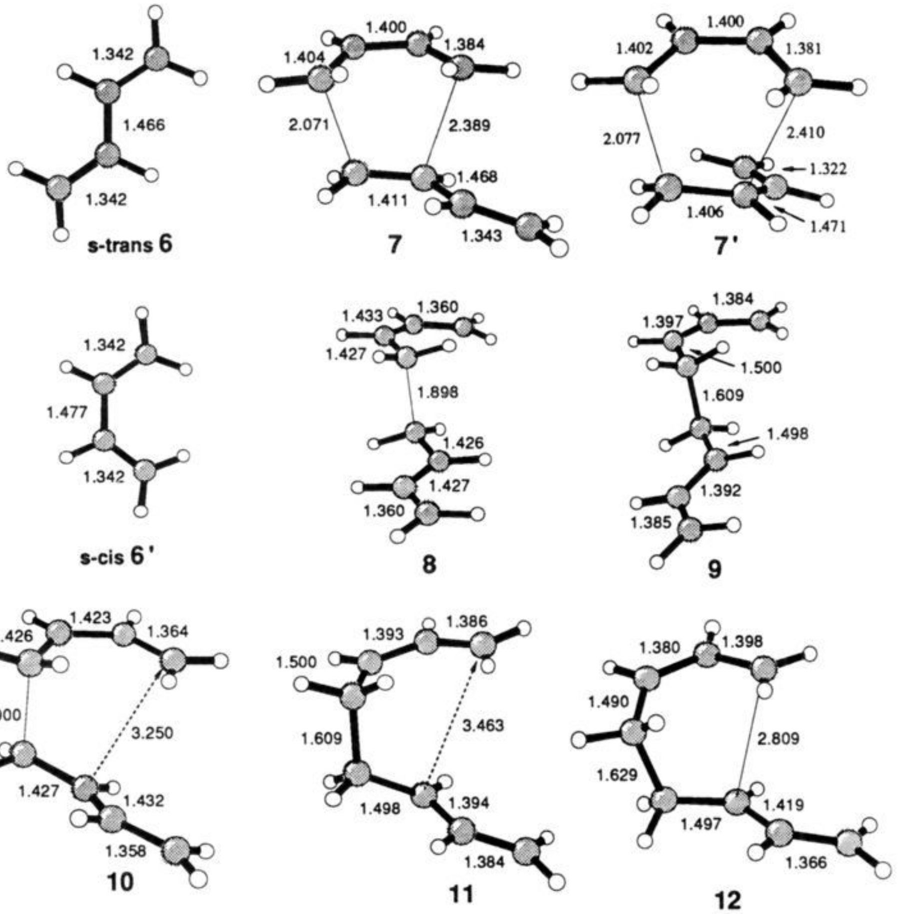

Figure 3. CASSCF/3-21G reactants (**6**, **6'**), concerted transition structures (**7**, **7'**), transition structures (**8**, **10**) for diradical formation, diradicals (**9**, **11**), and transition structure for biradical cyclization (**12**) for the butadiene dimerization. The bond lengths are in angströms.

