similar (difference <1%), since the larger spatial separation compared to the heteronuclear case reduces the effect of vibrational high-frequency modes. Hence, the averaging is dominated by more collective (low-frequency) motions, which are rather insensitive to the type of statistics. This means that, for the considered proton pairs, MD simulations and NMA give equivalent results on the influence of vibrational dynamics on cross relaxation.

The distribution of γ for *long-range backbone NOE/ROEs* is given in Figure 3. The centering of γ around 1.0 indicates an increased weight of radial fluctuations compared to the angular ones. Hence, the structurally important long-range NOE/ROEs are on average rather weakly perturbed by the normal-mode dynamics. On the other hand, geminal proton pairs, such as $H_{\beta1}$–$H_{\beta2}$ and $H_{\alpha1}$–$H_{\alpha2}$ (glycines), have γ values distributed around 0.8 (not shown). Consequently, their use for distance calibration tends to bias the long-range distances toward values that are slightly too small (around 4%) and corrects at the same time for the motionally scaled short-range NOE/ROEs of Figure 2, provided that the dominant dynamics lie in the fast time scale regime. The difference for γ between classical and quantum statistics becomes larger for geminal proton pairs but still remains below 3%.

4. Conclusion

The results presented here demonstrate for the protein BPTI that the very fast time scale motions, represented by normal modes, can have a considerable influence on both hetero- and homonuclear relaxation rates. This is consistent with experimental results obtained for other proteins.[3,15] A non-negligible difference of 4%–5% between quantum and classical statistics is found for heteronuclear C_α–H_α relaxation. This effect is to be considered and should be corrected for in the interpretation of heteronuclear relaxation data using classical simulations. Comparison between measured and calculated order parameters allows tests and eventual refinements of biomolecular force fields and might support the development of potentials of mean force to mimic solvent effects.[16] The influence of vibrational motions on averaged internuclear distances extracted from proton cross-relaxation data is small and should become noticeable only for the generation of very high resolution protein structures.

Acknowledgment. Dr. Benoit Roux is thanked for helpful discussion, Zoltan Mâdi for porting CHARMM to a Convex C2, and Prof. Dr. Richard R. Ernst for encouragement, discussion, and support. This work was financially supported by the Swiss National Science Foundation.

Registry No. BPTI, 9087-70-1.

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How "Stable" Is Cyclobutyne? The Activation Energy for the Unimolecular Rearrangement to Butatriene

Heather A. Carlson,† Geoffrey E. Quelch, and Henry F. Schaefer III*

Contribution from the Center for Computational Quantum Chemistry, University of Georgia, Athens, Georgia 30602. *Received June 28, 1991*

Abstract: The barrier height for the disappearance of the singlet ground state of cyclobutyne has been investigated using ab initio molecular quantum mechanical methods. Stationary-point geometries were determined using the two-configuration self-consistent-field (TCSCF) method in conjunction with double zeta plus polarization (DZP) basis sets. The transition state exhibits strong biradical behavior. At the DZ+P TCSCF level, the classical barrier for unimolecular rearrangement to butatriene is 55 kcal/mol. With configuration interaction including all single and double excitations with respect to both TCSCF reference configurations, the classical barrier is reduced to 51 kcal/mol. Significant further lowerings in the cyclobutyne barrier occur when coupled cluster (CC) methods are applied. Including all connected triple excitations with the CCSD(T) method, the classical barrier is reduced to 41 kcal/mol with the DZP basis. Further corrections for the inherent "two reference configuration" nature of the problem and for zero-point vibrational energy yield a final value of ~25 kcal/mol for the activation energy. Thus clyclobutyne is reasonably stable with respect to unimolecular isomerization to butatriene.

