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Effect of Basis Set Superposition Error (BSSE) upon ab Initio Calculations of Organic Transition States

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The transition states (TSs) for several organic reactions (concerted Diels−Alder, 1,2-H-atom shift in ethyl radical, and H-atom transfers from methane and propene to methyl radical) have been optimized on potential energy surfaces that include the counterpoise (CP) correction for basis set superposition error (BSSE). Various molecular orbit methods were used (Hartree−Fock (HF), second order Möller−Plesset, and density functional theory (DFT)) using basis sets varying in size from 3-21G to 6-311++G**. We show that the CP-optimized TSs obtained using small basis sets resemble those obtained using the larger basis sets both in energies and geometries. The geometry of the concerted Diels−Alder TS for ethylene and butadiene becomes more compact upon CP-correction, whereas the apparent TS for the 1,2-H-atom shift in ethyl radical is shown to be an artifact of BSSE (at least at the HF and DFT levels). The TSs for the radical abstraction reactions are shown to move toward product upon CP-optimization. The choice of fragments for the CP-correction is discussed.

Basis set superposition error has long been recognized as a serious problem when calculating the interactions between two (or more) species using ab initio molecular orbital calculations with basis sets substantially below the Hartree−Fock limit. This error occurs because the energy of each unit within an associated complex will be lowered by the basis functions of the others.

Although correction for basis set superposition error (BSSE) is often applied to the calculation of intermolecular complexes, it has rarely been applied to the calculation of the energies and never to the geometries of transition states (TSs). Nevertheless, many TSs involve interactions between molecules (or molecular fragments) that should lead to errors similar to those encountered for intermolecular complexes. For example, a butadiene and an ethylene approach each other in the TS for the simplest Diels−Alder reaction. The TS must suffer from BSSEs similar to those that have been long-established in H-bonding complexes, such as the water dimer.

The counterpoise (CP) correction proposed by Boys and Bernardi[1] continues to be the most prominent means of correcting for BSSE despite the fact that other methods for correcting this error have been discussed in the literature.[2] The CP method calculates each of the units with the basis functions of the other (but without the nuclei or electrons), using so-called “ghost orbitals”. With the use of the notation we have previously employed,[3] the CP-corrected interaction energy, $E^{\mathrm{CP}}_{\mathrm{interaction}}$, is stated in eq 1

$$E^{\mathrm{CP}}_{\mathrm{interaction}} = E_{\mathrm{super}} - \sum_{i=1}^{n} E_{\mathrm{m}^{i}_{\mathrm{opt}}} + \sum_{i=1}^{n} (E_{\mathrm{m}^{i}_{\mathrm{f}}} - E_{\mathrm{m}^{i*}_{\mathrm{f}}}) \qquad (1)$$

where the E_{m}’s represent the energies of the individual monomers. The subscripts “opt” and “f” denote the individually optimized monomers and those frozen in their supermolecular geometries and the asterisk (*) denotes monomers calculated with ghost orbitals. This method has proven to be somewhat controversial.[4] Nevertheless, van Duijneveldt has shown that CP rigorously corrects for BSSE in certain cases.[4h] The original procedure was conceived for molecules in fixed geometries and atoms. Geometric optimization was not considered. Equation 1 is a modification of the original procedure, which accounts for the changes in the geometries of the monomeric units upon forming the intermolecular complex. Traditionally, one applied CP correction as a single point correction to a previously optimized geometry of the complex.

BSSE introduces a nonphysical attraction between the two units. Thus, the CP correction generally makes intermolecular complexes less stable with longer intermolecular distances than apparent from the normally optimized structure. One should use CP to correct the optimized geometry as well as the interaction energy. We have recently developed a simple general method for optimizing geometries on CP-corrected potential energy surfaces (PES).[3] Others had previously optimized some surfaces using point by point calculations.[5] Several recent reports of geometric optimizations on BSSE-corrected PESs have appeared.[6]

In this paper, we examine the effect of optimizing the TSs of several simple organic reactions by applying our procedure for geometric optimization on CP-corrected PESs. We have chosen three different kinds of reactions that exemplify different effects of CP optimization for study: (1) the concerted Diels−Alder reaction between ethylene and butadiene, which has a reaction coordinate at the TS that is primarily the approach of the two fragments toward each other; (2) the 1,2-H-atom shift in ethyl radical, which *appears* to have a transition state with the H atom symmetrically placed with respect to the two carbons (but which may be an artifact of the calculations); and (3) two examples of the H transfer between organic radicals: the methyl radical and methane, which has a symmetric TS and a reaction coordinate that primarily involves motion of the H atom between the two carbons, and the methyl radical and propene, which has an unsymmetric TS in which the reaction coordinate

