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Ab Initio Calculation of the Reaction Path for the Addition of Singlet (¹A₁) Methylene to Ethylene

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Abstract: Ab initio calculations at the SCF level and with the inclusion of valence shell electron correlation in the CEPA (coupled electron pair approximation) scheme with a double ζ type basis plus polarization functions on carbon have been performed for the reaction path of the addition of singlet (ã ¹A₁) methylene to ethylene to yield cyclopropane. The energy is minimized with respect to all relevant geometrical parameters for fixed values of the approximate reaction coordinate. The reaction energy is accounted for to within the uncertainty of the experimental energy of CH₂ (ã ¹A₁). The energy along the reaction path decreases monotonically without a barrier. Hoffmann's prediction that the reaction path should be nonsymmetric is confirmed. The reaction starts with an electrophilic phase and is accomplished with a nucleophilic phase. In the two phases different geometrical arrangements and different internal geometries of the partners are favored.

I. Introduction

Methylene (CH₂) plays an important role as an intermediate in chemical reactions. Therefore, its electronic structure has received much attention.[2-7] The properties of CH₂ in low-lying electronic states as well as the difference in reactivity in these states were of particular interest.[4,5,8-13]

It is known from experimental studies[9,14-20] that the photolysis of ketene vapor or diazomethane leads primarily to methylene in highly excited singlet states. It is then deexcited in collisions with inert gas molecules to a mixture of CH₂ (¹A₁) and CH₂ (³B₁). The ratio of these two components depends on the conditions under which the photolysis is performed.

The CH₂ species is very reactive.[9,20,21] For example, with ethylene it reacts to form propylene and cyclopropane.[14-19] The relative yields of the products depend on the conditions of the reaction and it is possible to limit the yield of propylene to a very small fraction.[15] Furthermore, the attack of the CH₂ on the double bond in ethylene, which leads to cyclopropane, is sometimes stereospecific. The stereospecificity, or lack of it, depends on which of the two electronic states of CH₂ is in-

volved.[17-21] Some authors suggest that the singlet species should react in a single-step process to yield the three-membered ring stereospecifically while the triplet species should initially form a diradical intermediate which possesses only a small rotational barrier about single bonds, so that there is no stereospecificity in the second case.[5,8,10,16-23] This idea was probably first formulated by Skell and Garner[24] whereas Benson et al.[25,26] have suggested that an open-chain trimethylene is also involved in the singlet reaction. That the addition of triplet methylene to ethylene takes place via the trimethylene biradical[27,28] has been confirmed by theoretical investigations at the semiempirical[5,8] as well as at the ab initio level,[10,22] although the geometry of approach is not known in all its details.

For the addition of singlet methylene to double bonds the situation is not so straightforward from the theoretical point of view. According to the Woodward-Hoffmann rules cycloaddition of methylene to ethylene is forbidden if C_{2v} symmetry is preserved.[8] The orbital phase continuity principle of Goddard III leads to the same conclusions.[10] Bodor et al.[5] have

Table I. Optimized Values of the Geometrical Parameters; Distances in a_0 ($1a_0 = 0.529$ Å)

|	d							
	2.479	3	3.5	4	4.5	5	10	∞
CH_2 Group								
γ	0°	0°	0°	56.4°	90°	94.4°	150°	
$r_{C_3H_5} = r_{C_3H_6}$	2.030	2.012	2.014	2.044	2.075	2.078	2.085	2.088
$\angle H_5-C_3-H_6$	113.8°	122.4°	132.4°	119.8°	108.0°	106.7°	104.6°	104.6°
C_2H_4 Group								
r_{C-C}	2.862	2.766	2.702	2.571	2.517	2.502	2.484	2.486
$r_{C_1H_1}$	2.030	2.030	2.029	2.030	2.030	2.030	2.034	2.034
$\angle H_1-C_1-H_2$	113.8°	114.4°	115.5°	116.3°	116.2°	116.2°	116.0°	115.9°
α	30°	25.3°	19.9°	4.4°	0.9°	0°	0°	0°
β	30°	25.3°	19.9°	11.2°	4.5°	2.5°	0°	0°
δ	90°	90°	90°	90°	90°	90°	90°	
ϵ	90°	90°	90°	102.4°	94.5°	93.9°	90°	