Introduction

A question of long-standing interest[1-24] in physical organic chemistry is: "What is the smallest otherwise saturated cyclic hydrocarbon that can accommodate a $C\equiv C$ triple bond?" Experimentally, the smallest cycloalkyne that has been spectroscopically identified appears to be cyclohexyne, for which Wentrup, Blanch, Briehl, and Gross[22] recently assigned the $C\equiv C$ triple bond stretch to an infrared feature in the range 2090–2105 cm^{-1}. For cyclopentyne, Miller and Chapman[23] have very tentatively suggested that cyclopentyne may be the carrier of an infrared spectrum characterized by two strong bands at 2125 and 2077 cm^{-1}, a band of medium intensity at 1646 cm^{-1}, and two weak bands at 908 and 627 cm^{-1}. Experimental studies of cyclobutyne and its derivatives have proven to be inconclusive.[1,2]

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† CCQC Summer Undergraduate Fellow from North Central College, Naperville, IL.

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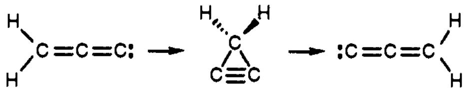
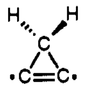
From the theoretical perspective it now seems reasonably clear[9,12] that singlet cyclopropyne is a transition state for the degenerate rearrangement of propodienylidene:

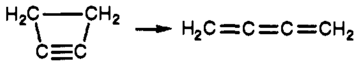


At the same time, it should be noted that triplet cyclopropyne



is a relative minimum on its potential energy hypersurface; clearly it does not incorporate a triple bond.

Although there is no convincing experimental evidence for the existence of cyclobutyne, theory[14,16] predicts that the singlet species is a genuine minimum. However, the critical unanswered question is the magnitude of the barrier for the unimolecular rearrangement of singlet cyclobutyne to lower energy C_4H_4 structures. For example, if this barrier proved to be less than 5 kcal/mol, the experimental identification of cyclobutyne might be exceedingly difficult. Accordingly, the goal of the present research is the prediction of the energy barrier for the disappearance of singlet cyclobutyne, to the lower energy butatriene molecule, i.e.,



Theoretical Approach

As discussed elsewhere,[14] the significant diradical character (roughly 15%) of the cyclobutyne ground state suggests a two-configuration self-consistent-field (TCSCF) starting point for theoretical studies. The appropriate two configurations are[14]

$$...3a_1^2 4a_1^2 3b_2^2 1b_1^2 4b_2^2 5a_1^2 6a_1^2 1a_2^2 2b_1^2 7a_1^2 \quad (1)$$

$$...3a_1^2 4a_1^2 3b_2^2 1b_1^2 4b_2^2 5a_1^2 6a_1^2 1a_2^2 2b_1^2 5b_2^2 \quad (2)$$

The small basis set used in the present research is the standard double zeta (DZ) set of Huzinaga[25] and Dunning,[26] designated C(9s5p/4s2p), H(4s/2s). The hydrogen s functions were scaled by a factor of 1.2; i.e., the primitive Gaussian orbital exponents α were multiplied by 1.44. The double zeta plus polarization (DZP) basis appends a set of six d-like functions ($\alpha_d = 0.75$) to each carbon atom and a set of p functions ($\alpha_p = 0.75$) to each hydrogen atom.

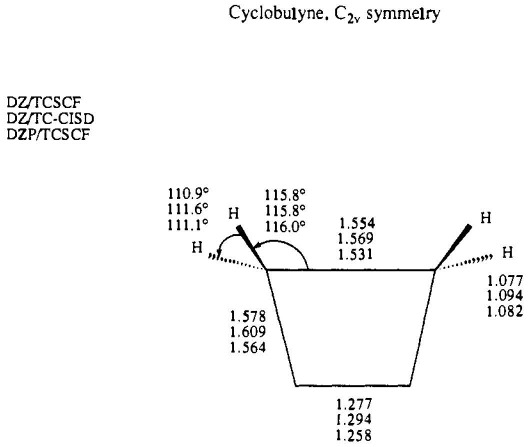


Figure 1. The equilibrium geometry of cyclobutyne predicted at four levels of theory. All bond distances are given in Å.

