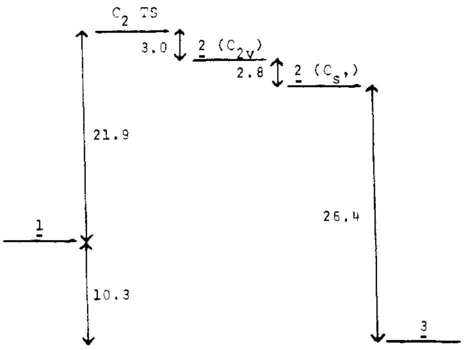

Figure 5. Relative MP2 energies (kcal/mol) of important stationary points on the $C_3H_6^{\bullet+}$ potential surface, after correction for zero-point energy differences. C_2 TS is the transition state for ring opening of **1**, **2** (C_{2v}) is the transition state for exchange of a methyl hydrogen with the hydrogen on the central carbon in **3**, and **2** ($C_{s'}$) is an intermediate, resulting from a 1,2-hydrogen shift in **3**, but separated from **3** by a barrier of <0.2 kcal/mol.

Most recently, Gross and co-workers have studied the gas-phase chemistry of **1**.[2] On the basis of this chemistry, they were able to verify the existence of a structural change in activated **1**; but they showed that the behavior of the species formed was different from that observed from **3**. Consequently, they suggested that activated **1** undergoes ring opening to form trimethylene radical cation (**2**). They were careful to note, however, that the radical cation formed from activated **1** might not be "a unique chemical species existing on a separate minimum on a potential surface" but rather might be a vibrationally excited form of **1** "with an enlarged C-C-C bond angle".[2]

As discussed above, our calculations find no evidence for a chemically significant minimum that corresponds to **2** on the $C_3H_6^{\bullet+}$ potential surface. The only species we have located that are calculated to have sufficient stability to be observed are **1** and **3**.

We calculate that the rearrangement of **1** to **3** is exothermic by 9.8 kcal/mol at the MP2 level, which increases to 10.3 kcal/mol after correction for zero-point energy differences. This is in reasonable agreement with an experimental value of slightly less than 13 kcal/mol.[38]

Because of the exothermicity of the rearrangement of **1** to **3**, as shown in Figure 5, the C_2 transition state for this reaction is predicted to be fully 32.2 kcal/mol above **3** in energy after zero-point energy corrections. Thus, formation of **3** by rearrangement of **1** should lead to radical cations possessing this much excess internal energy. Unless this energy were efficiently quenched, the chemistry of these vibrationally excited ions might differ significantly from that observed from relatively unenergized molecules of **3**.

Acknowledgment. We thank the National Science Foundation for support of this research, including a generous allocation of time at the San Diego Supercomputer Center, where many of these calculations were performed. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support.

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Transition Structures of Pericyclic Reactions. Electron Correlation and Basis Set Effects on the Transition Structure and Activation Energy of the Electrocyclization of Cyclobutene to Butadiene

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Abstract: Cyclobutene (**1**), *s-trans*-butadiene (**2**), and the conrotatory transition structure **3** of the electrocyclic ring opening of **1** have been located at the ab initio RHF and MP2 levels of theory and with semiempirical techniques. Geometries of all three structures are reasonably insensitive to changes in basis set or inclusion of electron correlation. At the RHF level and with MNDO and MINDO/3, activation energies and heats of reaction are overestimated, while at the AM1, MP2/6-31G*, MP2/6-31G*//RHF/3-21G, and MP4SDTQ/6-31G*//MP2/6-31G* levels they are in good agreement with the experimental values.