performed a MINDO/2 calculation of this "forbidden" reaction path and obtained a rather low barrier (6 kcal/mol). Hoffmann proposed a nonsymmetric approach for the addition of ($^1A_1$) CH_2 to ethylene both by qualitative arguments and as a result of his EHT calculations. On the other hand, San Yan Chu et al.[4] concluded from their limited CI calculations of the low-lying electronic states of CH_2 that the addition reaction may involve the $^1A_1{}^*$ excited state of CH_2. No fully optimized ab initio reaction path for the addition of singlet methylene to ethylene has been published so far. In order to state definitely whether or not the reaction has a barrier, a careful optimization of the geometrical parameters is necessary. The results of this geometrical optimization along the reaction coordinate turn out to be rather interesting.

II. The Method and Basis Set Used

For the geometry optimization we performed SCF calculations with a (7s,3p) Huzinaga basis, constructed from Gaussian lobes as described in ref 29, in the contraction (4,1,1,1/2,1) for carbon and a (3s) basis contracted to (2,1) for hydrogen. This basis is of "double ζ quality".

A multidimensional polynomial fit (with a program for which we are indebted to Professor R. Ahlrichs) was used for finding the minima of the energy along the reaction path. About 50 points were calculated for one d. (For the definition of d see Figure 1.)

For the optimized reaction path several SCF calculations were performed with d-type polarization functions ($\eta = 1.0$) on carbon and for some selected points, even calculations at PNO-CI and CEPA-PNO level, which take care of the most important effects of electron correlation. The PNO-CI and CEPA methods have been described elsewhere.[30,31] The basis, including polarization functions, has been found to be well
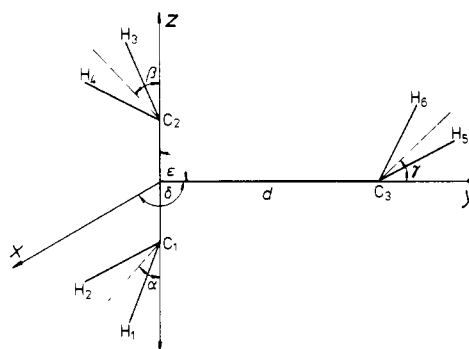
Figure 1. The geometrical parameters and the coordinate system used for the reaction ethylene + methylene → cyclopropane.

balanced for molecular calculations.[32,33] The computer program used is that described in ref 31.

III. Results and Discussion

In Table I the optimum geometrical parameters for different values of the "reaction coordinate" d are given. The meaning of these parameters is illustrated in Figure 1. The geometry optimization was done for fixed d at the SCF level without polarization functions. For the resulting optimized geometries calculations were then done with polarization functions on C and with the inclusion of electron correlation at different levels, the most reliable of which is CEPA (coupled electron pair approximation).[30,31] The different energy values are given in Table II.

Let us first discuss the reaction energy, i.e., the difference between the energies of cyclopropane and ethylene + methylene in their equilibrium geometries. The addition reaction

Table II. The Total Energy as Function of the Intersystem Distance d with the Other Parameters Optimized (See Table I) at Different Levels of Approximations (in au)

| d, a_0	Without polarization functions E_{SCF}	With polarization function on C				
		E_{SCF}	E_{IEPA}	E_{CEPA}	E_{CI}	E_{corr}^{CEPA}
2.479	−116.8927	−116.947 54	−117.428 54	−117.347 76	−117.302 88	−0.400 22
3.0	−116.8579	−116.901 26				
3.5	−116.7954	−116.830 20	−117.325 00	−117.236 00	−117.184 38	−0.405 80
4.0	−116.7711	−116.808 13	−117.275 40	−117.199 99	−117.150 85	−0.391 86
4.5	−116.7700	−116.807 79	−117.263 54	−117.191 12	−117.144 19	−0.383 33
5.0	−116.7670	−116.804 86				
10.0	−116.7583	−116.796 79				
20.0		−116.795 74	−117.241 76	−117.173 62	−117.126 78	−0.377 89
∞ [a]	−116.7578	−116.795 78	−117.241 76	−117.173 66	−117.145 55	−0.377 88