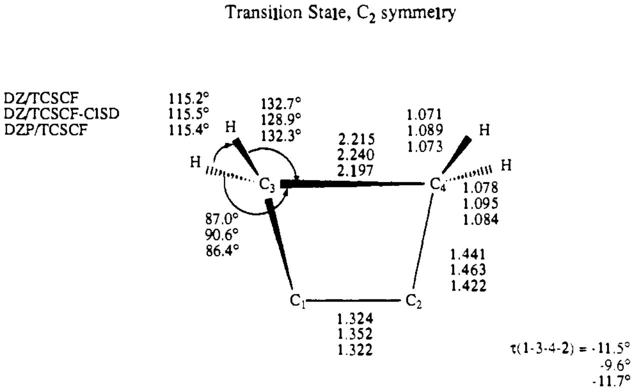


Figure 2. Transition state geometry for the unimolecular isomerization of cyclobutyne to butatriene. All bond distances are in Å.

Stationary-point geometries were optimized at the DZP TCSCF level for cyclobutyne, butatriene, and the transition state connecting them using analytic gradient techniques.[27] Although the butatriene results are not explicitly reported here, they may be obtained from the authors. Harmonic vibrational frequencies were evaluated at the same level of theory using analytic energy second derivative methods.[28] Stationary-point geometries were also located using the DZ TCSCF method and with configuration interaction including all single and double excitations with respect to both reference functions (1) and (2), that is, DZ TC-CISD.[29]

Using the DZP TCSCF stationary-point geometries, a number of higher level theoretical methods were used to predict the barrier height for the cyclobutyne rearrangement. With the DZP basis set, all configuration interaction and coupled cluster wave functions were constructed with the four lowest occupied SCF MO's (the carbon 1s-like orbitals) doubly occupied in all configurations. The single reference CISD[30] and CCSD[31] wave functions with the DZP basis set include 62 981 configurations for cyclobutyne and 123 203 configurations for the transition state. The DZP TC-CISD wave functions for cyclobutyne and the transition state include 124 816 and 244 452 configurations, respectively. Finally the CCSD(T) method,[32,33] which adds all connected triple excitations in a noniterative manner to the CCSD results, was also employed.

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Table I. Singlet Cyclobutyne at the DZP TCSCF Level of Theory[a]

		freq	IR int.	assignment
1	B_1	3338	36	in-phase CH_2 asym stretch (100)
2	A_2	3323	0	out-of-phase CH_2 asym stretch (99)
3	A_1	3264	52	in-phase CH_2 sym stretch (99)
4	B_2	3256	35	out-of-phase CH_2 sym stretch (99)
5	A_1	1910	17	triple-bond stretch (99)
6	A_1	1618	4	in-phase CH_2 scissor (66); in-phase CH_2 wag (−31)
7	B_2	1590	0	out-of-phase CH_2 scissor (68); out-of-phase CH_2 wag (−21)
8	B_2	1303	8	ring def (51); out-of-phase CH_2 wag (−48)
9	A_1	1296	8	in-phase CH_2 wag (75); unique CC stretch (−18)
10	A_2	1290	0	out-of-phase CH_2 twist (94)
11	B_1	1153	1	in-phase CH_2 rock (83)
12	A_1	1096	28	unique CC stretch (39); in-phase CC stretch (38); in-phase CH_2 wag (23)
13	A_2	1043	0	out-of-phase CH_2 rock (82)
14	B_2	957	2	out-of-phase C–C stretch (81)
15	A_1	912	104	in-phase C–C stretch (61); unique CC stretch (37)
16	B_1	850	3	in-phase CH_2 twist (73); in-phase CH_2 rock (27)
17	B_2	608	28	ring def (55); out of phase CC stretch (−34)
18	A_2	275	0	ring puckering (87)
				ZPVE = 41.58

[a] The vibrational assignments are quantified by the potential energy distributions (PED's) given in parentheses. Harmonic vibrational frequencies are given in cm^{-1}, infrared intensities in km mol^{-1}, and zero-point vibrational energy (ZPVE) in kcal mol^{-1}.

