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Theoretical Studies of Diels−Alder Reactions of Acetylenic Compounds

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Activation barriers in the Diels−Alder reactions of acetylenic systems have been calculated and discussed using the *ab initio* G2MS and IMOMO(G2MS:MP2) methods. Activation energies for the reaction of acetylene + butadiene and acetylene + cyclopentadiene are predicted to be 25.8 and 22.0 kcal/mol, respectively. Although the acetylene + butadiene transition state is more favorable in the interaction energy than the ethylene + butadiene transition state by about 3 kcal/mol due to secondary π orbital interactions, the stiffer acetylene + butadiene system requires about 5 kcal/mol more reactant distortion energy. Thus, overall, the acetylene + butadiene barrier is about 2 kcal/mol higher and the predicted rate is slower than ethylene + butadiene, consistent with experiment. For the reaction of acetylenedicarboxylic acid and cyclopentadiene, which possesses a very asymmetric transition state, the best IMOMO(G2MS:MP2) method predicts an activation barrier of 9.2 kcal/mol and reveals significant electronic effects of substituents outside the model system of acetylene + butadiene.

Introduction

The calculation of transition states involved in the Diels−Alder reaction has been difficult for theorists because high levels of electron correlation are necessary to accurately predict activation energies. Considerable effort has been expended and the results at various levels of theory have not been without controversy. In addition, arguments over the concerted or stepwise nature of [4+2] cycloadditions[1] have been protracted and a plethora of *ab initio*[2−4] and semiempirical[1,5] studies have been reported. Diels−Alder reactions of dienes with alkenes are important since the reaction allows for regiospecific, stereospecific, and enantiospecific synthesis of substituted cyclohexene ring systems. It is desirable to be able to predict theoretically reaction rates for these specific aspects of the chemistry.

Recently, high-level *ab initio* QCISD(T)[6] and G2-type[7] methods have been reported to accurately predict the activation energy for the reaction of ethylene + butadiene. With an increase in the number of heavy atoms, the QCISD(T) and CCSD(T) methods scale by approximately N^6 or N^7 and therefore it is not practical to use these methods for systems with more than 8 or 9 non-H atoms with even a moderate basis set. Thus, to accurately predict activation energies for Diels−Alder reactions with more than 10 non-H atoms in the case where high levels of electron correlation and basis set are required, a different strategy must be employed.

In the past, two approaches have generally been used to deal with large systems. Either high-level *ab initio* predictions are made on models of the real system or lower level *ab initio* predictions are made on the full system. Both methods have their limitations, as the former does not include electronic and steric effects of the substituents and the latter does not treat the correlation-dependent reaction center at a high enough level of theory. Ideally, a combination of the two methods is needed where high levels of electron correlation are used for the reaction center and substituent effects are included at a lower level of theory.

Recently, a multilayered approach has been introduced which divides a molecule into various segments and treats each layer by a different computational method both for energies and gradients. The ONIOM,[8] IMOMO,[9] and IMOMM[10] procedures are different integrated schemes which have been elaborated and tested. Using IMOMO as an example, the total integrated energy is a sum of the high-level model energy + the difference between the low-level real and low-level model energies. The IMOMO method has been used to accurately and relatively inexpensively predict activation energies for the Diels−Alder [4 + 2] cycloaddition reaction of dienes with olefins. For example, the reaction of maleic anhydride with 2-*tert*-

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butyl-1,3-butadiene (containing 15 non-H atoms) was examined where the six non-H atoms (and associated H atoms) at the reaction center were considered as the model system.[7] The high level extrapolation procedure, the G2MS method,[7] as will be explained later, was specifically developed to handle systems of 6−8 heavy atoms; thus it is ideally suited to use in conjunction with IMOMO, since the model system in this integrated method would seldom be larger than this. Previous studies[7,11] have indicated that IMOMO(G2MS:MP2), adopting the G2MS method for the high level and MP2 for the low level, gives good agreement with benchmark predictions and experimental data. In these studies, the hybrid B3LYP method also appears to predict activation barriers well using moderate basis sets, 6-31G or 6-31G*.