[a] Sum of the energies of the subsystems.
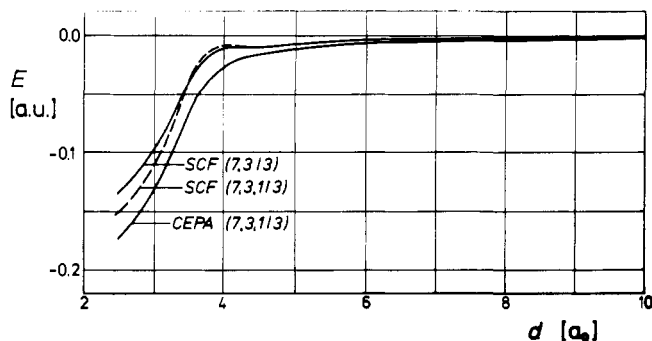
Figure 2. The interaction energy between ethylene and methylene as a function of the distance d in various approximations.

Figure 3. Variation of the angles γ and ϵ along the reaction path.

Figure 4. Variation of the CH bond length and the HCH angle of the CH_2 group along the reaction path.

is exoergic. At the SCF level with the small basis we get ΔE = 84.6 kcal/mol and with the larger basis (with polarization function on C) ΔE = 95.2 kcal/mol. It is well known[34] that it is imperative to include polarization functions on C if one wants to obtain acceptable energy differences between open-chain and cyclic molecules. However, correlation effects must be superimposed on these to obtain fully reliable values.[32] With CEPA we get ΔE = 109 kcal/mol. From a CI calculation (limited to double substitutions) we get 110.4 kcal/mol if we compare cyclopropane with the $(C_2H_4 + CH_2)$ system at a large internuclear separation $(20a_0)$, but only 98.7 kcal/mol if we take the sum of the energies of C_2H_4 and CH_2 as reference. This is an illustration of the fact[35,36] that the CI limited to double substitutions has an incorrect dependence on the number of electrons, but the resultant difficulties can be avoided if one compares only systems with the same number of electrons.[35]

Since the energy of CH_2 in its lowest singlet state is uncertain, the experimental reaction energy is not known accurately. The best value of the standard enthalpy of formation of CH_2 at 0 K is probably the theoretical result of ΔH_0 = 102 kcal/mol obtained by Kollmar,[37a] which agrees fairly well with some experimental estimates, especially the most recent one by Danon et al.[37b] (ΔH_{298} = 99.6 ± 0.8 kcal/mol). Using this value and the standard enthalpies of C_2H_4 and C_3H_6 as well as their zero-point energies[38] and an estimate of 10.5 kcal/mol for the zero-point energy of CH_2 we get an "experimental" value of the reaction energy of 105.4 kcal/mol, which differs by 3.6 kcal/mol from our CEPA value. In view of the smallness of our basis this is a fair agreement. It is not surprising that we overestimate the energy difference. With small basis sets aggregates of small systems are slightly favored with respect to the isolated systems. This effect is only expected to matter for small intersystem distances, and our CEPA curve should therefore be quite reliable for large and intermediate distances.

In Figure 2 the optimized energy is plotted as a function of d. One sees that the energy decreases monotonically with d in all three approximations. There is no barrier. This result is, however, only because all important geometrical parameters were varied. In our first pilot calculations where we optimized only the angle γ and interpolated the other geometrical parameters between initial and final states, a spurious local barrier was found, though it was lower in energy than for the separated reactants.