The character of the electronic wave functions at the cyclobutyne minimum and the transition state may be measured by the weights of the most important configurations appearing in the TC-CISD wave functions. For cyclobutyne, the coefficients of configurations (1) and (2) given above are 0.860 and −0.358, while that of the third most important configuration has a much smaller absolute value, 0.074. As expected, the transition state is more diradical-like, with the analogous two configurations having coefficients 0.705 and −0.589. Again the third configuration has a much smaller coefficient, of absolute value 0.080. Thus, both cyclobutyne and the transition state for unimolecular rearrangement to butatriene are qualitatively well-described by the TCSCF approximation.

Results and Discussion

A. Stationary-Point Geometries. Structures for cyclobutyne and the purported transition state to butatriene are given in Figures 1 and 2. Generally speaking, the reliable prediction of molecular geometries at moderate levels of theory involves a propitious cancellation of errors.[34] In this light, the DZP TCSCF structures are expected to be the most reliable of those reported here. However, comparison of DZ TCSCF with DZ TC-CISD structures should give us a realistic idea of the qualitative importance of correlation effects.

For cyclobutyne itself, the DZP TCSCF structure is very similar to the DZd TCSCF geometry of Fitzgerald and Saxe.[14] The latter basis set did not include p functions of the hydrogen atoms. The hydrogen p functions increase the C–H bond distances from 1.080 to 1.082 Å, and this is the largest structural difference between the DZd TCSCF and DZP TCSCF methods for cyclobutyne.

Our confidence in the DZP TCSCF structure for the cyclobutyne ground state arises from the expected near cancellation of two effects.[34] First, the use of much larger basis sets, such as TZ2Pf, will decrease the DZP TCSCF bond distances. However, the inclusion of correlation effects (perhaps via some high-level multireference CISD treatment) will increase the bond distances. The latter point is illustrated by comparison of the DZ TCSCF and DZ TC-CISD structures for cyclobutyne. The C≡C distance increases by 0.017 Å, the adjacent C–C by 0.031 Å, and the opposite C–C distance by 0.015 Å in going from TCSCF to TC-CISD.

The transition-state structures (Figure 2) display some interesting changes with respect to cyclobutyne. The formal C≡C triple bond in cyclobutyne is of length 1.258 Å, but increases to 1.322 Å at the transition state. For the product molecule butatriene, this central (a formal C=C double bond) carbon–carbon distance returns to 1.269 Å (all results, DZP TCSCF level of theory). Thus the initial C≡C bond increases and then decreases along the reaction pathway from cyclobutyne to butatriene. The fact that the formal triple bond in cyclobutyne is only 0.011 Å shorter than the formal double bond in butatriene is due to (a) the lengthening of the cyclobutyne triple bond due to its highly strained incorporation in the four-membered ring and (b) the shortening of the double bond from a normal value of ~1.34 Å due to the two adjacent double bonds in butatriene.

The cyclobutyne single bonds adjacent to the triple bond are of length 1.564 Å, a value reduced by 0.142 to 1.422 Å at the transition state. In the product butatriene molecule, these two distances are reduced by a further 0.110 to 1.312 Å. From this vantage point the transition state lies somewhat closer to the product butatriene than to the reactant cyclobutyne molecule. This result is, of course, contrary to Hammond's postulate[35] for an exothermic reaction such as cyclobutyne → butatriene.

The largest difference between cyclobutyne and the transition state occurs for the C–C single bond that is completely broken when butatriene is formed. This distance is 1.531 Å in cyclobutyne (a normal C–C single bond) but 2.197 Å at the transition state. This would also appear to be a finding that runs counter to Hammond's postulate.[35]

Our C_2 symmetry transition state is similar to that for the conrotatory opening of cyclobutene, in that it involves the out-of-plane, unstrained π bond in cyclobutyne. Since the in-plane, strained π bond still has appreciable diradical character in the C_2 transition state, the need for a two-configuration reference wave function for both the reactant and the transition state then becomes easier to understand.