The electrocyclic ring opening of cyclobutene (**1**) to form butadiene (**2**) is a pericyclic reaction that proceeds by a concerted, conrotatory pathway.[1] Many theoretical calculations of the transition-state geometry and energy of this system have been reported.[2-11] All calculated geometries of cyclobutene (**1**) and the transition state **3** are similar, regardless of the level of theory used. On the other hand, estimates of the activation energy differ rather widely. In order to carry out a general investigation of

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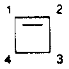
Table I. Geometries of Cyclobutene [Distances, Å; Angles, deg]



level	C_3–C_4	C_2–C_3	C_1–C_2	C_3–H	C_1–H	C_1–C_2–C_3	C_2–C_3–C_4	C_1–C_2–C_3–H
RHF/STO-3G	1.5649	1.5258	1.3142	1.0887	1.0817	94.7	85.3	115.3
RHF/3-21G	1.5934	1.5394	1.3264	1.0815	1.0683	95.0	85.0	114.6
RHF/4-31G	1.5758	1.5246	1.3256	1.0817	1.0691	94.7	85.3	115.3
RHF/6-31G	1.5743	1.5244	1.3305	1.0831	1.0706	94.6	85.4	115.4
RHF/6-31G*	1.5620	1.5150	1.3223	1.0855	1.0754	94.5	85.5	115.5
RHF/6-31G**	1.5620	1.5146	1.3222	1.0860	1.0755	94.5	85.5	115.5
MP2/3-21G	1.6142	1.5529	1.3576	1.0926	1.0820	94.7	85.3	114.4
MP2/6-31G*	1.5638	1.5118	1.3454	1.0950	1.0866	94.1	85.9	115.5
TCSCF/DZ[a]	1.578	1.533	1.362	1.083	1.071	94.0	86.0	
MINDO/3[b]	1.5372	1.5075	1.3489	1.1137	1.0977	93.6	86.4	118.0
MNDO[b]	1.5688	1.5241	1.3547	1.1038	1.0743	94.0	86.0	116.1
AM1[b]	1.5676	1.5219	1.3543	1.1089	1.0799	94.0	86.0	114.8
exptl[c]	1.566	1.517	1.342	1.094	1.083	94.2	85.8	

[a] From ref 9. [b] These structures have been reoptimized for this study with the AMPAC[25] and GAUSSIAN86 series of programs.[27] [c] From ref 28.

pericyclic reaction transition structures, we found it of interest to determine that level of theory at which reliable geometries and reaction energetics can be obtained. Additionally, we sought to make an accurate estimate of the relative error for a particular theoretical level. We report a systematic study of the effect of changes in basis set and the effect of electron correlation on the geometries and energetics of this pericyclic reaction. Geometries of **1–3** as well as activation energies and heats of reaction at many levels of theory, both semiempirical and ab initio, are presented and compared. Conclusions are made as to the levels of computation necessary for prediction of activation energies of related reactions.

Background

The experimental activation energy of the electrocyclic reaction of cyclobutene is 32.9 ± 0.5 kcal/mol.[12] In order to compare these experimental results to calculated energies, we have estimated the vibrationless activation energy, by subtracting the thermal vibration and zero-point energies, calculated at the RHF/3-21G level,[10] from the experimental energies. This gives a corrected activation energy of 34.5 kcal/mol. Similarly, the experimental heat of reaction has also been adjusted from −11.4[13] to −10.9 kcal/mol with the zero-point and thermal energy correction of 0.5 kcal/mol obtained at the same level. In the following discussions, the ab initio activation energies are compared to the vibrationless values of $\Delta E^{\ddagger} = 34.5$ kcal/mol and energy of reaction of $\Delta E_{rxn} = -10.9$ kcal/mol, while semiempirical comparisons are made with values of $\Delta H^{\ddagger} = 32.9$ kcal/mol and $\Delta H_{rxn} = -11.4$ kcal/mol.

