DFT Study of the Diels–Alder reactions between ethylene with buta-1,3-diene and cyclopentadiene

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A set of DFT methods (Xa, HFB, S-VWN, B-LYP, B-HandH and Becke3-LYP) has been used for the calculation of the transition states and energy barriers of the Diels–Alder reaction of ethylene with buta-1,3-diene and cyclopentadiene. The pure DFT methods overestimate the bond lengths, while the hybrid methods give values much closer to those obtained by conventional *ab initio* methods. The ratio of the σ-forming bonds to the π-breaking bonds is in excellent correlation to the predicted electronic energy barriers for these reactions. The local spin density approximation (S-VWN) fails completely giving a negative value for the classical energy barrier height for the addition of ethylene to buta-1,3-diene. On the other hand, the vibrational adiabatic barrier heights predicted by B-LYP/6-31G** and the hybrid Becke3-LYP/6-31G** theoretical models are in excellent agreement with available experimental data for both reactions.

The development of new approximations to density functional theory (DFT) over the past decade has provoked a wide interest in its application to a variety of areas in physics and chemistry. Besides structural determinations, it has been applied to the assignment of IR, UV, NMR and EPR spectra, and to other problems usually convered by *ab initio* methods.[1,2] Reaction barriers obtained by post-HF methods have proved to be reliable but are limited by the high computational cost which for MP2 calculations for example, scale to ON^4, for full MP3 O^2N^4 (O-occupied orbitals, N-basis functions). This is one of the major attractions of DFT that at a computational price of HF calculations, results of post-HF quality are obtained.[3]

It is of interest to study the prototypical Diels–Alder reaction of ethylene with buta-1,3-diene (BD) and cyclopentadiene (CPD) by DFT. The potential energy surface for these reactions has been studied in detail by means of various levels of quantum-mechanical methods[4] and experimental data for the activation energies is available.[5] After a decade of controversy involving a heated debate on the usefulness and quality of semiempirical *vs. ab initio* methods, the concerted mechanism of this reaction has been generally accepted. It has been shown, however, that the energy barriers calculated using Hartree–Fock theory are grossly overestimated, while at the second order Møller–Plesset correlation energy correction level they are underestimated. Consequently, the very expensive MP3 or even better MP4 or QCID levels are necessary even for this reaction. In view of the above, an evaluation of the performance of DFT methods is predicting the reaction barriers would be beneficial for the investigation of other all-carbon reactions.

Computational methods

All calculations were performed with the GAUSSIAN 92[6] implementation of density functional theory with the 6-31G** basis set. The optimizations were performed without geometric restrictions using the Flatter–Powell[7] method and the default GAUSSIAN convergence criteria. Standard search for transition-state structure was performed with the RHF method and an RHF/6-31G** optimized structure was used for all other optimizations. Frequency calculations were performed for all structures in order to determine the nature of the stationary points and by employing the harmonic approximations for the zero-point energies to calculate the vibrational adiabatic reaction barriers. All transition-state structures have one and only one imaginary frequency with motion along the reaction coordinate.

In the study of the reaction of ethylene with butadiene and cyclopentadiene a family of standard GAUSSIAN 92 DFT methods, including localized, non-localized or gradient-corrected, were used: Slater's exchange functional (Xa),[8] Becke's 1988 exchange functional (HFB),[9] Slater exchange with Vosko, Wilk and Nusair correlational functional (S-VWN), also known as local spin density approximation (LSDA),[10] and Becke's exchange with Lee, Yang and Parr correlation functional (B-LYP).[11] In addition to the pure methods, two hybrid methods were also employed: B-HandH,† and Becke3-LYP.‡

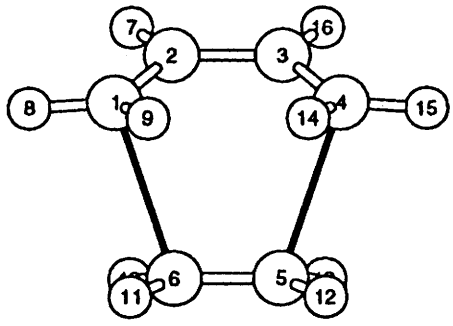
Results and discussion

Some of the geometric features (bond lengths l_{rs}, angles a_{rst} and dihedral angles d_{rstu}) of the transition states obtained by the various DFT methods for the addition of ethylene to buta-1,3-diene and the ethylene addition to cyclopentadiene are presented in Table 1. Values reported in the literature for the same transition states obtained by *ab initio* methods are also given in the same table.