The focus of this paper is the examination of Diels−Alder reactions of alkynes, and surprisingly few theoretical studies have been made on the reaction of acetylene with butadiene[12] or other dienes.[13] One of these studies of acetylene−butadiene by one of us[12b] reported transition state barriers ranging from 14.6 kcal/mol at the MP2/6-31G(d)//HF/6-31G(d) to 28.6 kcal/mol at the MP4SDQ/4-31G//HF/4-31G level of theory. It is now well-known that activation barriers from HF energies are too high and from MP2 calculations are usually too low. Thus even though the MP4SDQ results are based on a smaller basis set, these results are likely to be more accurate. In addition, the reaction of acetylenes with dienes are known to be slower than for the analogous reactions of ethylenes.[14] For the reaction of ethylene + butadiene, the barrier for that reaction has been measured[6,15] and falls within the range 25−27.5 kcal/mol. It would be expected that the barrier for acetylene + butadiene, though to our knowledge no measured values exist, will be higher than the barrier for the addition reaction with ethylene.

In the present paper, we have examined the parent reaction acetylene + butadiene using the G2MS method. An activation barrier for the reaction of acetylene + cyclopentadiene of 24.2 kcal/mol has been reported[16] and we now report calculations for this reaction. In addition, the Diels−Alder addition of acetylenedicarboxylic acid with cyclopentadiene is studied using the IMOMO(G2MS:MP2) approach as a model for the reaction of the methyl diester dimethyl acetylenedicarboxylate (DMAD) with cyclopentadiene, where an activation barrier of 13.8 kcal/mol[17] has been reported. DMAD is commonly used in Diels−Alder reactions because the electron-withdrawing ester groups increase the rate of the reaction and furthermore the product contains a new alkene which is activated for further elaboration by sequential Diels−Alder reaction.[18]

Computational Methods

Calculations were made with the Gaussian92[19] and Gaussian94[20] programs. Geometries were optimized at the B3LYP level[21] with the 6-31G or 6-31G(d) basis set,[22] and all stationary points were confirmed to be minima or transition states by vibrational frequency analysis. Zero-point corrections (ZPCs) at this level are included in any relative energies. Single-point energy predictions were made at a variety of levels including the G2MS level,[7] where

$$\mathrm{G2MS} = \mathrm{CCSD(T)/6\text{-}31G(d)} + \mathrm{MP2/6\text{-}311{+}G(2df,2p)} - \mathrm{MP2/6\text{-}31G(d)} + \mathrm{HLC}$$

and at the IMOMO(G2MS:MP2) level, where

$$E[\mathrm{IMOMO(G2MS{:}MP2)}] = E(\mathrm{G2MS,model}) + E(\mathrm{MP2,real}) - \mathrm{E}(\mathrm{MP2,model})$$

HLC in G2MS is an empirical higher order correction which is −3.8 kcal/mol for each doubly occupied molecular orbital. In all reactions studied in this paper, the number of doubly occupied orbitals is conserved; thus this empirical factor is not required. In the IMOMO method, the model system is acetylene + butadiene. The difference E(MP2,real) − E(MP2,model) is referred to as $\Delta E_{\mathrm{MP2}}(\mathrm{real}\leftarrow\mathrm{model})$ in the following discussions.

Results and discussion

A. Diels−Alder Addition of Acetylene + Butadiene and a Comparison with Ethylene + Butadiene. For the Diels−Alder reaction of acetylene + butadiene, the geometries of the reactants, transition state, and product optimized at the B3LYP/6-31G(d) level are depicted in Figure 1. Both *cisoid*- and *transoid*-butadiene were examined, but activation energies are quoted from the *transoid*-species. The vibrational analysis confirmed the following symmetries: *transoid*-butadiene, C_{2h}; *cisoid*-butadiene, C_2; acetylene, $D_{\infty h}$; transition state, C_s; product; D_{2h}. From *cisoid*-butadiene, the initial carbon−carbon bond lengths of 1.339 and 1.470 Å change to 1.370 and 1.393 Å in the transition state and to 1.507 and 1.335 Å in the 1,4-cyclohexadiene product. For acetylene, the initial triple bond length of 1.205 Å increases to 1.228 Å in the transition state and forms a double bond in the product with a bond length of 1.335 Å. The most interesting aspect is the newly formed bonds between the alkyne and diene. The infinitely separated reactants approach and both terminal bond distances in the transition state are 2.198 Å and are reduced to 1.507 Å in the product. The geometries of this transition state at three different levels of theory are shown in Figure 1. There is little difference between them. At the transition states