In an early study of the interconversion of **1** to **2**, Hsu and his co-workers probed both the conrotatory and disrotatory modes of ring opening with partial optimization of the reactant and transition structures.[2] The calculated activation energy for the conrotatory process is 77.5 kcal/mol at the RHF level and drops off to 47.3 kcal/mol with the inclusion of electron correlation. Both of these are significantly higher than the experimental value of 34.5 kcal/mol.[12] Dewar and Kirchner have used both MINDO/2 and MINDO/3 to study this reaction.[3] Other studies with MINDO/2,[4] MINDO/3,[5] MNDO,[5,6] AM1,[7] MNDOC,[5] MNDOC with CI,[5] and a combination of ab initio single-point calculations on PRDDO-optimized geometries[8] have all been reported. The MINDO/3 $\Delta H^{\ddagger}$ is 48.9 kcal/mol, the MNDO $\Delta H^{\ddagger}$ is 49.9 kcal/mol, and the AM1 $\Delta H^{\ddagger}$ is 35.3 kcal/mol. The other semiempirical calculations provide heats of activation similar to the MNDO value. The activation energy calculated by Halgren and Lipscomb at the STO-3G//PRDDO level is 85 kcal/mol.[8] Prior to our study, the highest level calculations are those of Breulet and Schaefer[9] who located the conrotatory transition structure with the use of an ab initio two-configuration SCF (TCSCF) procedure. They report activation energies that range from 35.8 kcal/mol with the inclusion of electron correlation (TCSCF+CI/DZ) to 42.9 kcal/mol with no CI but with the addition of polarization functions (TCSCF/DZ+P). Rondan and Houk[10,11] reported an activation energy of 41.6 kcal/mol at the RHF level with the 3-21G basis set. These authors also reported an activation energy of 36.6 kcal/mol calculated at the MP2/6-31G*//RHF/3-21G level.

It is clear from these studies that the calculated activation energy varies widely, covering a range of 36–88 kcal/mol. Structures differ little, regardless of the level of theory used. In a related study, Jensen and Houk have shown that the 3-21G geometries for the hydrogen 1,5-shift in (*Z*)-1,3-pentadiene are quite similar to structures obtained at the MP2/6-31G** level.[14] However, accurate activation parameters can be obtained only at very high levels of theory. The present work represents a parallel study for an electrocyclic reaction in which the reaction is not thermoneutral.

Results and Discussion

The geometries of **1–3** have been fully optimized with the STO-3G,[15] 3-21G,[16] 4-31G,[17] 6-31G,[18] 6-31G*,[19] and 6-31G**[19] basis sets at the restricted Hartree–Fock level and with the 3-21G and 6-31G* basis sets at the MP2 level of theory.[20] The geometries of **1** have been optimized in C_{2v} symmetry, while those of **2** and **3** have been optimized in C_2 and C_{2h} symmetry, respectively. The time required to find these geometries was dramatically reduced by using the 3-21G Hessian, calculated using analytical second derivatives, as the initial Hessian for subsequent optimizations. All geometries have been fully optimized with gradient techniques by Pople's GAUSSIAN82 series of programs.[21] Single-point calculations on **1** and **3** have been carried out at the MP2, MP3, MP4(DQ), MP4(SDQ), and MP4(SDTQ)/6-31G* levels on the MP2/6-31G*-optimized geometetries with the frozen-core approximation. Single-point calculations on the RHF/6-31G*