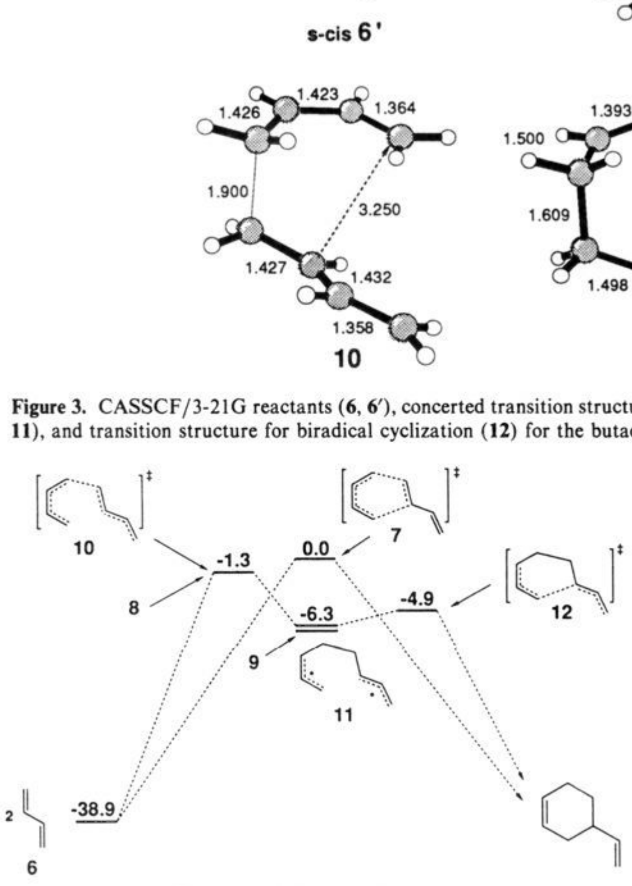

Figure 4. CASSCF/3-21G relative energies (kcal/mol) of reactants, transition structures, and diradical intermediates for butadiene dimerization.

At the CASSCF level, the concerted transition structure **2** is lower in energy than the stepwise transition structure by 5.8 kcal/mol with the 3-21G basis set and 1.9 kcal/mol with the 6-31G* basis set. On the CASSCF/3-21G potential energy surface, the concerted path is still favored by about 3.4 kcal/mol after zero-point energy (ZPE) corrections (Table I) calculated at the CASSCF/3-21G level. If the same ZPE correction is made to the CASSCF/6-31G* energy surface, the stepwise pathway is 0.5 kcal/mol below the concerted one. The calculated activation entropy (Table I) of the concerted transition structure **2** is 8 eu more negative than that of the stepwise transition structure, which favors the stepwise pathway in terms of lower activation free energy. Therefore, calculations at the CASSCF/6-31G* level predict a favorable stepwise pathway for the Diels–Alder reaction of butadiene with ethylene.

However, single point energy calculations at the RQCISD(T)/6-31G* level with the CASSCF/6-31G* geometries predict that the concerted transition structure **2** is 10 kcal/mol more stable than the stepwise transition structure **3** and 4 kcal/mol more stable than the biradical intermediate **4**. This RQCISD(T) method with a single determinant wave function offers a substantial improvement of the calculated relative energies as compared to RHF or even MP2/MP4 methods. In fact, the calculated activation energy (25.5 kcal/mol) is very close to the experimental value, much better than results from other calculations. The results with a UHF reference are almost identical. These results are summarized in Figure 2.

The results reported here provide interesting insights into the correlation energies of different species. The concerted transition state may be considered to be more unsaturated than the diradical or the transition state leading to it. That is, the concerted transition state has two partial σ-bonds, both quite long (2.2 Å), while the transition state leading to the diradical has only one partial σ-bond, which is more fully formed (1.8 Å). This is presumably the reason that dynamical correlation energy, calculated by QCI, corrects the energy of the concerted transition state more than the biradical or the transition state leading to it.

The QCI results predicted that the concerted pathway is lowest in energy and indicated that the MCSCF calculations overestimate the stability of biradical species relative to closed-shell species. A comparison between the CASSCF/6-31G* results and available

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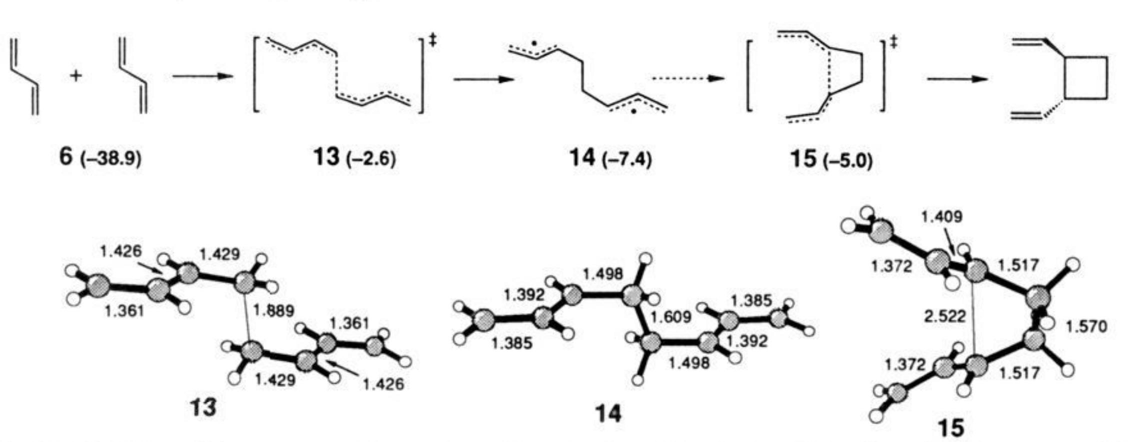

Figure 5. CASSCF/3-21G transition structures and intermediates of butadiene [2 + 2] dimerization. The bond lengths are in angströms. The energies relative to **7** are in parentheses (kcal/mol).