Figures 3-6 illustrate how the geometry varies along the "reaction path". The most important parameter is the angle γ, because a constant value γ = 0 during the reaction (with the other parameters interpolated) would mean that the system keeps C_{2v} symmetry, i.e., the reaction path would be that of the Woodward–Hoffmann-forbidden approach. In the important region $4a_0 \geqslant d \geqslant 6a_0$ the optimum γ is close to 90°, whereas for cyclopropane ($d \approx 3.5a_0$) one has γ = 0°. The
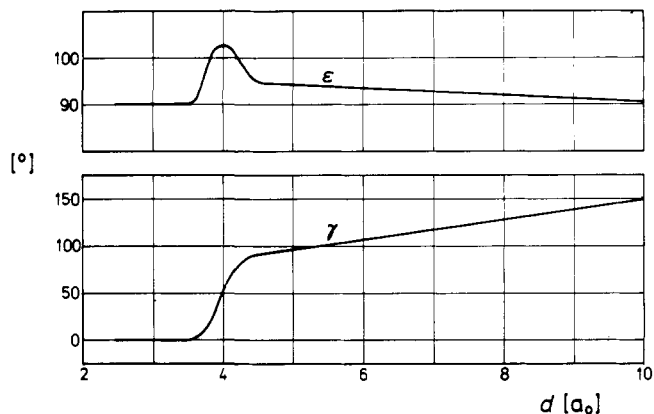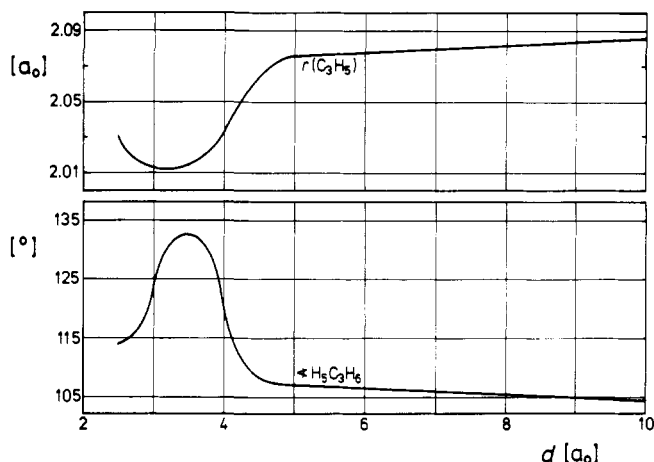
smooth increase of γ with d in the region $d \geqslant 5a_0$ should not be taken too literally, because for large d the energy varies very little with γ and the minimum is very shallow. At infinite separation it does not matter at all what the relative orientation of the reactants is. Moreover, the interaction energy at large distances is dominated by electrostatic terms and they may be poorly represented if the polarity of the CH bonds is even slightly incorrect.

Hoffmann[8] has suggested why γ should be close to 90° in the first phase of the reaction. It is due to the possibility of an attractive interaction by means of a charge transfer from the bonding π MO of ethylene to the empty π MO of methylene. This interaction is enhanced by a slight increase of ϵ, i.e., by an asymmetry in the C_1C_3 and C_2C_3 distances which one finds near d = 3.6a_0.

If we look at the variation of the C_1C_2 distance in ethylene we realize that near d = 3.5a_0 it is stretched about halfway to its final value.

We conclude that the first phase of the reaction, which takes place at $d \approx 4a_0$, is an electrophilic one during which electrons are transferred from ethylene to methylene. At the end of this phase the π AO of CH_2 is partially populated and the system is roughly described by a valence structure like that of the "half-formed cyclopropane" suggested long ago by Skell and
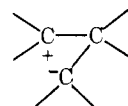
Garner,[24] who first postulated a two-phase mechanism for carbene insertion, which was later detected theoretically by Kollmar.[39]
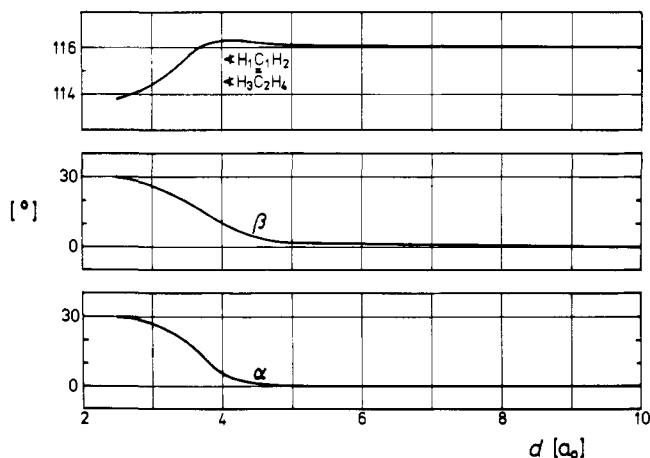
Figure 5. Variation of the angles α, β, and $H_1C_1H_3$ of the C_2H_4 group with d.
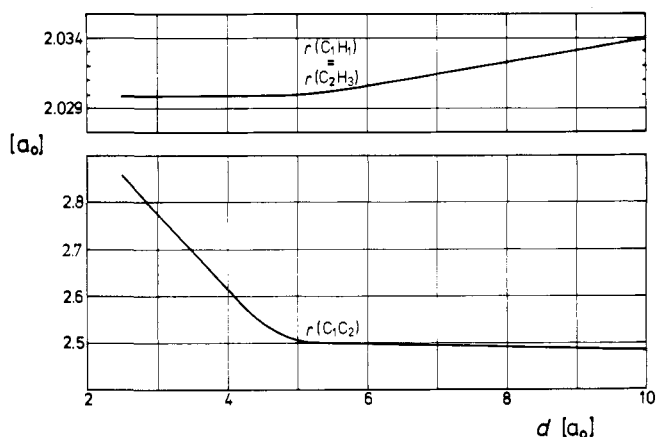