Inspection of the transition-state geometries given in Tables 1 and 2 show the inherent differences of the various DFT approaches. The earliest transition state for both reactions, as indicated by the largest values for the bonds forming between atoms l_{16}, and l_{45} (see structure in Table 2) is predicted by the S-VWN method. For the addition of ethylene to buta-1,3-diene the two newly forming bonds are 2.400 Å and for the addition to cyclopentadiene they are 2.367 Å. However, if the progress of the reaction is viewed not from the point of view of the bonds being formed but from the breaking of the π bonds (the diene or ethylene), a somewhat earlier transition state is predicted by Becke's 'half and half' method. This is a consequence of the fact that the latter is a hybrid method where the contribution of the Coulomb self-interaction of the electrons is lower than in the pure methods and all bonds are shorter.[12] The ratio of the new σ-forming bonds (l_{16}) to the π-breaking bonds (l_{12}) would be a better indication and is presented in Table 3. The earlier transition states have higher bond ratios (l_{16}/l_{12}) while the later

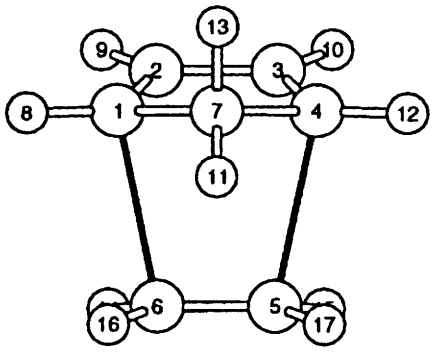
† A hybrid method proposed by Becke and includes 50% HF exchange and 50% Slater exchange (half and half), with no correlation functional.
‡ Becke's 3 parameter functional with non-local correlation provided by Lee, Yang and Parr expression.

Table 1 Structural parameters at the 6-31G** level for the transition state of the addition of ethylene to buta-1,3-diene



	l_{12}/Å	l_{16}/Å	l_{23}/Å	l_{56}/Å	a_{216}/°	a_{123}/°	d_{6123}/°
Xa	1.369	2.373	1.415	1.368	101.2	122.4	59.2
HFB	1.423	2.273	1.425	1.428	103.1	122.3	56.5
S-VWN	1.363	2.400	1.415	1.361	100.8	122.5	59.7
B-LYP	1.395	2.286	1.414	1.398	102.5	122.2	57.6
B-HandH	1.359	2.267	1.399	1.360	101.7	121.5	59.1
Becke3-LYP	1.383	2.268	1.406	1.386	102.3	122.0	57.9
HF/3-21G[4a]	1.370	2.210	1.395	1.376	102	121	
HF/6-31G*[4b]	1.377	2.201	1.393	1.383		121.5	
CASSSCF/3-21G[4c]	1.392	2.217	1.397	1.400			
CASSSCF/6-31G*[4c]	1.398	2.223	1.397	1.404			

Table 2 Structural parameters at the 6-31G** level for the transition state of the addition of ethylene to cyclopentadiene



	l_{12}/Å	l_{16}/Å	l_{23}/Å	l_{56}/Å	l_{17}/Å	a_{216}/°	a_{123}/°	a_{217}/°	d_{6123}/°	d_{7123}/°
Xa	1.386	2.342	1.413	1.369	1.495	98.2	109.0	107.3	74.5	15.0
HFB	1.440	2.240	1.424	1.431	1.550	101.2	108.9	105.9	73.1	21.0
S-VWN	1.379	2.367	1.412	1.361	1.489	97.8	109.0	107.5	74.7	13.7
B-LYP	1.412	2.260	1.413	1.400	1.523	100.3	109.0	106.4	73.4	19.1
B-HandH	1.374	2.251	1.396	1.360	1.486	99.0	108.9	107.1	77.0	16.8
Becke3-LYP	1.398	2.244	1.405	1.387	1.510	100.1	108.9	106.6	73.5	18.8
HF/31G*[4d]	1.389	2.193	1.392	1.382	1.506					

Table 3 Ratios[a] of the new σ-forming bonds (l_{16}) to the π-breaking bonds (l_{12}) in the transition states for the buta-1,3-diene to ethylene and cycloadditions of cyclopentadiene

	*r*1	*r*2	*r*3	*r*4	*r*5	*r*6
BD	1.733	1.597	1.761	1.639	1.669	1.640
CPD	1.689	1.555	1.716	1.600	1.638	1.605

[a] *r*1, *E*(XALPHA/6-31G**); *r*2, *E*(HFB/6-31G**); *r*3, *E*(SVWN/6-31G**); *r*4, *E*(BLYP/6-31G**); *r*5, *E*(BHandH/6-31G**); *r*6, *E*(BECKE3LYP/6-31G**).

transition states have lower ratios. It is apparent that S-VWN and not BHandH predicts the earliest transition states; the latest transition state is predicted by HFB for both reactions. The reactivity should follow a similar pattern, *i.e.*, the higher barrier would be expected to be obtained by the HFB while the lower by the S-VWN DFT method.