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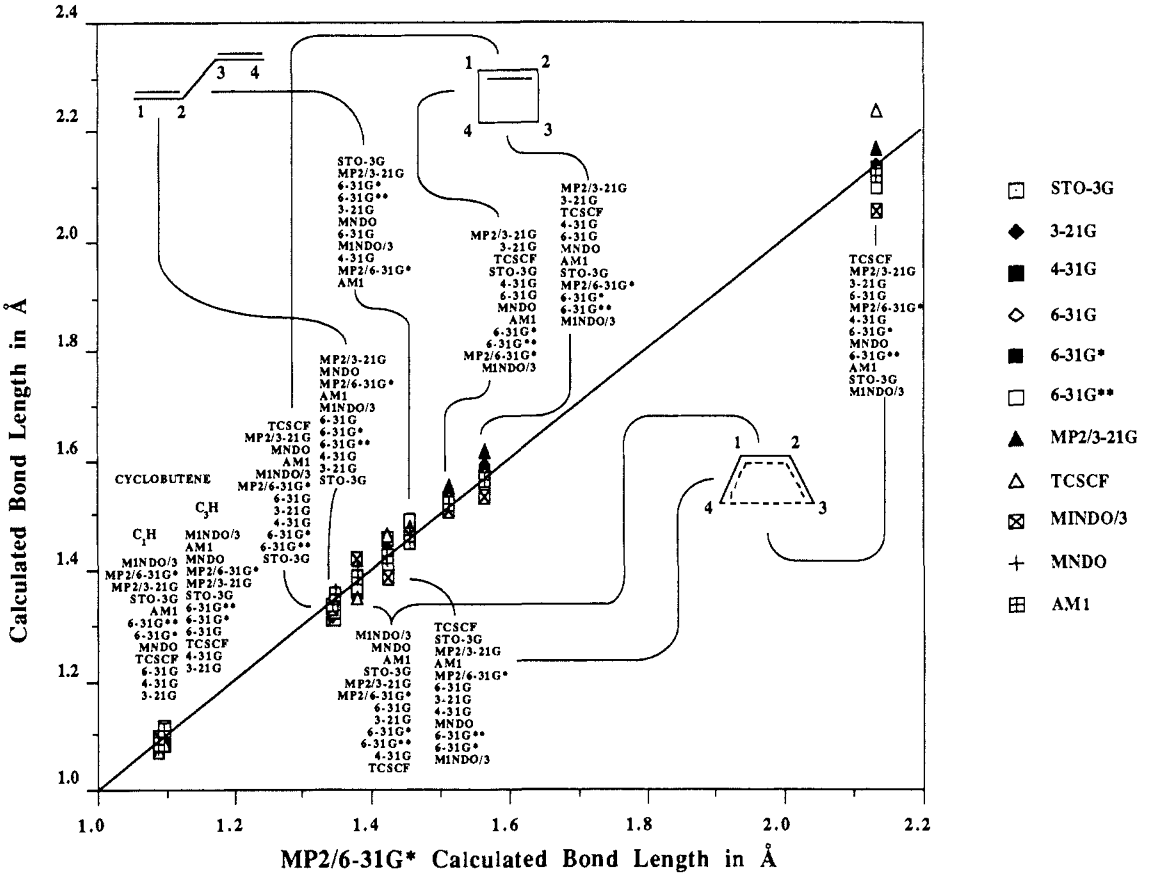
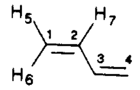


Figure 1. Bond lengths of **1**–**3** calculated at various levels versus MP2/6-31G* values.

Table II. Geometries of *s-trans*-1,3-Butadiene [Distances, Å; Angles, deg]



level	C_1–C_2	C_2–C_3	C_1–H_5	C_1–H_6	C_2–H_7	C_1–C_2–C_3	C_2–C_1–H_5	C_2–C_1–H_6	C_1–C_2–H_7
RHF/STO-3G	1.3134	1.4892	1.0812	1.0817	1.0844	124.1	122.0	122.0	120.2
RHF/3-21G	1.3204	1.4671	1.0724	1.0744	1.0757	124.0	121.5	121.8	119.9
RHF/4-31G	1.3219	1.4618	1.0714	1.0736	1.0756	124.3	121.9	121.9	119.6
RHF/6-31G	1.3275	1.4645	1.0726	1.0748	1.0767	124.3	121.8	121.8	119.5
RHF/6-31G*	1.3227	1.4676	1.0748	1.0766	1.0783	124.1	121.7	121.7	119.6
RHF/6-31G**	1.3221	1.4673	1.0750	1.0770	1.0786	124.1	121.6	121.7	119.6
MP2/3-21G	1.3479	1.4747	1.0852	1.0876	1.0907	123.8	121.9	121.6	119.7
MP2/6-31G*	1.3425	1.4563	1.0844	1.0863	1.0897	123.7	121.8	121.4	119.6
MINDO/3[b]	1.3295	1.4644	1.0992	1.1001	1.126	131.1	124.3	125.3	115.8
MNDO[b]	1.3444	1.4655	1.0893	1.0886	1.0963	125.7	122.2	124.4	118.7
AM1[b]	1.3348	1.4512	1.0974	1.0978	1.1042	123.4	122.1	122.8	120.7
exptl[c]	1.341	1.463	1.090	1.090	1.090	123.3	120.0	122.4	123.0