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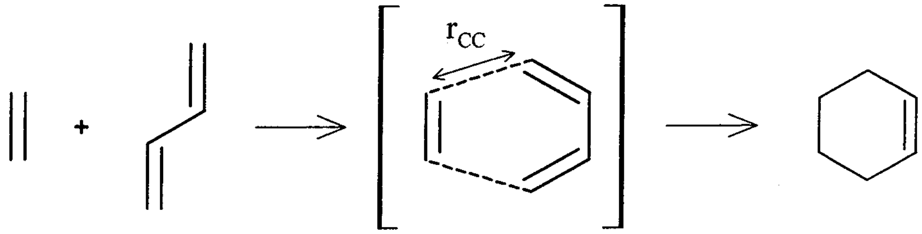
TABLE 1: Comparison of Normal and CP-Optimized TSs for the Diels−Alder Reaction between Ethylene and Butadiene



method	normal (uncorrected)			CP-corrected			difference		
	ΔE	$\Delta H^‡$	r_{CC}, Å	ΔE	$\Delta H^‡$	r_{CC}, Å	$\Delta\Delta E$	$\Delta\Delta H^‡$	Δr_{CC}, Å
HF/3-21G	33.21	34.58	2.2096	43.27	44.60	2.1949	10.06	10.02	−0.0147
HF/6-31G	40.70	41.86	2.2039	44.55	45.75	2.1962	3.86	3.89	−0.0077
HF/6-31G**	42.26	43.39	2.2002	45.83	46.99	2.1947	3.57	3.60	−0.0055
HF/D95**	43.75	44.80	2.2002	44.73	46.37	2.1983	0.97	1.57	−0.0019
HF/D95++**	43.84	44.89	2.1999	44.82	45.87	2.1980	0.98	0.98	−0.0018
HF/6-311++G**	45.39	46.50	2.1925	46.10	47.22	2.1910	0.71	0.72	−0.0015
B3PW91/3-21G	10.66	11.80	2.3280	18.46	19.66	2.2837	7.79	7.86	−0.0442
B3PW91/6-31G	17.35	18.37	2.2885	20.21	21.29	2.2772	2.86	2.92	−0.0113
B3PW91/6-31G**	16.30	17.29	2.2950	18.95	20.01	2.2863	2.65	2.72	−0.0087
B3PW91/D95**	17.42	18.22	2.2982	18.21	19.06	2.2938	0.78	0.84	−0.0044
B3PW91/D95++**	17.64	18.48	2.2974	18.32	19.22	2.2950	0.69	0.74	−0.0023
B3PW91/6-311++G**	18.43	19.39	2.2736	19.06	20.08	2.2703	0.63	0.69	−0.0033
B3LYP/6-311++G**	21.99	23.00	2.2469	22.54	23.62	2.2464	0.55	0.62	−0.0005
MP2/3-21G	15.70	16.81	2.2677	28.82	29.97	2.2182	13.12	13.16	−0.0495
MP2/6-31G	20.76	21.73	2.2557	28.55	29.58	2.2240	7.80	7.85	−0.0316
MP2/6-31G**	14.45	15.35	2.2832	21.46	22.42	2.2563	7.01	7.07	−0.0269
MP2/D95**	13.74	14.79	2.2997	19.60	20.72	2.2720	5.86	5.93	−0.0277
MP2/D95++**	12.66	13.65	2.2982	18.36	19.39	2.2773	5.70	5.74	−0.0209
MP2/6-311++G**	12.93	13.84	2.2936	16.87	17.80	2.2804	3.94	3.96	−0.0133

involves both the motion of the H atom relative to the carbons and the approach of the two fragments.

Methods

All molecular orbital (MO) calculations were performed using the Gaussian 98 suite of computer programs.[7] We obtained the CP-optimized TSs by converging to the geometrically optimized structures on the CP-corrected energy surface. Derivatives of the energy with respect to geometrical parameters were calculated using eq 2

$$\frac{\partial E^{\mathrm{CP}}_{\mathrm{interaction}}}{\partial p_j} = \frac{\partial E^{\mathrm{CP}}_{\mathrm{super}}}{\partial p_j} = \frac{\partial E_{\mathrm{super}}}{\partial p_j} + \sum_{i=1}^{n}\left(\frac{\partial E_{m_{\mathrm{f}}^{i}}}{\partial p_j} - \frac{\partial E_{m_{\mathrm{f}}^{i*}}}{\partial p_j}\right) \quad (2)$$

as previously described.[3] We used our CP optimizer program[8] to drive Gaussian 98 for the CP optimization. This program allows the user complete flexibility to specify the individual fragments of the associated complex. The charges and multiplicities of each fragment can be individually defined. Basis sets of varying complexity were used to illustrate the extent of the CP-optimization effect. We used basis sets varying in complexity from 321G to 6-311++G**. We report Hartree−Fock (HF) calculations, frozen core MP2 calculations, and density functional theory (DFT) calculations using the B3LYP and B3PW91 functionals. The B3PW91 method combines Becke's three-parameter functional,[9] with the nonlocal correlation provided by the Perdew−Wang expression,[10] whereas the B3PLYP combines the same Becke functional with correlation functional of Lee et al.[11]

Vibrational frequencies were calculated for all TSs to verify that they are first-order saddle points and to determine the enthalpies. The vibration frequencies for the CP-optimized structures were obtained from the CP-opt program using second derivatives calculated in a manner analogous to those of eq 1, as previously described.[3]

Results and Discussion

We first present and discuss the results for the individual reactions, followed by a general discussion.