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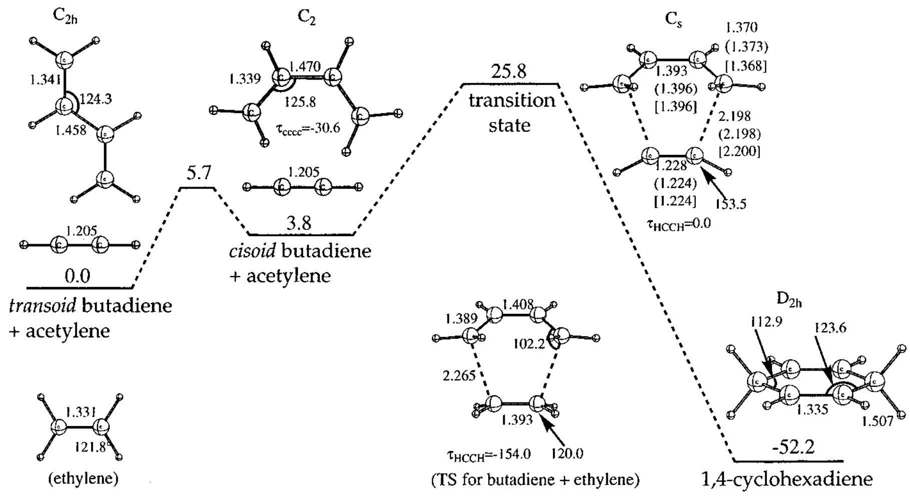

Figure 1. The potential energy profile and significant geometrical features of the reactants, transition state, and products in the Diels−Alder addition of acetylene to butadiene. Geometries are in Å and deg at the B3LYP/6-31G(d) level, as well as the HF/6-31G(d)[12b] (in parentheses) and HF/3−21G[12a] (in bracket) levels. Transition state geometry for ethylene + butadiene[7] is also shown for comparison. Relative single point energies in kcal/mol are listed at the highest G2MS level.

Table 1. Calculated Activation Barrier Heights, E_a, and Reaction Enthalpies, ΔH (in kcal/mol, including ZPC), for the Reactions of Acetylene + *transoid*-Butadiene and Acetylene + Cyclopentadiene, and Activation Barriers for Ethylene + *transoid*-Butadiene and Ethylene + Cyclopentadiene[a]

	butadiene			cyclopentadiene		
	acetylene		ethylene:[b]	acetylene		ethylene[b]
level	E_a	ΔH	E_a	E_a	ΔH	E_a
HF/6-31G(d)	47.1	−54.4	46.3	45.0	−20.9	41.4
MP2/6-31G(d)	22.7	−57.8	20.2	18.3	-31.1	14.1
MP2/6-311+G(2df,2p)	18.2	−54.2	16.5	15.0	−29.0	10.3
B3LYP/6-31G(d)	25.0	−56.7	22.7	25.7	−20.4	21.4
MP3/6-31G(d)	31.9	−59.2	29.6	29.0	−29.7	−
MP4(SDQ)/6-31G(d)	34.1	−57.0	31.7	29.8	−28.2	−
CCSD(T)/6-31G(d)	30.2	−55.8	27.6	25.3	−28.6	22.3
G2MS	25.8	−52.2	23.9	22.0	−26.5	18.5
Experiment	−	−	25.1−27.5	−	−24.2	23.7

[a] Geometries were optimized and ZPCs were calculated at the B3LYP/6-31G(d) level. [b]Reference 7.

for both acetylene and ethylene (also shown in Figure 1), the structures of both diene and dienophiles are rather close to those of the reactants and the forming C···C distances quite long, indicating that both transition states can be classified to be very early. Between acetylene and ethylene, the forming C···C bond distances for acetylene (2.198 Å) are shorter than for ethylene (2.265 Å),[7] showing that the acetylene transition state is later.