[a] From ref 9. [b] These structures have been reoptimized for this study with the AMPAC[25] and GAUSSIAN86 series of programs.[27] [c] Reference 29.

geometries of **1** and **2** are available at the MP4(SDTQ)/6-31G* level.[22] Stationary points found at the RHF level with the 3-21G basis set have been characterized by calculation of the force constants with analytical second-derivative techniques, indicating that **1** and **2** are indeed energy minima and that **3** is a transition structure. For a more complete comparison, geometries of **1**–**3** have been relocated with the MINDO/3,[23] MNDO,[24] and AM1[7] semiempirical methods by the AMPAC package.[25] They were also checked with these same techniques now available in the GAUSSIAN 86 package of programs.[26] These results, of course, are no different from those reported previously.[3-7]

As can be seen from Tables I–III the geometries of **1**–**3** are similar regardless of the level of theory employed. This is shown graphically in Figure 1, where the calculated bond lengths of all three structures are plotted versus the MP2/6-31G* calculated values.[27] We have chosen not to include the calculated C–H bond lengths of **2** or **3** for reasons of clarity. Energies are presented in Table IV.

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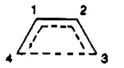
Table III. Geometries of Conrotatory Transition Structures [Distances, Å; Angles, deg]



level	C_3–C_4	C_2–C_3	C_1–C_2	C_2–C_3–C_4	C_1–C_2–C_3	C_3–C_2–H	C_1–C_2–C_3–C_4	C_4–C_1–C_2–C_3
RHF/STO-3G	2.1022	1.4555	1.3880	74.8	102.7	127.0	−15.6	22.7
RHF/3-21G	2.1384	1.4212	1.3692	73.4	104.4	126.2	−14.5	21.9
RHF/4-31G	2.1300	1.4187	1.3654	73.5	104.4	126.1	−14.1	21.2
RHF/6-31G	2.1333	1.4230	1.3694	73.6	104.3	126.1	−14.1	21.2
RHF/6-31G*	2.1298	1.4125	1.3680	73.5	104.3	126.0	−14.2	21.3
RHF/6-31G**	2.1280	1.4125	1.3680	73.5	104.2	126.1	−14.5	21.9
MP2/3-21G	2.1680	1.4477	1.3878	73.5	104.3	126.0	−14.2	21.3
MP2/6-31G*	2.1332	1.4233	1.3794	73.7	104.0	126.1	−14.8	22.2
TCSCF/DZ[a]	2.238	1.462	1.351	70.8	108.1		−16.4	
MINDO/3[b]	2.0591	1.3884	1.4181	75.8	102.1	126.8	−14.6	21.1
MNDO[b]	2.1290	1.4173	1.4022	74.3	103.5	127.1	−14.4	21.7
AM1[b]	2.1196	1.4278	1.3889	74.5	103.8	126.6	−12.3	18.7

[a] From ref 9. [b] These structures have been reoptimized for this study with the AMPAC[25] and GAUSSIAN 86 series of programs.[27]

Table IV. Energies of Optimization and Single-Point Energies at Selected Levels [ab Initio Energies, Hartrees; Semiempirical and Relative Energies, kcal/mol]