Figure 6. Variation of the CH and CC bond lengths of the C_2H_4 group with d.

At smaller distances a second, nucleophilic phase[39] takes place in which charge is transferred from the lone pair of CH_2 to the antibonding π MO of C_2H_4. For this phase of the reaction an angle $\gamma = 0°$ is more favorable. The nucleophilic interaction is enhanced by an opening of the $H_5C_3H_6$ angle of methylene to nearly its value in the triplet state, accompanied by a shortening of the C_3H_5 and C_3H_6 bond in methylene. One may say that at this stage the "valence state" of methylene is almost the one with the two nonbonding MOs singly occupied (as in the triplet state). The CH bond has more s character than in isolated singlet methylene and the "lone pair" has more p character and gets closer in energy to the "unoccupied" MO.

From Figure 2 one gets the impression that the electrophilic interaction has no appreciable energetic effect since the energy remains nearly constant between $d = \infty$ and $d = 3.5a_0$. One must not forget, however, that without this electrophilic interaction the potential would be repulsive and that this interaction is strong enough to overcompensate for the repulsion. It is essentially due to the strength of the electrophilic interaction that there is no barrier to the reaction.

From Figures 3–6 one may conclude that on further approach of CH_2 to C_2H_4 a third phase takes place where the system relaxes to cyclopropane in its equilibrium configuration. This is, however, essentially an artifact of our choice of the reaction coordinate and we must therefore comment on the reaction coordinate in this reaction.

In principle the construction of the path of steepest descent on the multidimensional potential hypersurface requires a full calculation of the hypersurface, which is, of course, prohibitive.

One still expects to get a good approximation to the reaction coordinate if one can separate the geometric parameters into a set A of coordinates that are "directly" involved in the reaction, a set B of coordinates that do vary during the reactions but which are not "directly" involved in the reaction, and finally a set C of coordinates that can be regarded as invariant during the reaction.

In the present case two new σ bonds (C_1C_3 and C_2C_3) are formed and a π bond (C_1C_2) is broken. This means that set A should consist of $r(C_1C_3)$, $r(C_2C_3)$, and $r(C_1C_2)$, or, equivalently, of d, ϵ, and $r(C_1C_2)$. From Figure 3 one concludes that ϵ should not be too crucial and that a two-dimensional surface with d and $r(C_1C_2)$ as independent parameters and the other coordinates optimized for every pair of d and $r(C_1C_2)$ should contain the information necessary to extract the reaction coordinate. It would even be preferable to replace d by $\bar{d} = \frac{1}{2}[r(C_1C_3) + r(C_2C_3)]$, since d does not correspond directly to any chemical interaction, although for large d, d and $\bar{d}$ do not differ much. Of course, for large d both d and $\bar{d}$ are excellent approximations to the reaction coordinate, but during the course of the addition reaction the reaction coordinate must be a mixture of d and $r(C_1C_2)$.