Concerted Diels-Alder Reaction between Ethylene and Butadiene. The activation energies $\Delta H^‡$'s and distances of the incipient bonds for various TSs optimized with and without CP correction using different MO methods are summarized in Table 1. We considered two fragments, ethylene and butadiene, in the CP-opt procedure. The TSs optimized with CP correction all have higher energies and *shorter incipient bond lengths* than the TSs optimized using the traditional procedure. The higher energies are a reasonable expectation based upon previous experience with intermolecular complexes, whose energies also increase (stabilization decreases) upon application of CP. However, intermolecular distances generally increase when these *complexes* are optimized on a CP-corrected surface. In these cases, removal of the nonphysical attraction (attributed to BSSE) between the molecules moves the minimum on the PES to a larger intermolecular separation.

For the TS in the DA reaction, we must consider the effect of the nonphysical attractive force upon the reaction coordinate, which has its maximum value at the TS (see Figure 1). At the TS calculated on the non-CP-corrected PES (point a in Figure 1), the gradient of the force along the reaction coordinate is zero (as for all of the other internal coordinates). The effect upon the reaction coordinate of the non-CP-corrected PES of *removing the nonphysical attraction* is equivalent to adding a repulsion of equal magnitude. This repulsion will increase along the reaction coordinate from reagents to product as the molecular fragments approach each other. If one imagines adding such a repulsion to the traditional PES (point d of Figure 1), the

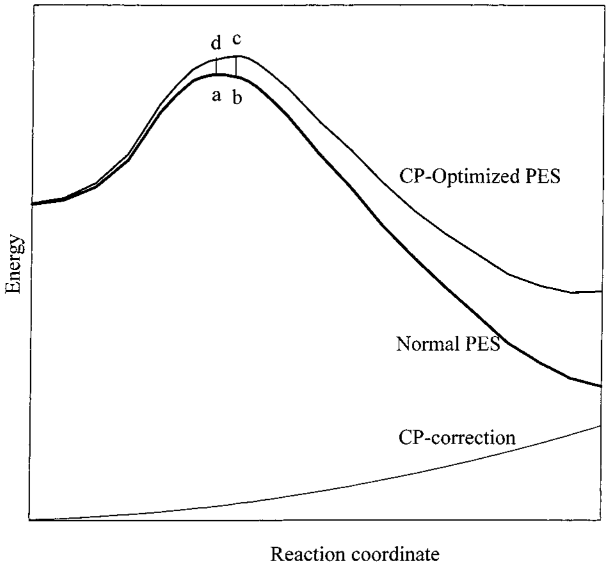
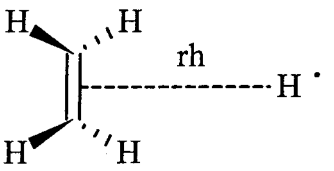


Figure 1. Comparison of normal and CP-optimized PESs for the Diels−Alder reaction between ethylene and butadiene. The CP-optimized surface can be understood as the sum of the normal (uncorrected) surface and the CP correction. Points a and c represent the optimized structures for the transition state on the normal and CP-optimized surfaces, respectively. Point b represents the CP-optimized structure on the normal surface. Point d represents the normal optimized structure on the CP-optimized surface.

TABLE 2: Hydrogen 1,2 Shift in the Ethyl Radical



method	normal (uncorrected)		CP-corrected		difference	
	ΔE^a	rh, Å	ΔE	*rh*, Å	$\Delta\Delta E$	Δrh, Å
HF/3-21G	−0.04	3.709	0.00	5.083	0.04	1.374
HF/6-31G	−0.03	3.961	0.00	5.376	0.03	1.414
HF/6-31G**	−0.03	3.933	0.00	5.258	0.03	1.325
HF/D95**	−0.01	4.322	0.00	5.626	0.01	1.303
HF/D95++**	−0.01	5.398	0.00	5.475	0.01	0.077
HF/6-311++G**	−0.00	6.131	0.00	6.131	0.00	0.000
B3PW91/3-21G	0.01	4.963	0.00	5.571	0.01	0.608
B3PW91/6-31G	0.00	6.201	0.00	6.201	0.00	0.000
B3PW91/6-31G**	0.00	6.097	0.00	6.097	0.00	0.000
B3PW91/D95**	0.01	4.619	0.00	6.499	−0.01	1.880
B3PW91/D95++**	−0.00	6.318	0.00	7.502	0.00	1.184
B3PW91/6-311++G**	0.01	6.019	0.00	7.813	−0.01	1.794
B3LYP/6-311++G**	0.04	3.576	0.05	3.660	0.01	0.084
MP2/3-21G	−0.06	3.632	0.00	5.072	0.06	1.440
MP2/6-31G	−0.04	3.868	0.00	5.356	0.04	1.488
MP2/6-31G**	−0.05	3.778	−0.00	5.080	0.05	1.302
MP2/D95**	−0.03	4.062	−0.00	5.211	0.03	1.148
MP2/D95++**	−0.03	4.508	−0.00	4.880	0.02	0.372
MP2/6-311++G**	−0.03	4.325	−0.01	4.534	0.02	0.208

[a] Energy with respect to separated ethylene and H atom (kcal/mol).

gradient of the reaction coordinate at the original TS will no longer be zero. Rather, it will become positive in the direction of the product. Upon moving along the reaction coordinate from the uncorrected TS toward product, this repulsive force increases, whereas the gradient of the uncorrected PES decreases. At some point on the product side of the original TS, the repulsive force will be exactly canceled by the downward slope of the uncorrected PES. This point becomes the new (CP-corrected) TS (point c in Figure 1). Because its reaction coordinate is on the product-side of the uncorrected TS, its incipient bond lengths will be shorter than those of the uncorrected TS.