Comparison between the DZ TCSCF and DZ TC-CISD transition-state structures suggests that correlation effects do not qualitatively change the nature of the stationary point. The introduction of TC-CISD modestly increases all transition-state bond distances, the differences ranging from 0.017 Å (the longer C_4–H distance) to 0.028 Å (the carbon–carbon distance that was the triple bond in cyclobutyne).

B. Stationary-Point Vibrational Frequencies. The DZP TCSCF harmonic vibrational frequencies, their assignments, and infrared intensities are reported in Table I. The IR intensities and potential energy distributions (PED's) were not obtained in the previous study[14] of cyclobutyne. Of greatest interest is the triple bond stretch, which fundamental should appear roughly 5% below the 1910 cm^{-1} DZP TCSCF harmonic vibrational frequency, i.e., at ~1810 cm^{-1}. The theoretical IR intensity of this fundamental is medium, namely, 17 km/mol.

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Table II. The Transition State from Singlet Cyclobutyne to Butatriene at the DZP TCSCF Level of Theory[a]

		freq	IR int.	assignment
1	A	3419	4	out-of-phase CH_2 asym stretch (85)
2	B	3419	5	in-phase CH_2 asym stretch (83)
3	B	3284	36	out-of-phase CH_2 sym stretch (80)
4	A	3281	8	in-phase CH_2 sym stretch (84)
5	A	1629	0	in-phase CH_2 scissor (89)
6	B	1613	4	out-of-phase CH_2 scissor (58); ring deformation (−40)
7	A	1338	5	triple-bond stretch (35); in phase CC stretch (21); out-of-phase CH_2 rock (−17); in phase CH_2 scissor (−15)
8	B	1321	7	out-of-phase CH_2 scissor (42); out of phase CH_2 rock (−21); out-of-phase CC stretch (−21)
9	B	1148	5	out-of-phase CH_2 wag (41); in phase CH_2 rock (−40)
10	A	1131	0	out-of-phase CH_2 rock (43); in phase C-C(23); in-phase CH_2 wag (−23)
11	A	1037	0	out-of-phase CH_2 rock (47); in phase CH_2 wag (27)
12	B	1021	13	out-of-phase CH_2 rock (57); ring deformation (−37)
13	A	864	175	C–C triple bond stretch (41); in phase CH_2 wag (−26)
14	B	755	8	in-phase CH_2 twist (56); out of phase CH_2 scissor (−27)
15	B	745	8	out-of-phase CH_2 wag (76); in phase CH_2 twist (21)
16	A	708	24	in-phase CH_2 wag (48); CC stretch (long) (−17)
17	A	408	39	ring pucker (80)
18	A	1140i	114	in-phase CC bond stretch (36); CC triple-bond stretch (−35)

ZPVE = 38.77

[a] The vibrational assignments are quantified by the potential energy distributions (PED's) given in parentheses. Harmonic vibrational frequencies are given in cm^{-1}, infrared intensities in km mol^{-1}, and zero-point vibrational energy (ZPVE) in kcal mol^{-1}.

Three of the four C–H stretching fundamentals are predicted to be of strong IR intensity, specifically 35, 36, and 52 km/mol. The highest predicted IR intensity (104 km/mol) is that for the harmonic vibrational frequency at 912 cm^{-1}, which is primarily (61%) an in-phase C–C stretch. The lowest predicted harmonic vibrational frequency occurs at 275 cm^{-1}, guaranteeing that cyclobutyne is a genuine minimum at this level of theory.

Table II reports the vibrational analysis for the DZP TCSCF transition state. The vibrational frequency along the reaction coordinate is substantial in magnitude (1140i cm^{-1}), indicating a fairly steep barrier at the top. The reaction coordinate is a mixed superposition of internal coordinates, namely, 36% in-phase C—C stretch plus 35% of what was the C≡C triple bond stretch. There is no question that this stationary point is a true transition state on the DZP TCSCF potential energy hypersurface.