computational level	E(cyclobutene)	E(TS)	E(butadiene)	$\Delta E^{\ddagger}$	E_{rxn}
experimental				34.5[a] ± 0.5	−10.9[b] ± 0.4
	Full Optimizations				
RHF/STO-3G//RHF/STO-3G	−153.040 29	−152.913 36	−153.020 36	79.7	−12.5
RHF/3-21G//RHF/3-21G	−154.030 72	−153.964 35	−154.059 46	41.6	−18.0
RHF/4-31G//RHF/4-31G	−154.667 94	−154.601 16	−154.699 96	41.9	−20.1
RHF/6-31G//RHF/6-31G	−154.832 30	−154.766 14	−154.864 57	41.9	−20.3
RHF/6-31G*//RHF/6-31G*	−154.899 62	−154.824 83	−154.916 54	46.9	−10.6
RHF/6-31G**//RHF/6-31G**	−154.900 98	−154.835 70	−154.930 32	46.5	−18.4
MP2/3-21G//MP2/3-21G	−154.393 57	−154.341 52	−154.419 10	32.7	−22.0
MP2/6-31G*//MP2/6-31G*	−155.429 33	−155.369 50	−155.441 71	37.6	−7.8
TCSCF/DZ//TCSCF/DZ[c]				39.4	
MINDO/3	33.0	82.0	31.9	48.9[d]	−1.1[d]
MNDO	31.0	80.8	29.0	49.9[d]	−2.0[d]
AM1	45.8	81.1	29.9	35.3[d]	−15.9[d]
	Single-Point Energies on Lower Level Geometries				
TCSCF+CISD/DZ//TCSCF/DZ[c]				35.8	
TCSCF/DZ+P//TCSCF/DZ[c]				42.9	
TCSCF+CISD/DZ+P//TCSCF/DZ[c]				42.4	
RHF/6-31G*//RHF/3-21G	−154.898 17	−154.824 60	−154.919 61	46.2	−13.5
MP2/6-31G*//RHF/3-21G	−155.407 75[e]	−155.349 43[e]	−155.420 69[e]	36.6	−8.1
MP2/3-21G//MP2/6-31G*	−154.338 40[e]	−154.333 79[e]		31.4	
MP2/6-31G*//MP2-6-31G*	−155.409 94[e]	−155.350 55[e]		37.3	
MP2/6-31G**//MP2/6-31G*	−155.458 11[e]	−155.399 45[e]		36.8	
MP3/6-31G*//MP2/6-31G*	−155.441 28[e]	−155.377 24[e]		40.2	
MP4(DQ)/6-31G*//MP2-6-31G*	−155.443 84[e]	−155.379 23[e]		40.5	
MP4(SDQ)/6-31G*//MP2/6-31G*	−155.448 42[e]	−155.385 00[e]		39.8	
MP4(SDTQ)/6-31G*//MP2/6-31G*	−155.468 04[e]	−155.409 79[e]		36.6	

[a] From ref 12. Corrected for the unscaled 3-21G ZPE correction of 1.6 kcal/mol. [b] From ref 13. Corrected for the unscaled 3-21G ZPE correction of 0.5 kcal/mol. [c] From ref 9. [d] These values should be compared to a $\Delta H^{\ddagger}$ of 32.9 kcal/mol and ΔH_{rxn} of −11.4 kcal/mol. [e] Energy calculated with the frozen-core approximation.

That the cyclobutene geometries are similar can be seen from the geometries presented in Table I. The maximum deviation of the geometries is less than 0.08 Å for bond lengths, less than 1.5° for bond angles, and about 3.6° for the torsional angles. The C_1–C_2 bond length is shortest with the STO-3G basis set (1.314 Å) and longest at the TCSCF level (1.362 Å). The C_2–C_3 and C_3–C_4 bond lengths are longest for the MP2/3-21G geometry (1.553 and 1.358 Å, respectively) and shortest for the MINDO/3 geometry (1.508 and 1.349 Å, respectively). The three C–C bond lengths as calculated with the 3-21G basis set are all longer than those calculated with the STO-3G basis set. Use of the 3-21G basis set gives a C_3–C_4 bond length that is longer than the experimental value[28] (1.593 vs 1.566 Å), while the C_1–C_2 bond length of 1.326 Å is in better agreement with the experimental value of 1.342 Å than is the STO-3G value of 1.314 Å. Increasing the size of the basis set causes a shortening of the C_3–C_4 bond but has little effect on the other bond lengths. Addition of polarization functions causes a further shortening of the C_2–C_3 and C_3–C_4 bonds, while inclusion of correlation causes a lengthening of the C_1–C_2 bond. The geometries calculated at either the semiempirical AM1 or the correlated ab initio MP2/6-31G* levels are in excellent agreement with the experimental geometry.[28] The MP2/3-21G geometries appear to deviate most from experimental geometries.