The HF calculations all predict activation parameters that are significantly higher than the MP2 and DFT calculations, in accord with previous reports. The effects of CP correction increase in the order HF < DFT < MP2 both for an increase in activation and a decrease in incipient bond length. We had previously noted that the single-point CP correction for the TS of the DA reaction between butadiene and cyclopropene is quite large when quadratic configuration interaction (QCI) is used.[12] The effects diminish as the basis sets increase in complexity, as expected.

For large basis sets, only the B3LYP calculations are reasonably consistent with the experimental activation energy. The kinetics of the gas-phase reaction between ethylene and butadiene were determined at temperatures between 760 and 921 K.[13] An Arrhenius plot in this temperature range gave and activation energy of 27.5 (extrapolated to 25.1 at 0 K) kcal/mol. Because of the high temperatures employed in the experimental study, there is reason to believe that a significant fraction of the reaction follows a stepwise rather than concerted reaction. The $\Delta S^{\ddagger}$ for the former should be significantly less-negative, making the stepwise reaction more competitive at high temperatures.[14] B3LYP/6-31G* calculations on the reaction between ethylene and butadiene place the stepwise (biradical) TS only 3.4 kcal/mol higher than the concerted TS.[15] Therefore, the expected activation energy for the concerted reaction might be a few kcal/mol less than the experimental value.

Hydrogen 1,2 Shift in the Ethyl Radical. The 1,2-sigmatropic shift of an H atom in the ethyl radical is a symmetry-forbidden process because the lowest unoccupied molecular orbital (LUMO) of the ethylene has a nodal plane that bisects the C−C bond axis. Thus, the hydrogen 1s orbital has zero overlap with the LUMO as it crosses the nodal plane (at the presumed TS). One may reasonably question whether a TS exists for this reaction or whether the system would preferentially dissociate into ethane and a H atom. In this case, the PES for ethylene plus an H atom would have two valleys for approach of an H atom to either carbon, separated by a ridge that increases in magnitude as the H atom approaches the ethylene. This situation is qualitatively similar to that previously proposed for the differentiation of the reaction paths for coupling versus disproportionation of two ethyl radicals.[16] Simple MO calculations do predict a well-defined TS (only one imaginary frequency which connects the two equivalent ethyl radicals) for this process. There is a slight increase in energy as the H atom is removed to infinite distance from its position in the TS. The obvious question arises: Does this TS owe its existence to weak bonding of the H atom to orbitals of the ethylene other than the LUMO, or is the apparent TS simply an artifact on the PES caused by BSSE?

To answer this question, we optimized the geometry of a system in which a H atom is constrained to the plane that perpendicularly bisects the C═C bond of ethylene (the nodal plane of the LUMO). A minimum found in this plane should correspond to a TS for the 1,2 shift. The results of the calculations are collected in Table 2. The ΔE values in this table refer to the stabilization of the TS relative to separated ethylene and a H atom. Inspection of Table 2 shows that HF, MP2, and DFT calculations with small basis sets all predict a well-defined TS with a distance of about 3.6−3.7 Å between the H atom and the midpoint of the C═C bond. The energies for removal

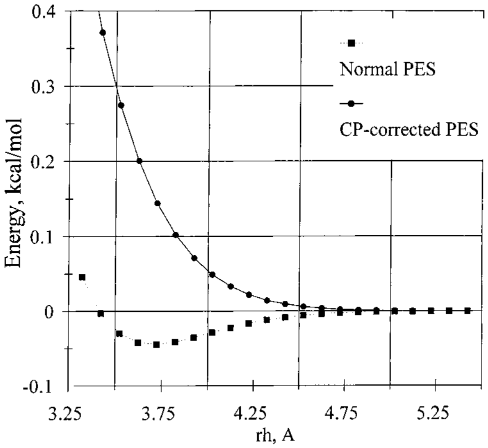


Figure 2. Comparison of the normal and CP-corrected PESs for the H migration in ethyl radical at the HF/3-21G level. The figure represents a cross section of the surface in a plane that bisects and is perpendicular to the C=C bond, whereas rh is the distance between the midpoint of the C=C bond and the H atom (see Table 2).

of the H atom are about 0.5 kcal/mol. As the basis sets become more complex within a series, the predicted distance between the H atom and the midpoint of the C=C bond increases to values as large as 7 Å (B3PW91/6-311++G**) with an ΔE of about 15×10^{-3} kcal/mol.