Table I. Calculated Energies and Entropies for the Diels–Alder Reaction of Butadiene with Ethylene (Relative Energies in kcal/mol Are Shown in Parentheses)

molecule(s)	CASSCF/3-21G –energy (au)	CASSCF/3-21G ZPE (kcal/mol)	CASSCF/3-21G S(298K eu)	CASSCF/6-31G* –energy (au)	RQCISD(T)[a] 6-31G*	UQCISD(T)[a] 6-31G*
1	231.74899[b] (–37.3)	89.8[c]	119.4[d]	233.03574[b] (–43.8)	–25.5	–29.4
2	231.68960 (0.0)	93.4	76.2	232.96590 (0.0)	0.0	0.0
3	231.68033 (5.8)	91.0	82.6	232.96291 (1.9)	10.2	9.8
4	231.68356 (3.8)	91.4	84.0	232.97089 (–3.1)	4.3	0.9
5[e]	231.78159 (–57.7)	97.4	75.0			

[a] Relative energies (kcal/mol) of frozen core single point energy calculations on the CASSCF/6-31G* geometries. Energies of **2**: –233.76785 (au, RQCISD(T)); –233.75912 (au, UQCISD(T)). [b] Single point energy of butadiene with ethylene 6 Å apart. [c] Sum of individual ZPEs. [d] Sum of individual entropies. [e] Cyclohexene boat conformation. The more stable chair is ~6 kcal/mol more stable.[29]

Table II. Calculated Energies and Entropies at the CASSCF/3-21G Level (Relative Energies in kcal/mol Are Shown in Parentheses)

molecule	–energy (au)	ZPE (kcal/mol)	S(298 K) (eu)
butadiene + butadiene (**6**)	308.23588[a] (–38.9)	112.4[b]	134.4[c]
7	308.17392 (0.0)	115.1	88.9
7′	308.17360 (0.2)	114.1	91.4
8	308.17599 (–1.3)	113.5	93.6
9	308.18449 (–6.6)	114.0	95.5
10	308.17595 (–1.3)	113.8	92.3
11	308.18399 (–6.3)[d]	114.2	89.1
12	308.18168 (–4.9)	114.6	88.8
13	308.17806 (–2.6)	113.3	94.4
14	308.18570 (–7.4)	113.7	96.5
15	308.18192 (–5.0)	113.9	91.2
16	308.17036 (+2.2)	118.6	77.8
17	308.17830 (–2.7)	116.7	82.6

[a] Single point energy of two butadienes that are 6 Å apart. [b] Sum of individual ZPEs. [c] Sum of individual entropies. [d] This structure has one small imaginary frequency of 16i cm^{-1}.

experimental evidence also indicates that MCSCF calculations without dynamical electron correlation energy corrections overestimate the stabilities of biradical species. For example, we have found experimentally that the reactions of *cis*- or *trans*-1,2-dideuterioethylene with 1,1,4,4-tetradeuteriobutadiene proceed stereospecifically to afford the cis and the trans adducts, respectively, with less than 1% scrambling of stereochemistry, if any.[1b] The observed high stereospecificity could involve a stepwise mechanism only if the ring closure of the biradical intermediate were at least 100-fold faster than the rate of rotation of the methylene radical center. However, the ring closure of a stabilized biradical intermediate involved in the butadiene–ethylene reaction is unlikely to be faster than cyclization of 1,4-butanediyl to cyclobutane, and the latter occurs only after almost complete scrambling of stereochemistry arising from rotation of the terminal methylene groups.[26] If it were formed, the biradical intermediate in the butadiene–ethylene reaction would undergo extensive rotation of the deuterated terminal methylene before cyclization to cyclohexene. The barriers to rotation of primary radical centers are less than 0.4 kcal/mol,[27] as compared to a rotational barrier of 2–3 kcal/mol[14] predicted for **4** to achieve the proper orientation for ring closure. There may also be a free energy barrier of 1–2 kcal/mol required for a biradical ring closure due to the unfavorable entropy of cyclization.[23,28] Therefore, a concerted mechanism, not a stepwise biradical mechanism, is consistent with the experimental stereochemistry of the butadiene–ethylene reaction. In order to account for the observed high stereospecificity of the butadiene–ethylene reaction, the concerted stereospecific pathway is required to have an activation energy at least 3.7 kcal/mol lower than that for a stepwise pathway.[1b] This estimate is also in the range of Doering's energy of concert of 2–7 kcal/mol based upon thermochemical analyses.[6] A 3.4 kcal/mol energy preference for the concerted pathway calculated at the CASSCF/3-21G level is in reasonable agreement with these estimates, while the CASSCF/6-31G* calculations overestimate the stabilities of biradical species.