From an electronic structure perspective, perhaps the most interesting aspect of the transition state vibrational analysis is the fact that the cyclobutyne C≡C stretch at 1910 cm^{-1} has disappeared. For cyclobutyne this feature falls between the lowest C–H stretch (3256 cm^{-1}) and the in-phase CH_2 scissor (1618 cm^{-1}). For the transition state there is no such feature in this interval of the vibrational spectrum. When we look through the PED's to find pieces of the C≡C stretch, 35% appears at 1338 cm^{-1}, 41% at 864 cm^{-1}, and 35% in the reaction coordinate. Thus the C≡C stretch, so clearly defined for cyclobutyne (99% of the 1910 cm^{-1} PED), has been scattered in three directions at the transition state.

Tables I and II also report the zero-point vibrational energies (ZPVE's), which are evaluated as one-half the sum of the harmonic vibrational frequencies. The cyclobutyne ZPVE (41.58 kcal) is 2.81 kcal greater than that of the transition state (38.77 kcal). In simple transition-state theory, this means that the activation energy E_a should be 2.8 kcal *less than* the classical barrier height.

C. The Classical Barrier Height. Table III gives the total energies and classical barrier heights obtained with the different theoretical methods, all using the double zeta plus polarization (DZP) basis set. Recall that 2.8 kcal/mol (the DZP TCSCF difference in ZPVE's) must be subtracted from each classical barrier in Table III to yield an estimate of the activation energy.

The DZP single configuration SCF and TCSCF classical barriers are 71.6 and 54.5 kcal/mol, respectively. This decrease of 17.1 kcal/mol is all the more noteworthy when one recalls[14] that the second configuration is very important for cyclobutyne itself. The coefficients of configurations (1) and (2) in the DZP TCSCF wave function for the transition state are 0.781 and −0.625, respectively, indicating a remarkable degree of biradical character.

Table III. Total Energies (in hartrees) and Classical Barrier Heights (in kcal mol^{-1}) at the SCF, TCSCF, Single-Reference CISD, Two-Reference CISD, CCSD, and CCSD(T) Levels of Theory with the DZP Basis Set for Cyclobutyne and the Transition State[a]

level of theory	cyclobutyne	transition state	classical barrier
SCF	−153.575 29	−153.461 18	71.6
TCSCF	−153.632 07	−153.545 15	54.5
CISD	−154.063 46	−153.954 61	68.3
CISD+Q	−154.136 66	−154.035 34	63.6
TC-CISD	−154.090 38	−154.009 50	50.8
TC-CISD+Q	−154.153 55	−154.078 83	46.9
CCSD	−154.150 92	−154.065 59	53.5
CCSD(T)	−154.180 88	−154.114 99	41.3

[a] All energies were evaluated at the DZP/TCSCF stationary-point geometries.

The single configuration CISD classical barrier is 68.3 kcal/mol, only 3.3 kcal/mol below the single configuration SCF value. Anticipating (see below) that the true barrier is much lower, it is clear that the single reference CISD method does quite poorly. The situation is reminiscent of the ozone ground state, where CISD starting from a single reference function is equally impotent.[36] Similarly, adding the Davidson correction for unlinked quadruple excitations[37] is still inadequate in lowering the classical barrier to a reasonable value. This result, labeled DZP CISD+Q in Table III, is 63.6 kcal/mol, or 4.7 kcal/mol below the CISD prediction.

The two-reference (using TCSCF molecular orbitals) CISD classical barrier is 50.8 kcal/mol, or 3.7 kcal/mol below the TCSCF result. The fact that the TC-CISD barrier is fully 17.5 kcal/mol below the single reference CISD result shows how poorly the latter method does in describing the critical second configuration (2) at the transition state. The coefficients of the first two configurations in the TC-CISD wave function are 0.726 and −0.569, again indicating the strong diradical character of the transition state. Appending a Davidson correction[38] to the TC-CISD result gives a classical barrier 3.9 kcal/mol lower, namely, 46.9 kcal/mol.