Optimization of these structures on the CP-corrected surfaces appeared to give TSs with much longer H atom−carbon separations and very low E_a's. However, frequency calculations indicated these structures not to be true TSs. For these CP-opt calculations, the fragments considered were ethylene and a hydrogen atom. The gradients of the TSs continue to decrease as the H atom moves away from the ethylene (Figure 2); however, the surface had become so flat that the gradients of the energy with respect to this distance had become effectively zero (thus satisfying the programs convergence criterion). Clearly, this is a case where the *qualitative* appearance of the PES changes when it is calculated with CP correction.

One should note that another saddle point for H transfer in ethyl radical exists. This structure, which has the H atom much more tightly bound to the ethylene, can be thought of as an H atom forming a stabilizing interaction with the π-bonding orbital of and *excited* ethylene. Removal of the H atom via dissociation of the H atom along a path that preserves the plane of symmetry leads to an excited triplet state of ethylene,[17] clearly an endoergonic process (see Figure 3). Because H transfer via this saddle point will surely be more ordered, thus of higher free energy, than the dissociation of the H atom on the ground-state surface, the associated saddle point cannot be properly called a TS for a thermal reaction. Nevertheless, we have calculated the CP-corrected saddle point for this process at two levels: HF/6-31G and B3LYP/6-311++G**. In this case, the two fragments used for the CP-optimization procedure are an H atom and a triplet ethylene. Because the normal coordinate which separates the H atom from the triplet ethylene has a rapidly increasing slope, the CP correction on the PES is minimal. The optimization of this point on the CP-optimized surface is noteworthy because it is the first example to our knowledge where CP optimization has been performed using an excited state of one of the fragments in the complex.

The energies of the CP-corrected saddle point are +18.45 and −0.44 kcal/mol compared to those of separated (ground state) ethylene for the HF and DFT CP-optimized species, respectively. At the lower level of calculation, this saddle point is considerably higher than those of the dissociated species, implying that it could reasonably be neglected. However, the more sophisticated calculation suggests this saddle point is energetically equivalent to the separated species. The necessarily more negative entropy for this saddle point makes it an extremely unlikely candidate for the TS on a free energy surface.

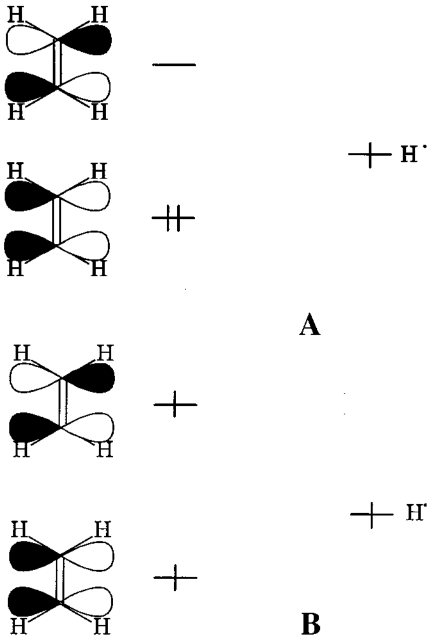
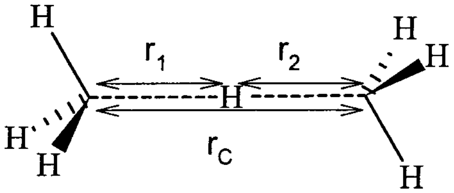


Figure 3. Orbital interaction diagrams for ethylene plus a hydrogen atom in the plane perpendicular to and bisecting the C=C bond. (A) ground singlet-state ethylene plus H; (B) excited triplet-state ethylene plus H.

H-Atom Transfer from Methane to the Methyl Radical. For this and the following reaction, three fragments were considered for the CP-opt procedure: a hydrogen atom and the two appropriate radicals (two methyls or a methyl and an allyl). Using only two fragments (i.e., a methyl radical and methane) for the CP-opt procedure would destroy the symmetry of the TS, as noted by Mayer.[18] However, it is entirely appropriate to use the three fragment system because the quasithermodynamic-state properties of the TS should be independent of whether it be formed from a methyl radical and methane or two methyl radicals and a hydrogen atom.

In this process, the reaction coordinate involves: (a) the approach of the reactants, (b) the transfer of the H atom, and (c) the separation of the products. All MO methods that we have tried predict the reaction coordinate at the TS to primarily involve the motion of the migrating H atom between the C's. The distance between the C's remains relatively insensitive to the reaction coordinate at the TS. Nevertheless, the nonphysical force caused by BSSE should affect the distance between the C's at the TS. Removing this force would cause the C···C separation to increase at the TS. If the C···C separation is greater, the H atom would traverse a larger distance during its migration. Consequently, the H atom would have decreased overlap with each C at the TS. Thus, one would expect the calculated activation energy to increase after CP correction is applied to the PES. The results collected in Table 3 and displayed in Figure 4 confirm these expectations. The activation parameters in the table refer to the energy differences between the TS and the reagents calculated using the same three fragments. Thus, methane is calculated using the CP-optimization procedure with a methyl radical and an H atom as the two fragments. This breaks the symmetry of methane but provides a continuous potential-energy surface for the H-transfer reaction.