At the highest G2MS level of theory using the B3LYP/6-31G(d) geometries, the activation energy for the reaction of acetylene + *transoid*-butadiene is calculated to be 25.8 kcal/mol, and the reaction is predicted to be exothermic by 52.2 kcal/mol, as shown Table 1. These are to be compared with the corresponding energies of 23.9 and 36.7 kcal/mol for ethylene + *transoid*-butadiene.[7] The calculated energies (with ZPC) of reaction for both systems are in good agreement with the experimental enthalpies of reaction, −55.0 and −39.9 kcal/mol. The predicted increase in the activation energy (1.9 kcal/mol) on going from ethylene to acetylene is consistent with the observed decrease in reactivity, though no experimental value for the acetylene reaction has been reported. It is very interesting to notice that the acetylene reaction is more exothermic but has a higher barrier than the ethylene reaction, in disagreement with the Hammond postulate. As was discussed above, the transition states for both reactions are very early, and the barrier height is obviously not decided by the exothermicity but rather by the energetics in the early stage of the reaction.

Table 2. Distortion and Interaction Energies (in kcal/mol) for the Diels−Alder Additions of Ethylene + *cisoid*-Butadiene and Acetylene + *cisoid*-Butadiene at the B3LYP/6-31G(d) Level without ZPC[a]

	ethylene + butadiene		acetylene + butadiene	
distorted reactants	+7.9	+16.1	+11.8	+17.3
distortion energy	+24.0		+29.1	
interaction energy	−6.9		−9.8	
activation energy (E_a)[b]	+17.1		+19.3	

[a] The zero-point correction raises the activation energy by 2.2 kcal/mol in the ethylene + butadiene reaction and 2.3 kcal/mol in the acetylene + butadiene reaction. [b]Note the activation energy (E_a) here is from the *cisoid* conformation (the *transoid*-species is 3.4 kcal/mol more stable than *cisoid*).

The activation barrier in a Diels−Alder reaction can be regarded as the net effect of the distortion energy, the energy required to distort the geometries of reactants to those of the transition state, and the interaction energy between the distorted fragments.[23] Table 2 shows these energies for both ethylene and acetylene + *cisoid*-butadiene at the B3LYP/6-31G(d) level without ZPC. There is a larger distortion energy, 29.1 kcal/mol, in the acetylene + butadiene reaction than 24.0 kcal/mol in the ethylene + butadiene addition. Of the 5.1 kcal/mol difference in favor of the ethylene reaction, 1.2 kcal/mol comes from the distortion of the common *cisoid*-butadiene and 3.9 kcal/mol comes from the difference in distortion energies between acetylene and ethylene. Acetylene is stiffer than ethylene and requires more energy to distort from its equilibrium geometry to that at the transition state. If the C···C distance dependence of the diene-dienophile interaction is assumed to be the same, the larger distortion energy for acetylene should make the transition state later and the activation barrier higher.

The more favorable interaction energy of −2.9 kcal/mol in the acetylene reaction (−9.8 kcal/mol) compared to the ethylene reaction (−6.9 kcal/mol) is in part due to

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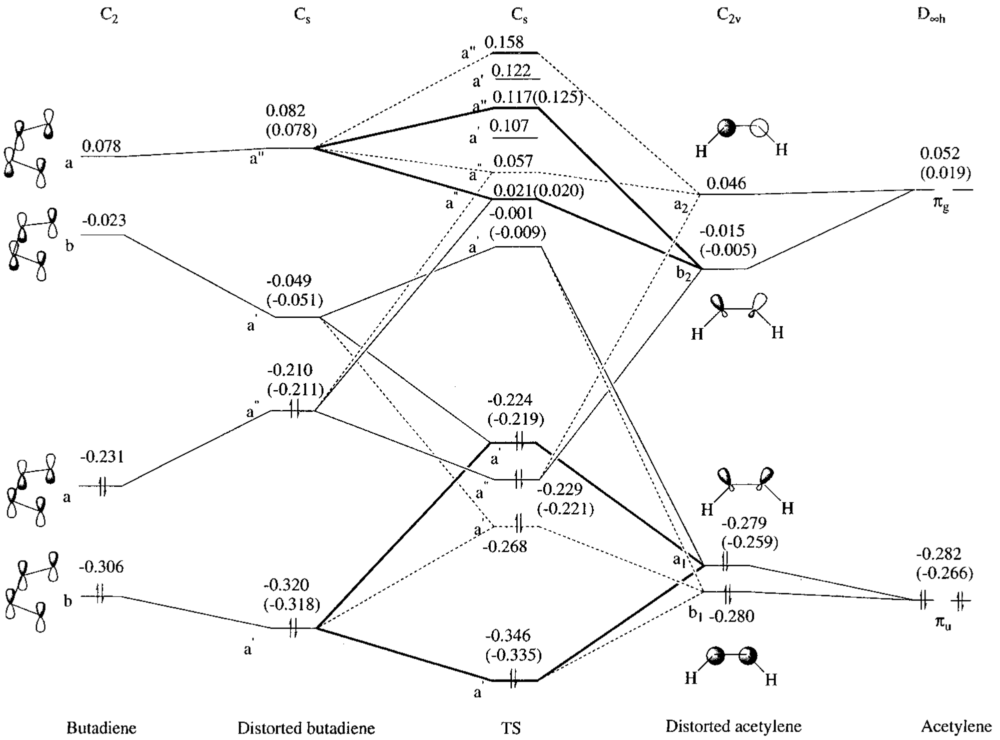