CASSCF calculations underestimate considerably the heat of reaction of ethylene plus butadiene to form cyclohexene. As shown in Table I, the reaction is calculated by CASSCF/3-21G to be exothermic by only 26 kcal/mol,[29] as compared to an experimental value of 40 kcal/mol. RHF/3-21G calculations predict an exothermicity of 38 kcal/mol. The error in the CASSCF calculation is due to different extents of electron correlation for the active space including π and π^* orbitals of butadiene and the active space involving σ and σ^* orbitals in

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[29] The half-chair conformation of cyclohexene is found experimentally and computationally to be more stable than the boat by ~6 kcal/mol. Anet, F. A. L.; Freedberg, D.; Houk, K. N.; Storer, J. W. *J. Am. Chem. Soc.* **1992**, *114*, 10969.

cyclohexene. The active space including π and π^* orbitals returns more correlation energy than the active space involving the σ and σ^* orbitals in the product; the π–π^* active space has smaller energy gaps between the ground state and excited state configurations and thus more mixing of excited configurations than is the case for a σ–σ^* active space. As an illustration, we carried out calculations on the bond energies of the π-bond in ethylene and the σ-bond in ethane using the CASSCF(2e,2o)/3-21G method. The rotational barrier of ethylene is calculated to be 66 kcal/mol, in good agreement with the experimental value of ~65 kcal/mol.[30] That is, inclusion of non-dynamical correlation energy is adequate to give proper relative energies of a π-bond and two radical centers. By contrast, the calculated bond dissociation energy of ethane to form two methyl radicals 10 Å apart is 82 kcal/mol, which is about 6 kcal/mol smaller than the experimental value.[31] The underestimation of the CC σ-bond dissociation energy of ethane is due to the fact that the CASSCF calculations underestimate the correlation energy of ethane relative to two radicals. It is likely, therefore, that correlation energies within the CASSCF formalism are treated in an unbalanced manner for reactive intermediates and transition structures where σ and σ^* orbitals of fully formed bonds are included in the active space of some of these species but not the others. Taken together, these results indicate that the energies of **2**, **3**, and **4** are somewhat between those calculated by CASSCF and QCISD(T) calculations. Relative energies of 0, 5, and 3 kcal/mol are consistent with calculations and experiments.

Butadiene Dimerization. As found here and elsewhere for the Diels–Alder reaction of butadiene with ethylene, our calculations show that the butadiene dimerization can have both stepwise and concerted pathways. Figure 3 shows the transition structures and biradical intermediates located for the Diels–Alder butadiene dimerization. There are several possible conformations for the concerted transition structures. We found at the RHF/3-21G level that the exo transition structure with *s-trans*-butadiene as a dienophile is the most favorable one. This is 1 kcal/mol more stable than the *s-trans* endo transition structure. The *s-cis* exo and endo transition structures are 0.8 and 1.4 kcal/mol, respectively, above the *s-trans* exo structure. For the CASSCF studies, only the *s-trans* structures were studied. We located an endo transition structure for *s-cis*-butadiene and an exo transition structure for *s-trans*-butadiene reacting with the diene at the CASSCF level of theory. The exo transition structure **7** is only 0.2 kcal/mol more stable than the endo transition structure **7′**. This is in minor disagreement with the experimentally observed slight endo selectivity of the butadiene dimerization (endo/exo ratio of 59:41 at 1 bar)[8b] and also to the calculated endo preference of the Diels–Alder reactions of cyclopentadiene with various dienophiles.[32] There is no evidence from energy or geometry of any effect of secondary orbital interactions on the stereochemistry. The concerted transition structure **7** is quite asynchronous; the two forming partial σ-bonds are 2.07 and 2.39 Å. The stepwise mechanism may involve the formation of the biradical intermediate **9** through the transition structure **8**, followed by bond rotation and biradical ring closure. This stepwise mechanism is predicted to be favored by 1.3 kcal/mol over the concerted pathway.