Table II shows that the geometries of *s-trans*-butadiene are also similar by the different techniques. The C–C bond lengths deviate by less than 0.04 Å, while the angles deviate less than 4° in all cases except one (the MINDO/3 geometry). The STO-3G geometry has double-bond lengths of 1.313 Å, the same as the length of an isolated double bond and shorter than the experimental value of 1.341 Å.[29] The C_2–C_3 bond length of 1.489 Å is longer than the experimental value[29] of 1.463 Å. The 3-21G geometry has a C_2–C_3 bond length of 1.467 Å, which is close to the experimental value. However, the double bonds (1.320 Å) are still somewhat

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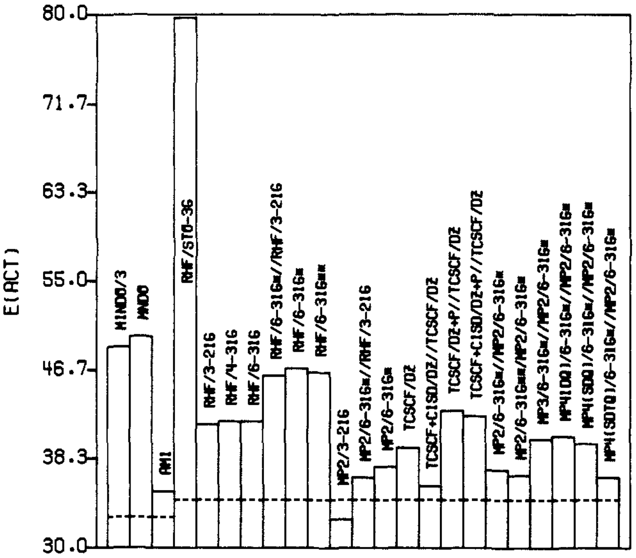

Figure 2. Comparison of calculated activation energies at several levels of theory. The dashed line indicates the value of the activation energy for comparison purposes. The semiempirical values are compared to $\Delta H^{\ddagger}$ = 32.9 kcal/mol. The ab initio values are compared to $\Delta E^{\ddagger}$ = 34.5 kcal/mol.

short, relative to the experimental value. Inclusion of electron correlation with the 6-31G* basis set gives a C_1–C_2 bond length of 1.343 Å and a C_2–C_3 bond length of 1.456 Å. Both of these are in good agreement with the experimental values. The MINDO/3 geometry estimates the C–C–C angle at 131.1°, which is much larger than the experimental value of 123.3°. Other than this, all the geometries for *s-trans* butadiene are in good agreement with experimental values.

Like **1** and **2**, little variation is seen in the transition-structure geometries obtained by different methods (see Table III). For convenience, the geometries are numbered following the cyclobutene numbering scheme. The largest deviation in the bond lengths is seen in the elongated C_3–C_4 bond where the geometries differ by about 0.2 Å. The TCSCF geometry is "latest" (most bond breaking) at 2.238 Å, while the MINDO/3 geometry is "earlier" at 2.059 Å. The C_3–C_4 bonds of the remaining calculations are all within 0.07 Å of each other. The C_1–C_2 and C_2–C_3 bond lengths show smaller variability, differing by less than 0.08 Å in all the structures. It is interesting to note that, with the TCSCF procedure, the C_1–C_2 bond length is shorter in the transition structure (1.351 Å) than in the ground state (1.362 Å), but this is due to the fact that the ground-state double-bond length is much too long. It is also interesting that only in the MINDO/3 geometry is the C_2–C_3 bond length shorter than the C_1–C_2 bond length. This indicates a reaction progress greater than would be inferred from the C_3–C_4 bond length, which is the shortest with MINDO/3. In all cases, the nonplanarity of the carbon skeleton is pronounced. The C_1–C_2–C_3–C_4 dihedral angle ranges from 12° to 16°, and the C_4–C_1–C_2–C_3 dihedral angle varies from 19° to 23°.