Figure 2. A correlation diagram for the most significant frontier orbitals in the Diels–Alder addition of acetylene + *cisoid*-butadiene. The orbital energies (in au) are for calculations at the B3LYP/6-31G(d) level. The geometry and energy of the distorted butadiene and acetylene are at their transition state geometries but separated infinitely. The bold lines indicate occupied–occupied and unoccupied–unoccupied interactions, the normal lines occupied–unoccupied interactions, and the dotted lines secondary orbital interactions. The corresponding orbital energies for the ethylene + *cisoid*-butadiene reaction are shown in parentheses.

the shorter forming C···C bond and in part due to the result of secondary orbital overlaps associated with the π-orbital of acetylene orthogonal to the forming σ-framework. The correlation diagram for acetylene + butadiene for the more important interacting frontier orbitals is shown in Figure 2. Of the major frontier orbital interactions, the occupied orbital–occupied orbital interaction between the fully symmetric b-orbital of *cisoid*-butadiene and one of the π_u-orbitals of acetylene (a_1) leads to the a′-orbital with energies of −0.346 au, which is 0.011 au lower than that for ethylene + butadiene. The 'nonbonding' orthogonal π_u-orbital (b_1) increases in energy from −0.280 au in the distorted fragment to −0.268 au in the transition state. Both of these changes can be considered as the result of the secondary interaction between the orthogonal π_u-orbital (b_1) of acetylene and the b-orbital of butadiene.

B. Addition of Acetylene to Cyclopentadiene. The additions of ethylene and acetylene to cyclopentadiene have both been studied experimentally and the activation barriers for the former reaction are reported to be 23.7 ± 0.2[24] or 24.5 kcal/mol[25] and for the latter, 24.2 kcal/mol.[24] The similarity of E_a for these two reactions is surprising since it is generally thought that alkynes react more slowly in Diels–Alder reactions than analogous alkenes.[14] The activation barrier has been calculated at different levels of theory, as shown in Table 1; the highest level method, G2MS, predicts an activation barrier for ethylene + cyclopentadiene of 18.5 kcal/mol.[7]

For the acetylene + cyclopentadiene reaction, the important geometrical features of the transition state optimized at the B3LYP/6-31G level are shown in Figure 3B and should be compared with those for acetylene + butadiene in Figure 1. The transition state for acetylene + cyclopentadiene is also symmetrical (C_s). The carbon–carbon bond length in the acetylene moiety in the transition state is only slightly longer (1.247 Å) than for free acetylene (1.205 Å) and the forming terminal bond is long (2.255 Å), consistent with an early transition state, relative to the acetylene + butadiene case.