In the present case the determination of a two-dimensional energy surface would have required too much computer time. However, a study of this kind has been performed for the closely related addition reaction of CH_2 to H_2 by Kollmar[39] in the CNDO approximation and by Kollmar and Staemmler[40] in an ab initio study (see also ref 46). One can conclude from these studies that in the first part of the reaction the valley of the potential surface corresponds to large variations of d and small variations of $r(C_1C_2)$, and in the second part to large variations of $r(C_1C_2)$ and small variations of d, i.e., that in the second part of the reaction $r(C_1C_2)$ is closer to the real reaction coordinate. This means that one would get a more realistic picture of the minimum energy path if one regarded $r(C_1C_2)$ as the reaction coordinate in the nucleophilic phase and optimized the other parameters for constant $r(C_1C_2)$.

Anyway, the basic results of our calculations will not be affected by such a procedure. The energy curves of Figure 2 would become somewhat steeper near $d = 3a_0$. In other words, in this region our curves do not follow the minimum energy valley exactly.

We have already mentioned the reaction of $CH_2 + H_2$ to yield CH_4. In fact, this reaction, which has been studied theoretically by several authors,[39–46] resembles in many respects that of the present paper. It also proceeds in a nonsymmetric way since the C_{2v} reaction path is Woodward–Hoffmann forbidden. It also exhibits subsequently an electrophilic and a nucleophilic phase. A difference between the two reactions may be that the reaction methylene + ethylene → cyclopropane definitely has no barrier, while it is not certain whether a barrier exists for the reaction $H_2 + CH_2 → CH_4$. This difference may be partly due to the fact that in our case there are more internal degrees of freedom that can be relaxed, and partly to the smaller electron affinity of H_2 as compared to ethylene as well as to the stronger resistance of H_2 to breaking of its bond relative to that of the π bond in ethylene. Although one can put forward several reasons to explain why the reaction of ethylene + methylene → cyclopropane should be less liable to have a barrier than the reaction of hydrogen + methylene → methane, the most recent and most sophisticated studies of the latter reaction[40,46] suggest that even here there is no barrier.

One of the major points emerging from our study is that along the minimum energy path several geometrical parameters vary considerably in the course of the reaction. Although these variations are easily interpreted in terms of chemical concepts, one should resist the temptation to believe that the reaction really follows this path. Among the possible reactive

Table III. Bond Contributions to the IEPA Correlation Energy (Negative, in au)

Molecule :	C₂H₄			CH₂	C₃H₆
Basis[a] :	(7,3/3)	(7,3,1/3)	(9,5,1/5)	(7,3/3)	
Ref :	This paper	45	45	This paper	
ϵ_c[b]	0.024 65	0.025 11	0.025 85	0.033 22	0.024 29
ϵ_h	0.023 70	0.030 06	0.030 21	0.024 38	0.023 68
ϵ_{cc}[c]	0.032 87	0.034 52	0.035 25		0.015 21
ϵ_{ch}[d]	0.013 02	0.013 92	0.014 80	0.018 23	0.013 41
ϵ_{hh}[d]	0.013 30	0.014 38	0.014 93	0.014 30	0.013 21

[a] The notation refers to the number of primitive functions in the basis; (7,3,1/3) means, e.g., 7 s lobes, 3 p lobes, and 1 d lobe for carbon and 3 s lobes for hydrogen. [b] The subscript c refers to a CC bond or a lone pair on carbon, or in ethylene to one of two equivalent banana bonds, h to a CH bond. [c] ϵ_{ab} is the interorbital correlation energy (sums of the corresponding singlet and triplet contributions) between the bond orbitals a and b. [d] Only those interorbital contributions between bonds are indicated which have at least one atom in common. The other contributions are smaller by an order of magnitude.

trajectories on the potential surface the ones that are close to the minimum energy path may be rather unlikely due to dynamic reasons, in particular if this path corresponds to a rather complicated motion. We think that information about this "reaction path" is useful nevertheless.