TABLE 3: Hydrogen Transfer from Methane to the Methyl Radical[a]



method	normal (uncorrected) ΔE	$\Delta H^\ddagger$	r_1,r_2, Å	CP-corrected ΔE	$\Delta H^\ddagger$	r_1,r_2, Å	difference ΔE(TS)	$\Delta\Delta E$	$\Delta\Delta H^\ddagger$	Δr_1,Δr_2, Å
HF/3-21G	27.20	26.22	1.3562	30.97	29.36	1.3676	5.18	3.77	3.15	0.0114
HF/6-31G	29.69	28.34	1.3555	30.84	29.44	1.3582	1.63	1.15	1.10	0.0027
HF/6-31G**	29.73	28.39	1.3560	30.71	29.30	1.3578	1.46	0.98	0.91	0.0018
HF/D95**	30.61	29.10	1.3547	31.12	30.62	1.3558	1.12	0.51	1.51	0.0011
HF/D95++**	30.61	29.11	1.3551	30.86	29.35	1.3563	0.52	0.24	0.25	0.0012
HF/6-311++G**	30.53	29.08	1.3569	30.71	29.25	1.3578	0.34	0.17	0.17	0.0009
B3PW91/3-21G	11.35	10.29	1.3446	15.57	13.88	1.3554	5.67	4.22	3.59	0.0108
B3PW91/6-31G	13.88	12.43	1.3430	15.27	13.22	1.3458	1.91	1.38	0.79	0.0028
B3PW91/6-31G**	13.76	12.21	1.3431	14.96	13.02	1.3455	1.75	1.20	0.81	0.0024
B3PW91/D95**	14.31	12.67	1.3416	15.02	13.00	1.3429	1.52	0.71	0.33	0.0013
B3PW91/D95++**	14.48	12.83	1.3414	14.70	12.66	1.3425	0.46	0.21	−0.17	0.0011
B3PW91/6-311++G**	14.84	13.22	1.3423	15.01	13.39	1.3431	0.27	0.17	0.17	0.0008
B3LYP/6-311++G**	15.34	13.72	1.3468	15.49	1 13.97	1.3475	0.24	0.15	4 0.25	0.0007
MP2/3-21G	21.14	20.05	1.3435	25.93	24.25	1.3606	7.15	4.79	4.21	0.0171
MP2/6-31G	22.97	21.42	1.3442	25.13	23.02	1.3530	3.50	2.16	1.60	0.0088
MP2/6-31G**	20.81	19.22	1.3241	22.74	20.60	1.3308	3.30	1.94	1.38	0.0067
MP2/D95**	20.57	18.92	1.3225	22.20	20.50	1.3303	3.17	1.63	1.58	0.0078
MP2/D95++**	20.36	18.61	1.3226	21.78	20.10	1.3303	2.62	1.42	1.49	0.0077
MP2/6-311++G**	19.77	17.90	1.3265	20.69	18.85	1.3320	1.79	0.92	0.95	0.0055

[a] Transition state, kcal/mol. ΔE(TS) indicates ΔE for TS only. $\Delta\Delta E$ and $\Delta\Delta H^\ddagger$ are activation parameters where CP optimization is applied to the reactants as well as the TS.

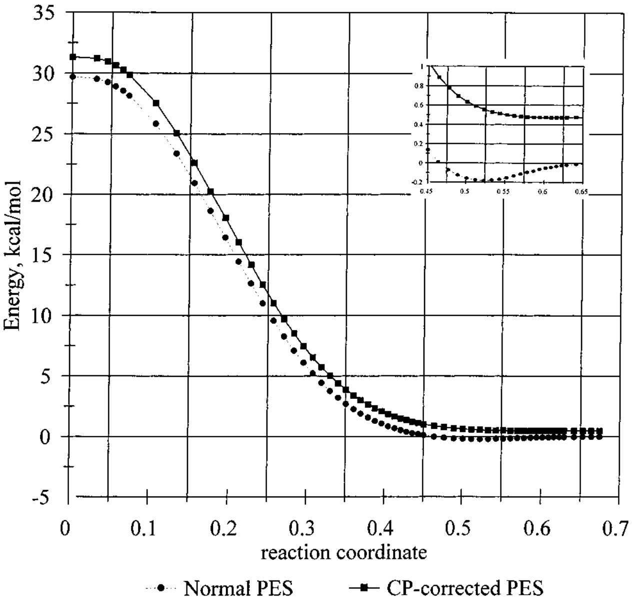


Figure 4. Normal and CP-corrected PES for the $H_3C-H-CH_3$ system (HF/6-31G). To perform a scan, distance r_1 was gradually increased while the rest of the system was optimized, whereas the single-point CP correction was performed for every optimized geometry. The ratio $(r_1 - r_2)/r_c$ is used as the reaction coordinate to generate the graph. The inset shows a magnified version of the region for $(r_1 - r_2)/r_c = 4.5-6.5$. Note the minimum is on the uncorrected PES only. See Table 3 for definitions of parameters.