As already mentioned and reported in the literature, a general feature of the bond lengths by DFT methods compared with *ab initio* methods is the fact that they are overestimated. This is best illustrated by the 'most stable' bond length in the transition states, the single bond between the two double bonds in the diene, l_{23}. The HF and post HF methods are in excellent agreement predicting a value of 1.393–7 Å for the buta-1,3-diene and a very close 1.392 Å for the cyclopentadiene reaction even though the calculations were not performed with the same basis set (Tables 1 and 2). The bond length obtained by the various DFT methods are spread over a wider range with the same basis set, from 1.399–1.425 Å for the first reaction and 1.396–1.424 Å

Table 4 Total energies[a] of the species involved in the reaction

	*E*1/Hartree	*E*2/Hartree	*E*3/Hartree	*E*4/Hartree	*E*5/Hartree	*E*6/Hartree
ethylene	−77.362 57	−78.046 25	−78.130 46	−78.543 39	−77.931 26	−78.593 80
	0.049 13	*0.048 43*	*0.049 73*	*0.049 70*	*0.052 48*	*0.051 11*
s-*cis*-BD	−153.651 67	−154.948 88	−155.085 87	−155.907 64	−154.728 28	−155.996 08
	0.082 07	*0.080 63*	*0.082 85*	*0.082 78*	*0.087 75*	*0.085 23*
s-*trans*-BD	−153.657 46	−154.954 71	−155.091 61	−155.913 63	−154.733 20	−156.001 64
	0.082 02	*0.080 70*	*0.083 00*	*0.082 80*	*0.087 70*	*0.085 24*
CP	−191.274 51	−192.830 50	−192.992 75	*−194.006 60*	−192.576 1	−194.110 6
	0.089 39	*0.087 37*	*0.090 48*	*0.089 85*	*0.095 63*	*0.092 63*
TS BD	−231.012 52	−232.950 97	−233.219 33	−234.424 10	−232.644 54	−234.559 69
	0.134 39	*0.132 98*	*0.135 73*	*0.136 37*	*0.144 01*	*0.140 31*
TS CP	−268.633 37	−270.829 44	−271.124 14	−272.519 99	−270.493 35	−272.672 45
	0.141 78	*0.139 47*	*0.143 31*	*0.143 25*	*0.151 95*	*0.147 59*

[a] *E*1, *E*(XALPHA/6-31G**); *E*2, *E*(HFB/6-31G**); *E*3, *E*(SVWN/6-31G**); *E*4, *E*(BLYP/6-31G**); *E*5, *E*(BHandH/6-31G**); *E*6, *E*(BECKE3LYP/6-31G**). Zero-point vibrational energy corrections given in italics.

Table 5 Classical and vibrational adiabatic barrier heights[a] (kcal mol^{-1}) for the Diels–Alder reaction of ethylene

	E_a1	E_a2	E_a3	E_a4	E_a5	E_a6	E_{exp}
s-*cis*-BD	1.08	27.71	−1.88	16.90	9.41	18.94	
	3.08	***30.17***	***0.09***	***19.34***	***11.78***	***21.44***	
s-*trans*-BD	4.71	31.37	1.72	20.66	12.50	22.43	
	6.75	***33.79***	***3.60***	***23.09***	***14.90***	***24.92***	25.1[15]
CPD	2.33	29.69	−0.58	18.83	8.79	20.05	
	4.37	***31.99***	***1.36***	***21.15***	***11.20***	***22.46***	23.7[4c]
Δ*E*(BD–CPD)	2.38	1.80	2.24	1.94	3.70	2.46	3.8

E_a1, *E*(XALPHA/6-31G**); E_a2, *E*(HFB/6-31G**); E_a3, *E*(SVWN/6-31G**); E_a4, *E*(BLYP/6-31G**); E_a5, *E*(BHandH/6-31G**); E_a6, *E*(BECKE3LYP/6-31G**). [a] Given in bold italic.

Table 6 Classical barrier heights[a] (kcal mol^{-1}) for the Diels–Alder reaction of ethylene with buta-1,3-diene

	E_a7[4a]	E_a8[4a]	E_a9[4a]	E_a10[4a]	E_a11[4a]	E_a12[4b]	E_a13[4b]
s-*trans*-BD	35.9	45.04	16.58	26.86	28.57	29.4	25.5

[a] E_a7, *E*(HF/3-21G); E_a8, *E*(HF/6-31G*); E_a9, *E*(MP2/6-31G*//HF/6-31G*); E_a10, *E*(MP3/6-31G*//HF/6-31G*); E_a11, *E*(MP4SDQ/6-31G*//HF/6-31G*); E_a12, *E*(UQCISD(T)/6-31G*//CASSCF/6-31G*); E_a13, *E*(RQCISD(T)/6-31G*//CASSCF/6-31G*).