The energetics at various levels of theory for both the activation barrier and the reaction enthalpy for the reaction of acetylene + cyclopentadiene are shown in Table 1. The B3LYP/6-31G(d) level (including ZPC) predicts an activation energy of 25.7 kcal/mol and a reaction enthalpy of −20.4 kcal/mol. This activation energy is 1.5 kcal/mol larger than the experimental value. The HF/6-31G(d) method overestimates the activation barrier, and larger basis sets at the HF level have been reported to increase the barrier.[7] MP2/6-31(d) underestimates the barrier (18.3 kcal/mol), while it is further lowered at the MP2/6-311+G(2df,2p) level (15.0 kcal/mol). The higher order perturbation method significantly increases the activation energy to 29.0 kcal/mol at the MP3/6-31G(d) level and appears to be converging to the MP4(SDQ)/6-31G(d) value of 29.8 kcal/mol. The effect of the triples in the coupled cluster expansion is significant as the activation energy at the CCSD level of 30.0 kcal/mol is lowered to the CCSD(T) value of 25.3 kcal/mol. The basis set correction in the highest G2MS scheme leads to a lowering of this activation energy by 3.3 kcal/mol to a predicted activation energy of 22.0 kcal/

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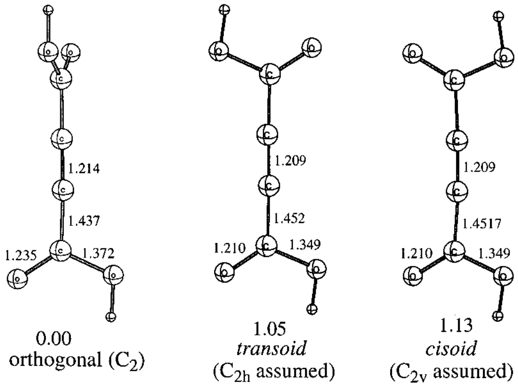
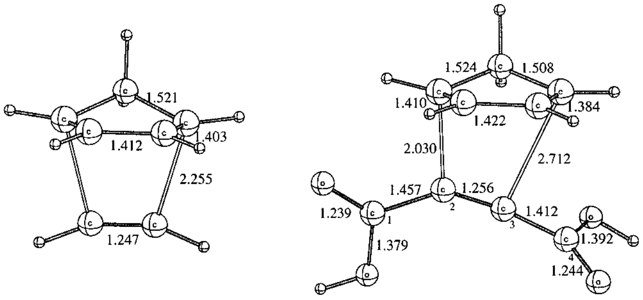


(A) three structures of acetylenedicarboxylic acid



(B) transition state for acetylene + cyclopentadiene

(C) transition state for acetylenedicarboxylic acid + cyclopentadiene

Figure 3. Important bond distances (in Å) of (A) the three structures of acetylenedicarboxylic acid, (B) the transition states for the Diels−Alder addition of acetylene + cyclopentadiene, and (C) that of acetylenedicarboxylic acid + cyclopentadiene, optimized at the B3LYP/6-31G level. The relative energies of the three structures of acetylenedicarboxylic acid are given in kcal/mol at the B3LYP/6-31G(d) + ZPC(B3LYP/6-31G) level.

mol, which is 2.2 kcal/mol lower than experiment. The enthalpy of the reaction is calculated to be −26.5 kcal/mol at the G2MS level. The exothermicity of this reaction is considerably less than that for acetylene + butadiene and reflects the higher energy of norbornadiene relative to reactants compared with cyclohexadiene relative to butadiene + acetylene.

The reaction of acetylene + butadiene has a calculated activation barrier of 25.8 kcal/mol (G2MS), which is 3.8 kcal/mol larger than that predicted for the reaction of acetylene with cyclopentadiene (22.0 kcal/mol) (see Table 1). This parallels the theoretical predictions for the reaction of ethylene and butadiene and cyclopentadiene where the values have a similar difference (5.4 kcal/mol at G2MS[7]). In general, these results would be expected, given that reactions beginning from *transoid*-butadiene would be slower than that from cyclopentadiene where the ring is locked into the more reactive *cisoid*-conformation. However, experiments for the cycloaddition of ethylene to butadiene and cyclopentadiene indicate a decrease by *ca.* 2 kcal/mol (25.1 kcal/mol for the former and 23.7 kcal/mol for the latter), and we suggest that new and more accurate experimental determination of activation energies for many of these Diels−Alder reactions be made.