Table IV shows the activation energies and energies of reaction for the full optimizations and selected single-point calculations at several levels of theory. A graph of the activation energies is given in Figure 2. The activation energy at the STO-3G level is 79.7 kcal/mol, which is 45.2 kcal/mol above the experimental value of 34.5 kcal/mol.[12] The energy of reaction is −12.5 kcal/mol, which is in fair agreement with the experimental heat of reaction of −10.9 kcal/mol.[13] The 3-21G activation energy is 41.6 kcal/mol, and the energy of reaction is −18.0 kcal/mol. The enormous lowering of the activation energy by introducing a split-valence basis presumably reflects a much better representation of the long partial bond in the transition structure. The activation energy rises slightly upon increasing the basis set size and peaks at 46.9 kcal/mol with the 6-31G* basis set. We estimate that the activation energy of the Hartree–Fock limit will be about 47 kcal/mol.

The energy of reaction decreases to −20.3 kcal/mol with the 6-31G basis set, rises to −10.6 kcal/mol with inclusion of polarization functions on the carbon atoms, and drops significantly to −18.4 kcal/mol with inclusion of polarization functions on the hydrogens. No estimate of the energy of reaction at the Hartree–Fock limit is possible from these data. Intermediate levels of theory accidentally give values near the experimental value.

The MP2/3-21G activation energy is nearly correct, indicating that incomplete recovery of correlation energy with the 3-21G basis set cancels out the inadequacies of such a small basis set. The energy of reaction of −22.0 kcal/mol at this level is too negative. The MP2/6-31G* activation energy of 37.6 kcal/mol is 3 kcal/mol higher than the experimental value, as is the energy of reaction of −7.8 kcal/mol. The AM1 $\Delta H^{\ddagger}$ of 35.3 kcal/mol and ΔH_{rxn} of −15.9 kcal/mol are close to the experimental values of 32.9 and −11.4 kcal/mol, respectively. The best estimate of the activation energy with ab initio techniques is the 36.6 kcal/mol value estimated at either the MP4(SDTQ)/6-31G*//MP2/6-31G* level or the MP2/6-31G*//RHF/3-21G level. The inclusion of the triples in the MP4 calculations has a large effect and lowers the calculated activated energy by 3.2 kcal/mol! The energy of reaction at the MP4(SDTQ)/6-31G*//RHF/6-31G* level of −9.4 kcal/mol[19] is unlikely to differ much with the use of the MP2/6-31G*-optimized structures.

Table IV shows that the ability to reproduce the activation energy of this reaction is not related to the ability of reproducing the ΔH_{rxn}. This can be seen with the STO-3G values of −12.5 kcal/mol for the energy of reaction and 79.7 kcal/mol for the activation energy. The energy of reaction is nearly correct, but the activation energy is 150% too high. Likewise, the calculated activation energy at the MP2/3-21G level is quite reasonable, but the energy of reaction is incorrect by more than 10 kcal/mol.

Conclusion

Reliable geometries for the cyclobutene to butadiene electrocyclic ring opening are found with several basis sets at the RHF level of theory, with semiempirical methods, and with the inclusion of electron correlation with relatively large basis sets. The MINDO/3, MNDO, and STO-3G activation energies are too high. The ab initio activation energies are generally too high and approach the Hartree–Fock limit of about 47 kcal/mol. Inclusion of electron correlation corrects the activation energy to near the experimental value. The MP4(SDTQ)/6-31G*//MP2/6-31G* activation energy of 36.6 kcal/mol is in good agreement with experiment ($\Delta E^{\ddagger}$ = 34.5 kcal/mol). The AM1 $\Delta H^{\ddagger}$ of 35.3 kcal/mol is within 2.5 kcal/mol of the heat of activation of 32.9 kcal/mol. Single-point calculations at the MP2/6-31G* level on the 3-21G-optimized geometries also give energetics that are in good agreement with experiment.

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