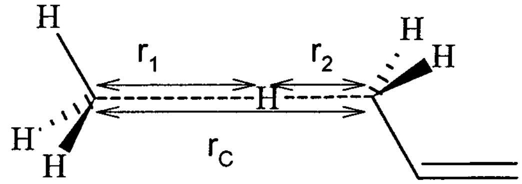
Because the changes in activation energies upon CP optimization derive both from the energetic change in the TS and the methane, the change in the energy of the TS alone, ΔE(TS), is included in Table 3 along with the changes in the activation parameters. Once again, the effect of CP correction upon the TS decreases as the basis set becomes more complex. Also, the effect is greater for MP2 than it is for HF or DFT calculations.

HF calculations greatly overestimate the activation parameters for this reaction, whereas the best DFT calculations predict a $\Delta H^\ddagger$ very close to the experimental[19] value of 14.9 kcal/mol for abstraction from methane by $CD_3\bullet$. The MP2 calculations also predict $\Delta H^\ddagger$'s that are higher than those of the experimental reports. There may be a contribution from H-atom tunneling that would make the calculated $\Delta H^\ddagger$ higher than that derived from experimentally measured rates. However, the apparently small deviations from linearity of the Arrhenius plots suggest tunneling to be unimportant. Nevertheless, Truhlar[20] has suggested that there may be increased tunneling as the system approaches the TS. Such a situation could be consistent with the experimental Arrhenius plots.

In addition to the effect upon the TS, BSSE has another noticeable effect upon the PES. The methyl radical and methane molecule are calculated to form a weak complex when small basis sets are used. This phenomenon is illustrated in Figure 4 (inset) for the PES calculated at the HF/6-31G level. As is noted in the figure, CP correction removes this (apparently anomalous) minimum on the PES.

H-Atom Transfer from Propane to the Methyl Radical. This reaction is similar to the H transfer for methane to the methyl radical. However, it does not have a symmetrical PES because the products (methane and an ally radical) are more stable than the reactants. The Hammond postulate dictates that the TS should be earlier along the reaction path than for the previous reaction. Thus, one might reasonably expect the reaction coordinate at the TS to involve the approach of the two reactive carbon centers, as well as, movement of the H atom between these centers. As in the case of the DA reaction, the gradient of the reaction coordinate will be positive at the traditionally optimized TS (because the two molecular fragments

TABLE 4: Hydrogen Transfer from Propene to the Methyl Radical[a]



	normal				CP-corrected				difference				
method	ΔE	$\Delta H^{\ddagger}$	rc, Å	$r1/r2$, Å	ΔE	$\Delta H^{\ddagger}$	rc, Å	$r1/r2$, Å	ΔE(TS)	$\Delta\Delta E$	$\Delta\Delta H^{\ddagger}$	Δrc,Å	$\Delta(r1/r2)$, Å
HF/3-21G	20.34	18.70	2.738	1.1001	24.55	22.26	2.769	1.0965	5.77	4.22	3.56	0.030	−0.0036
HF/6-31G	22.55	20.48	2.746	1.1031	23.77	21.11	2.753	1.1028	1.76	1.22	0.63	0.008	−0.0003
HF/6-31G**	23.80	21.78	2.742	1.0912	24.86	22.84	2.747	1.0909	1.59	1.06	1.06	0.005	−0.0003
HF/D95**	25.09	22.93	2.736	1.0850	25.64	23.48	2.739	1.0846	1.27	0.55	0.55	0.003	−0.0003
HF/D95++**	25.08	22.93	2.737	1.0849	25.38	23.23	2.740	1.0843	0.58	0.30	0.30	0.002	−0.0005
HF/6-311++G**	25.13	23.07	2.741	1.0845	25.34	23.28	2.742	1.0842	0.38	0.21	0.21	0.002	−0.0003
B3PW91/3-21G	5.44	4.52	2.733	1.1822	9.99	8.41	2.758	1.1656	6.25	4.55	3.89	0.024	−0.0166
B3PW91/6-31G	8.01	6.72	2.739	1.1846	9.44	7.56	2.746	1.1828	2.11	1.43	0.83	0.008	−0.0018
B3PW91/6-31G**	8.06	6.64	2.736	1.1775	9.32	7.90	2.741	1.1761	1.94	1.26	1.26	0.005	−0.0013
B3PW91/D95**	8.79	7.28	2.730	1.1716	9.56	7.46	2.733	1.1704	1.78	0.77	0.18	0.003	−0.0012
B3PW91/D95++**	9.00	7.47	2.730	1.1710	9.29	7.74	2.732	1.1698	0.59	0.29	0.27	0.002	−0.0012
B3PW91/6-311++G**	9.29	7.79	2.732	1.1708	9.51	8.02	2.733	1.1700	0.36	0.22	0.23	0.001	−0.0008
B3LYP/6-311++G**	9.80	8.29	2.736	1.1574	9.99	8.49	2.737	1.1568	0.31	0.19	0.20	0.001	−0.0006
MP2/3-21G	20.72	20.56	2.689	1.0542	26.10	25.33	2.733	1.0515	8.30	5.38	4.76	0.043	−0.0026
MP2/6-31G	23.46	22.89	2.698	1.0621	25.81	24.66	2.721	1.0621	4.16	2.35	1.78	0.023	−0.0000
MP2/6-31G**	19.77	19.23	2.656	1.0539	21.97	20.86	2.673	1.0535	3.93	2.20	1.63	0.017	−0.0004
MP2/D95**	19.62	19.03	2.651	1.0469	21.56	20.39	2.669	1.0461	3.94	1.94	1.37	0.018	−0.0008
MP2/D95++**	19.16	18.56	2.652	1.0468	21.08	19.90	2.669	1.0454	3.38	1.92	1.34	0.017	−0.0014
MP2/6-311++G**	18.24	17.64	2.659	1.0474	19.46	18.28	2.672	1.0467	2.31	1.22	0.65	0.013	−0.0006