C. Addition of Acetylenedicarboxylic Acid to Cyclopentadiene and the Application of the IMOMO(G2MS:MP2) Method. The addition of dimethyl acetylenedicarboxylate (DMAD) to cyclopentadiene has been studied experimentally and the activation energy reported to be 13.8 kcal/mol,[17] which is significantly lower than for the reaction of acetylene with cyclopentadiene, where the experimentally determined activation barrier is 24.2 kcal/mol and the theoretically predicted value at the G2MS level is 22.0 kcal/mol. The lower activation energy is a measure of the electron-withdrawing effects of the carboxylate groups of DMAD.

Modeling the reaction of DMAD encounters some convergence difficulty because of nearly free rotation of the methyl groups which produces a very flat potential energy surface. To avoid this difficulty, we have adopted the diacid analog, acetylenedicarboxylic acid, in the present study. We have examined three different conformers of acetylenedicarboxylic acid, namely the *cisoid*, the *transoid*, and the orthogonal. The acid groups on each end of the triple bond can both conjugate to one of the π-systems in *cisoid*- and *transoid*-conformers, or each to a different π-system in the orthogonal conformer. The three conformers have been examined in detail. The C_{2v} (*cisoid*) and C_{2h}-constrained (*transoid*) optimized structures at the B3LYP/6-31G level, shown in Figure 3A, both have one small imaginary frequency ($<100i$ cm^{-1}) and are transition states for rotation around the acetylenic bond. Slight distortions of the geometry to break the symmetry lead to the orthogonal optimized isomer in C_2 symmetry, which is probably the global minimum, about 1 kcal/mol lower than the *cisoid*- and *transoid*-structures.

The transition state geometry for the reaction of acetylenedicarboxylic acid with cyclopentadiene optimized at the B3LYP/6-31G level is depicted in Figure 3C. The transition state is extremely asymmetric with the two forming σ-bonds of 2.030 and 2.712 Å. At the transition state, the π-orbital of one of the carboxyl groups (containing C^4 in Figure 3C) overlaps with the forming σ-bonds, while the π-orbital of the other carbonyl (containing C^1) is perpendicular and retains overlap with the second, nonreacting π-bond of the acetylene moiety. The forming σ-bond on C^2, away from the interacting C^4O_2H group, is much shorter (2.030 Å) than that (2.712 Å) on C^3, adjacent to the interacting C^4O_2H group. The length of the C^3−C^4O_2H bond that is conjugating with the forming σ-bond is short, 1.412 Å, while the length of the C^2−C^1O_2H bond that is conjugating with the nonreacting acetylene π-orbital is long, 1.457 Å. These structural features of the present asymmetric transition state are consistent with those of the asymmetric transition state found for the Diels−Alder reaction between acrolein ($OC^1HC^2H{=}C^3H_2$) and 2-methyl-1,3-butadiene.[8] Here the forming σ-bonds overlaps with the π-orbital of the carbonyl group, and the forming σ-bond on C^3 (away from the carbonyl) is much shorter (2.049 Å) than that (2.587 Å) on C^2 (adjacent to the carbonyl). This asymmetry of the transition is obviously the electronic effect of the electron-withdrawing carbonyl substituent, which makes the dienophile carbon atom further away from the substituent more positively charged and more reactive.

The reaction system of cyclopentadiene with acetylenedicarboxylic acid, consisting of 13 non-H atoms, is computationally too large for direct application of any G2-type procedure for extrapolation of correlation and basis set effects. As discussed previously,[7] the IMOMO scheme using a G2-type method for the reaction center and a lower level MO method for the substituent effects is the method of choice that should allow for a reasonable prediction of the barrier height for the reaction. This *three-dimensional* IMOMO-G2-type approach[7] allows for

Table 3. Predicted Activation Energies (in kcal/mol) at Various IMOMO and Standard MO Levels[a] for the Diels−Alder Addition of Acetylenedicarboxylic Acid with Cyclopentadiene, at the B3LYP/6-31G-Optimized Geometries and Including ZPC(B3LYP/6-31G)

	lower level		
higher level	HF	MP2	B3LYP
B3LYP			14.1
HF	32.7	−	
MP2	8.2	7.7	
MP3	17.5	17.0	
MP4	18.7	18.2	
CCSD(T)	13.9	13.4	
G2MS	9.7	9.2	
$\mathrm{MP4_{model}}$	29.5		
$\mathrm{CCSD(T)_{model}}$	24.7		
$\mathrm{G2MS_{model}}$	20.5		
DHF(real←model)-10.8			
DMP2(real←model)-11.3			
Experiment[b]	13.8		