In the butadiene–ethylene reaction, there is no biradical intermediate when the forming radical centers are close enough to interact. By contrast, in the butadiene dimerization, a two-step pathway with geometry very much like the concerted transition state also exists.

Transition structure **10** is the same in energy as **8**. It leads to the biradical intermediate **11**, which is the same in energy as **9**. Both are *cis,trans* bis-allyl biradicals. Transition structure **10** has a forming σ-bond length of 1.9 Å, while there is no bonding between the other termini that are 3.25 Å apart. The biradical **11** has the newly formed σ-bond length of 1.61 Å and a long distance (3.46 Å) between the other termini which become bonded in cyclohexene. It is nearly a minimum, although harmonic vibrational frequency analyses indicate a very small imaginary vibrational frequency of $16i$ cm^{-1} corresponding to the essentially barrierless rotation of the *s-trans* allyl moiety around the C3–C4 bond. Biradical **11** undergoes ring closure via transition structure **12** to form vinylcyclohexene. Transition structure **12** is extremely early, similar in structure to the biradical with a very long (2.8 Å) forming single bond. It is interesting to note that the first formed σ-bond is stretched by 0.02 Å in the ring closure transition structure. This geometrical change presumably allows closer approach of the centers involved in the formation of the second bond.

The identical energies of **8** and **10** and of **9** and **11** provide the information that there is no interaction between radical centers at distances >3.25 Å. The fact that **12** is a transition structure provides an interesting (although not necessarily universal) value of 2.8 Å for the length of a forming bond in the transition state of biradical closure.

The existence of both concerted and stepwise mechanisms with similar conformations in the butadiene dimerization is particularly interesting; this has been claimed for the butadiene–ethylene reaction by Dewar,[11a] although apparently this claim has now been repealed.[1e] However, we found in the butadiene–ethylene reaction that attempted optimization of a similar asynchronous structure like **11** leads to collapse to the synchronous transition structure. This difference between the two systems is the result of an extra allylic stabilization of the biradical intermediate in the butadiene dimerization as compared to the biradical involved in the butadiene–ethylene reaction.

It is very interesting that at the CASSCF/3-21G level, the addition of a vinyl group destabilizes the concerted transition state **2** by 1 kcal/mol, stabilizes the transition state **3** leading to the diradical intermediate by 5.5 kcal/mol, and stabilizes the diradical intermediate **4** by 8.8 kcal/mol. While these numbers are likely to change at higher computational levels, they are in accord with expectation.

At the CASSCF/3-21G level, the calculated barrier for the ring closure of biradical **11** via **12** is only 1.4 kcal/mol, while there is a 5 kcal/mol barrier to cleavage of the first formed σ-bond in **11**. Therefore, for the stepwise pathway, the first transition structure **10** leading to the formation of biradical intermediate **11** is considerably higher in energy than the transition structure of radical ring closure. Overall, the stepwise transition structure is slightly favored by 1.3 kcal/mol as compared to the concerted transition structure **7**. All of these energetics are compared in Figure 4.

Since the biradical pathway competes favorably in this case, we also searched for other more stable biradical intermediates. Indeed, there are many potential biradical intermediates, with *s-cis* or *s-trans* arrangements of each butadiene moiety and gauche-plus, gauche-minus, or anti arrangements about each newly formed σ-bond. CASSCF calculations show that the transition structure, **13**, leading to a *trans,trans* biradical intermediate **14** is about 1 kcal/mol more favorable than **8** and **10** (Figure 5). This *all-trans* transition structure **13** is predicted to be 2.6 kcal/mol lower in energy than the concerted transition structure at the CASSCF/3-21G level. The *trans,trans* biradical **14** is more stable than the *trans,cis* biradical **11** by about 1 kcal/mol, and there is a similar 5 kcal/mol barrier for the cleavage of *trans,trans* biradical to two butadienes. However, since there is a substantial barrier to rotation in an allyl radical,[26,27] the *trans,trans* biradical intermediate **14** can only readily form *cis*- or *trans*-divinylcyclobutane upon ring closure. A transition structure **15** was located for the ring closure of a *trans,trans* biradical intermediate to form *trans*-divinylcyclobutane. As expected for the recombination of a biradical, this transition