[a] Transition state, kcal/mol. ΔE(TS) indicates ΔE for TS only. $\Delta\Delta E$ and $\Delta\Delta H^{\ddagger}$ are activation parameters where CP optimization is applied to the reactants as well as the TS.

are approaching each other). Thus, the CP-optimized TS will be somewhat closer to product. The progress along the reaction coordinate can be measured by the relative C···H distances for the breaking and forming bonds. Because the TS is early, the ratio of the breaking to forming C···H bond distances should be <1. As one moves toward the product along the reaction coordinate, this ratio will increase. The data in Table 4 show that this ratio at the TS increases upon CP optimization of the TS. Propene was calculated with the CP-optimization procedure using an allyl radical and a H atom (see discussion above for the methyl radical plus methane) We have already seen (from the previous discussion) that the H atom transfer is facilitated by a close approach of the reactive carbon centers. This distance increases upon CP optimization of the TS causing increases in the calculated activation parameters.

As in the case of the previous reaction, the HF calculations give activation parameters that are much too high. The best DFT calculations give results in accord with the reported experimental[19] value of 7.7 kcal/mol for $\Delta H^{\ddagger}$.

General Discussion

Clearly, CP-corrected surfaces lead to noticeable improvements in the geometrically optimized TSs obtained with relatively small basis sets. The geometries and associated activation energies become closer to those obtained with larger basis sets. The CP corrections to these parameters tend to diminish as the basis sets are improved. These observations may be contrasted with the earlier suggestion by Lendvay and Mayer that CP correction is inappropriate for the optimizations of TSs.[18] They quite correctly noted that certain choices for the fragments used in the CP correction calculation would be inappropriate. In particular, they criticized two applications of CP to TSs.[21] For example, had we used two fragments (CH_4 and CH_3•) for the methane/methyl H-transfer reaction, we would have obtained an inappropriate, unsymmetrical TS. However, a flexible choice of the fragments will usually allow reasonable CP calculations of the TS, at least for cases where all fragments are neutral. Nevertheless, the seemingly arbitrary nature of the fragment choices bear some detailed discussion.

Because the TS is defined by transition-state theory as a quasithermodynamic state, it is approximated to have the associated thermodynamic state-functions. Thus, the First Law can be applied to the TS. As a consequence, one can construct the TS from any fragments, not simply from the reagents and products. Clearly, the BSSE will depend on the choice of fragments, just as it will depend on the choice of a basis set. Thus, the extent of the BSSE and the CP will differ somewhat depending upon how the fragments are chosen. In principle, the TS could be constructed from the individual atoms. This would lead to a different BSSE. Although CP is not usually now applied to the construction of molecules from atoms, it is noteworthy that this was the original application by Jansen and Ros.[1c]

One can consider the choice of the basis set in an analogous manner. Typically, nucleus-centered Gaussians are used to construct basis sets. These lead to obvious assignments of these Gaussians to the atom on whose nucleus it is centered and the molecular fragment to which this nucleus belongs. However, other choices for a basis functions exist and have been used. For example, Gaussians can be placed along the bond axes between the atoms. If such a bond were broken into two fragments, the arbitrary decision must be made to associate the bond Gaussian with one of the two fragments. If the other functions in the basis set were sufficient to provide HF-limit calculations for the original structure, as well as, each of the two fragments, the energy of bond rupture would be insensitive to the assignment of the bond Gaussian to one or the other fragment. The use of inadequate nucleus-centered Gaussian basis sets presents an analogous problem. Because the basis set of the first fragment is inadequate, it borrows density from the bases of the other fragment. Thus, the apparent basis functions of the second fragment are also being used by the first fragment. In fact, these basis functions on the second fragment are also basis functions of the first (just as the bond Gaussian was). This problem will disappear as the originally inadequate basis set is improved. Obviously, this is simply another way of describing BSSE phenomenologically. In any case, any reasonable construction of the TS from fragments suitably chosen to preserve the essential properties of the TS (i.e., correct symmetry) should lead to an improvement in the TS calculated with relatively small basis sets. The correction should tend to disappear as the basis set is improved. We see that the choice of both the fragments and basis sets used to construct a molecular complex will influence the calculated energies and geometries of the molecular complex when the basis sets are inadequate but not when they are complete. Even the aforementioned TS for the CH_4/CH_3• H-atom transfer will converge to the correct TS on the CP-optimized surface as the HF limit is approached.

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