Table 7 Classical barrier heights (kcal mol^{-1}) for the Diels–Alder reaction of ethylene with cyclopentadiene

	E_a14	E_a15	E_a16	E_a17	E_a18
CPD	30.06	39.74	39.66	10.57	22.34

E_a14, *E*(HF/3-21G); E_a15, *E*(HF/6-31G//HF/3-21G); E_a16, *E*(HF/6-31G*); E_a17, *E*(MP2/6-31G*//HF/6-31G*); E_a18, *E*(MP3/6-31G*//HF/6-31G*).

for the second reaction. They are longer by up to 0.028 Å, and the hybrid methods, as already discussed, give much better results than the 'pure' methods.

The total energies and the corresponding zero-point vibrational corrections of the species involved in the reaction, ethylene, s-*cis*-buta-1,3-diene, s-*trans*-buta-1,3-diene, cyclopentadiene, as well as the two transition states (TS) are given in Table 4.

The calculated classical and vibrational adiabatic barrier heights as well as the experimental values for the reaction of ethylene with buta-1,3-diene and ethylene and cyclopentadiene are given in Table 5. For comparison the energy barriers calculated by various non-correlated and correlated *ab initio* theoretical models are presented in Tables 6 and 7.

As presented in Table 5, the different theoretical models give a wide range of electronic activation energies for these reactions. The worst performance is by the S-VWN method which for the classical barrier height for the ethylene cycloaddition to cyclopentadiene predicts the transition state to be relatively more stable than the reactants. Only the introduction of the zero-point correction raises the vibrational adiabatic height to a positive value but is still over 22 kcal mol^{-1} below the experimental value. This is not unexpected in view of previous results obtained with this method for energy barriers.

The predictions of the two methods without correlation functionals, Xa and HFB, are the reverse of each other, the former greatly underestimates the barriers giving values close to S-VWN. The latter overestimates them, although not as much as Hartree–Fock theory where values well over 10 kcal mol^{-1} are obtained for Diels–Alder reactions especially when larger than minimal basis sets are used (Tables 6 and 7).

B-LYP and the hybrid Becke3-LYP give the best results, to within a few kcal mol^{-1} of the experimental values. However, in view of the fact that the experimental error for the addition of ethylene to buta-1,3-diene is rather high, (±2 kcal mol^{-1}) and when scaled to 0 K as are the calculated results,§ the predicted energy barriers are in excellent agreement. B-LYP has been previously reported to give acceptable results in predicting the energy barriers for radical hydrogen abstractions such as $CH_4 + CH_3 \longrightarrow CH_3 + CH_4$.[13] Unfortunately, this cannot be generalized since poor results have been reported for the

§ The experimental value for the ethylene addition to buta-1,3-diene is 27.5 kcal mol^{-1}. For estimated activation barrier of 25.1 ± 2 kcal mol^{-1} at 0 K, see 4c.

reactions $H + H_2 \longrightarrow H_2 + H$, $CH_4 + H \longrightarrow CH_3 + H_2$ and $CH_4 + {}^3O \longrightarrow CH_3 + OH$.[14]

It should be noted that the reactivity closely follows that predicted from the ratio of the newly forming σ-bonds to the breaking π-bonds. The reactivity is inversely dependent on this ratio; this applies to both reactions. However, it applies only to related reactions, *i.e.*, where the reaction centres are structurally similar.

All applied approximate DFT methods predict that the cycloaddition of ethylene to cyclopentadiene has a lower energy barrier than the same reaction with buta-1,3-diene. The difference in the energy barriers of the two reactions (Table 5) is 3.8 kcal mol^{-1}, and all DFT methods are to within 2 kcal mol^{-1} of this value, the hybrid 'half and half' giving the best result. The kinetic measurements of these reactions give rise to a larger uncertainty than this calculated value. Nevertheless, this is an important finding that may be useful when comparing the relative energy barriers for reactions which do not have experimentally available data.

Conclusions

In conclusion it can be stated that the bond lengths for the transition states obtained by the applied approximate DFT methods are overestimated. This is especially true for the 'pure' methods, while the hybrid DFT methods seem to be satisfactory for predicting the molecular structures. The ratio of the forming σ-bonds to the breaking π-bonds is a good indicator of the progress of the reaction and consequently, correlates to the predicted electronic energy barriers for these reactions. However, this indicator can be used only for structurally similar reaction centres.

The predicted classical energy barrier height and the corrected vibrational adiabatic barrier height are usually understimated by most of the applied methods, where S-VWN for the first reaction yields a negative value. Two theoretical models, B-LYP/6-31G** and Becke3-LYP/6-31G**[15] gives values for the barrier heights within the experimental errors from the kinetic measurements for these reactions.

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