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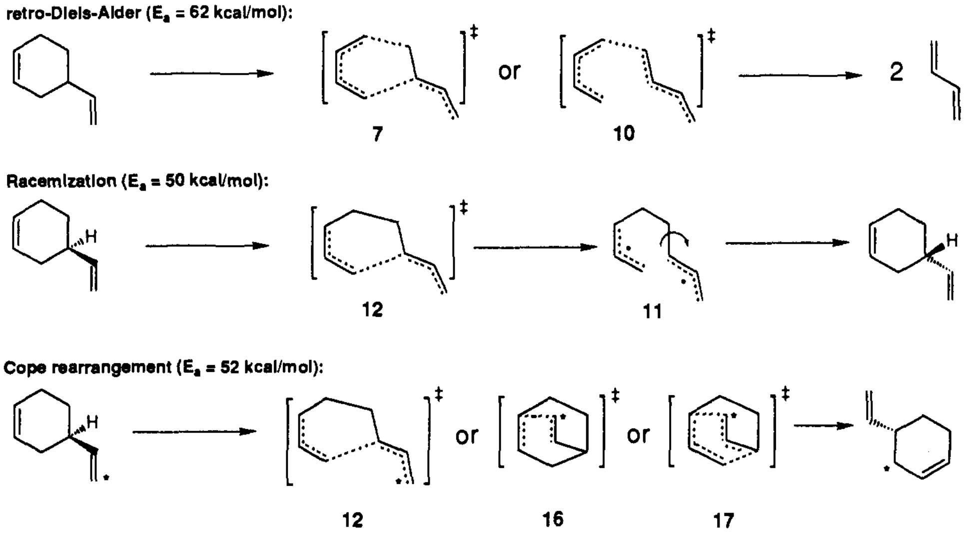

Figure 6. Thermal reactions of vinylcyclohexene.

structure is a very early one involving a long forming σ-bond (2.52 Å), and its energy is only 2–3 kcal/mol above the biradical minimum.[33] Radical ring closure from the biradical is again kinetically favored over reversion to butadiene, although closure of the four-membered ring is predicted to be 1 kcal/mol more difficult than closure to a six-membered ring from **11**.

Experimental studies on the Diels–Alder dimerization of butadiene so far offer no simple conclusions about the relative energetics of concerted and stepwise mechanisms. Benson's early estimates of the heats of formation of the transition state led to the conclusion that this reaction is not a concerted process but a two-step process[5c] and suggested that the butadiene dimerization involves a biradical intermediate that cyclizes to 4-vinylcyclohexene.[5b] Doering and co-workers, however, by a careful thermochemical analysis involving more experimental data showed that the mechanism of this reaction is likely to be concerted, perhaps two-stage, but not two-step.[5a] On the basis of studies of stereochemistry and activation volumes of this reaction, Klärner and Krawczyk concluded that the reaction is concerted.[8b] The CASSCF calculations we have performed predict that concerted and stepwise mechanisms are comparable in energy with the latter slightly more favorable. However, there seems to be an overestimate of biradical stability again in our calculations, since the formation of biradical **14**, which will lead to divinylcyclobutane, is predicted to be the most favorable process, yet divinylcyclobutane is formed to the extent of only 8% in the dimerization of butadiene.[8a]

Additional experimental data are available on the energies of other transition states and diradical species on the C_8C_{12} surface. Comparisons can be made between the calculated and experimental activation energies of three thermal reactions of 4-vinylcyclohexene (Figure 6). These comparisons are particularly useful because all the experimental values are based upon a single starting reactant and there is no need to estimate any thermodynamic values. Vinylcyclohexene undergoes a retro-Diels–Alder reaction to form butadiene, with a measured activation energy of 62 kcal/mol.[3b] This must involve concerted transition structure, **7**, or the transition structure for the second bond cleavage, **10**. Optically active 4-(*exo*-dideuteriovinyl)cyclohexene undergoes both Cope rearrangement and racemization with much lower activation energies of 50–52 kcal/mol.[5a,34] The racemization reaction must involve the σ-bond cleavage of vinylcyclohexene to form a bis-allyl biradical **11**, followed by ring closure after a rapid single bond rotation in the bis-allyl biradical. The stepwise retro-Diels–Alder reaction of vinylcyclohexene should also involve the same bis-allyl biradical, which then undergoes a subsequent cleavage of the second σ-bond to give two butadiene molecules. On the basis of these experimental activation energies, one would expect at least a 12-kcal/mol difference in energy between the transition state for the first σ-bond cleavage and that for the second bond cleavage of vinylcyclohexene. Transition structure **12** corresponds to the first σ-bond cleavage in the racemization reaction, and transition structure **10** corresponds to the second σ-bond cleavage involved in the stepwise retro-Diels–Alder reactions of 4-vinylcyclohexene. Our calculations show only a 4–5 kcal/mol difference in energy between **10** and **12**, which is considerably less than the experimental estimate of 12 kcal/mol. The discrepancy here may be due to the unbalanced treatment of correlation energies in calculations of **12** where the σ–σ^* orbitals were included in the active space.