The coupled cluster approach[39,40] provides an independent window into the problem of the barrier to cyclobutyne isomeri-

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zation. The DZP CCSD barrier is 53.5 kcal/mol, or 14.8 kcal/mol below the comparable CISD result. It is abundantly clear that the CCSD method does a much better job of describing the transition state than does CISD. There is an ambiguity, however, concerning whether this substantial lowering of the CISD barrier is due to (a) recovery of that part of the correlation energy that is included in the TCSCF treatment or (b) recovery of that part of the correlation energy due to unlinked clusters, which are treated to infinite order (in the sense of perturbation theory) by CCSD.

Connected triple excitations, included for the first time in the CCSD(T) method,[32,33] significantly lower the barrier to cyclobutyne disappearance. The CCSD(T) classical barrier is 41.3 kcal/mol, or 12.2 kcal/mol below the CCSD result. But is this 41.3-kcal/mol barrier the ultimate result? For a number of classic "multireference problems", including the molecular structure of FOOF,[41] the CCSD(T) gives success where all simpler reference-based methods fail. However, for the vibrational frequencies of ozone, Watts, Stanton, and Bartlett[42] have recently shown that the CCSD(T) predictions deviate significantly from the more complete CCSDT method. Since the cyclobutyne transition state is a more serious two-reference problem than the ozone ground state, there is reason for concern here.

Conclusions

One conclusion from the present work is that it would be very helpful to develop two reference (TCSCF) CCSD and CCSD(T) methods for systems like the cyclobutyne transition state. Taken at face value, our most reliable theoretical prediction here is from the DZP CCSD(T) method, 41.3 kcal/mol for the classical barrier and 38.5 kcal/mol for the activation energy. However, the question remains as to how effectively the CCSD and CCSD(T) methods pick up the profound orbital relaxation effects that are readily incorporated in the simple TCSCF wave functions.

An extreme limit is to assume that the CCSD(T) method is completely ineffective in recovering the TCSCF contribution to the barrier for cyclobutyne isomerization. From the difference between SCF and TCSCF classical barriers, this contribution is (71.6 − 54.5) = 17.1 kcal/mol. From the difference between CISD and TC-CISD barriers, the analogous contribution is (68.3 − 50.8) = 17.5 kcal/mol. Finally, from the Davidson-corrected CISD and TC-CISD results, this contribution is (63.6 − 46.9) = 16.7 kcal/mol. The consistency of these differences shows clearly that neither CISD nor CISD + Q is able to recover the contribution at the transition state due to the second configuration in the TCSCF treatment.

Taking the above extreme limit, TC-CISD+Q minus CISD+Q, we may subtract 16.7 kcal/mol from the CCSD(T) activation energy to yield $E_a \sim 21.8$ kcal/mol. This is, of course, a radical attempt to simulate the result of a TC-CCSD(T) theoretical treatment. We do consider $E_a \sim 21.8$ kcal/mol to represent a conservative lower limit[43] to the activation energy for unimolecular isomerization of cyclobutyne to butatriene.

A more reasonable guess of the cyclobutyne isomerization activation energy might be 25 kcal/mol. Such an activation energy is still sufficiently high that cyclobutyne should be "makeable" under suitable conditions, despite the fact that it lies ~78 kcal/mol above the C_4H_4 global minimum, vinylacetylene. The cyclobutyne situation is far different from that established theoretically for the three-membered ring cyclopropyne, which is no more than a transition state for the degenerate rearrangement of propadienylidene.

Acknowledgment. This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Fundamental Interactions Branch, Grant DE-FG09-87ER13811. We thank Professor Wesley D. Allen and Dr. Michael D. Miller for communication of their unpublished results for cyclopentyne. We thank Professor Gustavo E. Scuseria for his addition of the CCSD(T) method to the system of programs PSI.

Registry No. Cyclobutyne, 1191-94-2; butatriene, 2873-50-9.

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