[a] Values where lower level and higher level are same are standard MO calculations, and the rest are IMOMO(High level: Lower level) calculations. All IMOMO energies can be calculated from the energy components (in italic) in the second half of the table. For instance, E_a(IMOMO(G2MS:MP2)) = 9.2 = $E_a(\mathrm{G2MS_{model}})$ + E_a(DMP2(real←model)) = 20.5 + (−11.3). [b] [b] For DMAD + cyclopentadiene. Reference 17.

extrapolation for correlation and basis set effects of the model (reaction center) at the G2MS level, as well as for steric and electronic effects in the real←model step in the IMOMO procedure. In the present study, the model was chosen to be acetylene + butadiene, the minimum reaction center for a Diels−Alder reaction consisting of six non-H atoms. The most reliable energy prediction is to be made from the IMOMO scheme which takes the G2MS energy [CCSD(T)/6-31G(d) + MP2/6-311+G(2df,2p) − MP2/6-31G(d) + HLC] for the model and the MP2/6−31G(d) energy for the real system.

For this reaction, the activation energy at the pure B3LYP MO level is predicted to be 14.1 kcal/mol, in excellent agreement with experiment. As before, pure HF and MP2 methods overestimate and underestimate, respectively, the activation barrier, as shown in Table 3. Various IMOMO schemes have also been used for evaluation of the activation energy, as shown in Table 3. As seen in the second half of Table 3, while the barrier of the model system at high levels of theory is high, 20 kcal/mol or more, the correction (Δ*E*(real←model)) to the barrier due to the steric and electronic effects of the substituents in the real acetylenedicarboxylic acid system has large negative values, −11.3 and −10.8 kcal/mol for MP2 and HF, respectively, and lower the overall barrier. This is mainly due to the electronic effect of the two CO_2H groups, as was discussed above in connection to the transition state structure. A correlation of an asymmetric transition state with a reduction in the activation barrier has been noticed before.[3]

The prediction at our highest level IMOMO(G2MS:MP2) leads to an activation barrier of 9.2 kcal/mol for acetylenedicarboxylic acid + cyclopentadiene, which is somewhat lower than the reported experimental value of 13.8 kcal/mol for DMAD + cyclopentadiene.[17] The origin of the larger-than-expected error is not known but may be attributable to the fact that the treatment at a level higher than MP2 is needed to properly take into account the electronic effects of the two carbonyl groups. It has been pointed out by a referee that this error might be due to steric effects of the methyl groups which are absent in our calculation. It has been predicted before that each of these groups has an approximate 2 kcal/mol steric effect.[12a]

Conclusions

The G2MS and IMOMO(G2MS:MP2) methods have been used to predict activation barriers for various Diels−Alder reactions. The standard reaction of acetylene + butadiene led to a predicted activation barrier of 25.8 kcal/mol at the best G2MS level. This value is 1.9 kcal/mol higher than the analogous ethylene + butadiene reaction at the same level and supports the slower rate of reaction for acetylene + butadiene.[14] The correlation diagram for the reaction of butadiene with acetylene in comparison with that for ethylene shows the importance of secondary orbital interactions in the reaction of acetylenic dienophiles. The energy analysis indicates that, while the interaction energy at the transition state is about 3 kcal/mol more favorable for acetylene + butadiene, as suggested by the secondary orbital interaction, the distortion of the reactants (in particular, of the stiffer acetylene in comparison to ethylene) is about 5 kcal/mol less favorable, making the acetylene + butadiene reaction slower than the ethylene + butadiene reaction. For the reaction of acetylene with cyclopentadiene, the G2MS predicted activation energy of 22.0 kcal/mol agrees well with the experimental value of 24.2 kcal/mol. The IMOMO(G2MS:MP2) method applied to the reaction of acetylenedicarboxylic acid with cyclopentadiene (containing 13 non-H atoms) with a very asymmetric transition state predicted a much lower activation barrier of 9.2 kcal/mol, in comparison with those with symmetric transition states.

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Supporting Information Available: The Cartesian coordinates and total energies of the transition state and product structures are available (3 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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