Alternatively, the retro-Diels–Alder reaction of vinylcyclohexene can take place via a concerted mechanism, and thus the observed 12 kcal/mol difference in activation energies corresponds to the energy gap between the concerted transition state (**7**) and that of the first σ-bond cleavage (**12**). Again, our calculations show only a 4–5 kcal/mol difference in energy between **7** and **12**. The discrepancy between experimental and calculated values may be attributed to the low level of theory used or to the poor assumption that the transition state for the racemization is **12**.[35] If that assumption is correct, then there should be a barrier of at least 12 kcal/mol for the bis-allyl radical to dissociate into two butadiene molecules.

The Cope rearrangement, which has an observed activation energy of 52 kcal/mol (Figure 6), might occur by several mechanistic pathways. The first is a stepwise one that occurs by breaking the σ-bond via **12** to form a bis-allyl radical, followed by collapse of the diradical to form product. This is similar to the racemization process as discussed earlier. Another stepwise mechanism involves the formation of a biradical intermediate via an asynchronous transition structure **16**, while the concerted process involves a synchronous transition structure **17** of C_2 symmetry. All three pathways of this type have been studied extensively for the parent Cope rearrangement of 1,5-hexadiene. The latest MCSCF/6-31G* calculations by Dupuis, Murray, and Davidson suggest that the pathways analogous to **16** and **17** are of comparable energy. Earlier MCSCF calculations with the 3-21G basis set predicted the concerted pathway like **17** to be most favorable.[13a]

The active space used here for the CASSCF calculations on transition structures **16** and **17** was eight electrons in eight orbitals; six of the orbitals correspond to orbitals involved in the bond

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(33) Closure of bis-allyl radical **14** gives *cis*-divinylcyclobutane or *cis*-cyclooctadiene, but the energy of **14** should differ little from a similar bis-allyl biradical that cyclizes to *trans*-divinylcyclobutane via transition structure **15**.

(34) Doering, W. v. E.; Brenner, D. M. *Tetrahedron Lett.* **1976**, 899.

(35) Attempts to locate a chair transition structure for the bond homolysis of chair vinylcyclohexene have so far been unsuccessful.

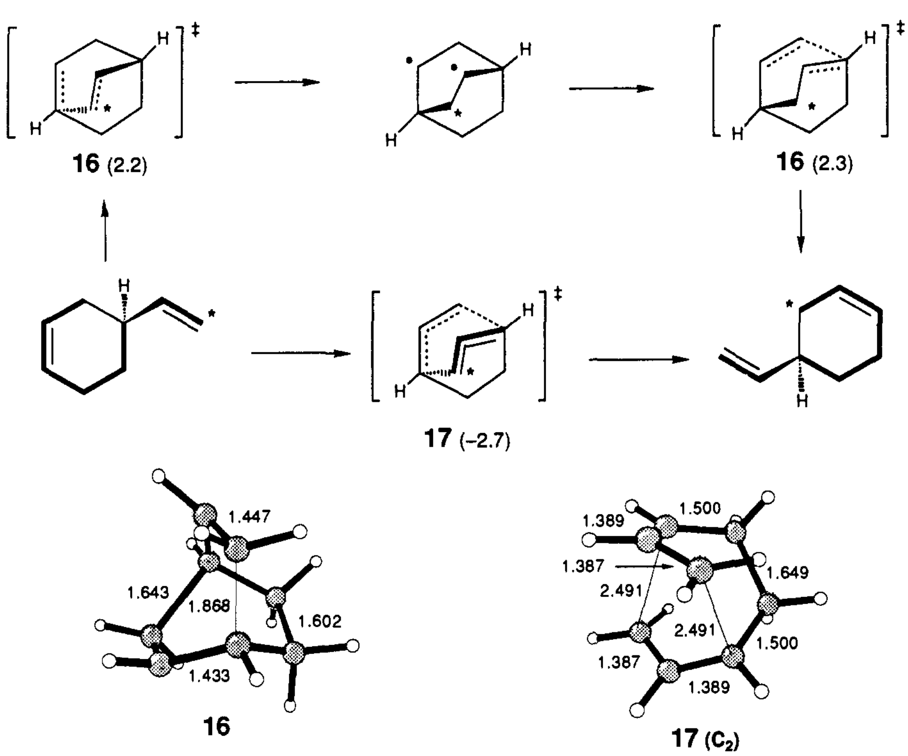

Figure 7. CASSCF/3-21G geometries of transition structures **16** and **18** for the stepwise and concerted Cope rearrangements of vinylcyclohexene. Bond lengths are in angströms, and energies relative to **7** are shown in parentheses (kcal/mol).

breaking and formation and the other two correspond to the σ and σ^* orbitals of the bridge CC bond. In contrast to the Cope rearrangement of 1,5-hexadiene, where the chair conformation is more favorable than the boat, only the boat transition structures can be achieved in the vinylcyclohexene case. The optimized structures are shown in Figure 7. The transition structure **16** for the stepwise Cope rearrangement is predicted to be 5 kcal/mol higher in energy than the concerted transition structure **17**. The transition structure **17** is predicted to be 2.7 kcal/mol more stable than the transition structure of the concerted Diels–Alder reaction. The experimental measurements, however, show that the Cope rearrangement is 12 kcal/mol more favorable than the retro-Diels–Alder transition structure. Once again, there might be a problem of balance with treatments of various reaction intermediates and transition structures by CASSCF methods which underestimate the stability of the Cope transition structures.

Transition structure **17** is quite unusual, since the forming and breaking bond lengths (2.49 Å) are longer than is usually found in pericyclic transition states. Indeed, the energy of **17** is calculated to be only 2 kcal/mol higher than that for the single bond cleavage, **12**, most likely due to the steric repulsion required to move the vinyl groups of vinylcyclohexene into the crowded arrangement necessary for formation of the new σ-bond.

Conclusion

We have shown that the geometries of various intermediates and transition structures are more sensitive to electron correlation than to the basis set once it is expanded beyond the 3-21G basis set. The potential energy surface is influenced significantly by basis set and electron correlation, and even relative energies cannot be reliably predicted within 3 kcal/mol. With respect to the concerted transition structures, biradical species treated by MCSCF calculations including strong σ–σ^* orbitals in the active space are artificially too high in energy, which may compensate for the effect of dynamical electron correlation that should raise the energy. Transition structures leading to the biradical intermediates should become higher in energy if dynamical electron correlations are included. Overall, the MCSCF calculations unrealistically favor the stepwise biradical pathway by 2–3 kcal/mol for the Diels–Alder dimerization of butadiene.

One would not expect the calculations done at the current level of theory to be exact enough to offer a conclusive distinction among various mechanisms of the Diels–Alder dimerization of butadiene. Nevertheless, the results appear to be converging pleasingly to the experimental results. For the Diels–Alder reaction of butadiene with ethylene, there are two mechanisms, with the synchronous concerted process favored by 5 kcal/mol over the stepwise. The stepwise process occurs only through an anti 1,4-diradical (vinyl-substituted) which is protected from cyclization only by the rotational barrier around the 2,3 bond.

For the butadiene dimerization, the concerted process is likely to be favored slightly over the stepwise, and a variety of diradicals exist with relative energies dictated by steric effects. The only serious discrepancy between theory and experiment involves the relative energies of transition states **10** and **7** relative to **12** and **17**. Theory puts these two classes of transition state within 2–4 kcal/mol of each other, while experiment places **7** and **10** about 10 kcal/mol higher in energy than **12** and **17**. This discrepancy could arise from basis set insufficiencies, or the greater correlation energy of **12** and **17**—a result we deem unlikely based upon considerations in this paper—or to problems in experimental measurement of the activation energy for the retro-Diels–Alder reaction of vinylcyclohexene.

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