IV. Analysis of Correlation Effects

A special analysis of the effects of electron correlation on the reaction surface is useful, because unlike for larger systems in this particular case calculations including electron correlation were possible. It is therefore interesting to know what we can learn for larger systems where a direct calculation of correlation effects is prohibitive.

We must admit that the basis used here is smaller than the smallest basis used in ref 47. In fact we could not afford to use p AOs on the H atoms. As can be seen from Table III this leads to a poor representation of the correlation energy of the CH bonds, but has very little effect on the other contributions to the correlation energy. Since the number of CH bonds does not change during the reaction, we are confident that the change in correlation is rather well accounted for.

In Table III the individual contributions of the bonds and their interaction to the correlation energy are collected. We get new evidence for the observation[47] that comparable bonds yield similar contributions to the correlation energy if comparable bases are used. Unusual values are easily explained. The lone pair in CH₂ is, of course, different from a CC bond; the interaction between two banana bonds in ethylene is different from that between two CC σ bonds in cyclopropane.

As is seen from Table IV the correlation energy of cyclopropane is larger in absolute value than the sum of the correlation energies of ethylene and methylene. This is so in all three approximations: IEPA (independent electron pair approximation), CEPA (coupled electron pair approximation), and CI (configuration interaction limited to double substitutions).

It is convenient to analyze this difference in IEPA, because E_{corr}^{IEPA} is directly a sum of pair contributions.

One sees easily that the change in correlation energy on going from C₂H₄ + CH₂ to C₃H₆ is dominated by the change in the number of neighboring CC bonds. This number is 1 (interaction between two banana bonds) in C₂H₄ + CH₂ and 3 in C₃H₆. If one assumes an average value for the interorbital correlation between two C–C bonds of 0.015 au, one gets a rough estimate that the change of correlation energy should be of the order of 0.03 au. Of course, in reality, the situation is more complicated, because all contributions change somewhat, but there is not doubt about the main reason for the change of correlation energy.

Along the path from CH₂ + C₂H₄ to C₃H₆ the correlation energy changes in a nearly monotonic fashion, although there seems to be a slight maximum at $d = 3.5a_0$. An increase of the correlation energy with decreasing distance between two subsystems is rather general and is due to the fact that the dispersion (or van der Waals) attraction is automatically included in the correlation energy but is lacking at the SCF level.

Since the effects of electron correlation are far from negligible the question arises whether one is justified in performing the geometry optimization at the SCF level, i.e., whether it is likely that correlation affects the equilibrium geometry. In fact this is not to be expected, since the correlation energy is much less sensitive to changes in the other geometrical parameters than to changes in d, and even this dependence is small. It is true that SCF calculations are unable to describe correctly the dissociation of a bond like that of H₂ in the reaction CH₂ + H₂ → CH₄. SCF calculations tend to favor geometries with small H–H distances (i.e., distances only slightly larger than the H₂ equilibrium distance). A careful investigation by Kollmar and Staemmler[40] has shown that the reaction path remains nearly unaffected by correlation. In our example no bond is fully

Table IV. Correlation Energy (Negative, in au) of C₂H₄ and C₂H₂ Compared with That of C₃H₆ in Different Approximations (1 au = 627.7 kcal/mol)

	C₂H₄	CH₂	C₂H₄ + CH₂[a]	C₃H₆	Difference[b]
IEPA	0.313 27	0.132 74	0.446 01	0.481 00	0.034 99
CEPA	0.264 69	0.113 19	0.377 88	0.400 22	0.022 34
CI	0.242 11	0.107 66	0.349 77	0.355 34	0.005 57
CI			0.331 04[c]		0.024 30
IEPA (intra)	0.144 10	0.081 98	0.226 08	0.214 95	−0.011 13
IEPA (inter, c.b)[d]	0.163 63	0.050 76	0.214 39	0.246 18	0.031 79
IEPA (inter, d.b)[e]	0.005 54	0.0	0.005 54	0.019 92	0.014 38

[a] Sum of the correlation energies of the isolated subsystems. [b] Change in the correlation energy on formation of cyclopropane. [c] Energy of C₂H₄ + CH₂ at an intersystem distance $d = 20a_0$. [d] c.b. = close bonds, i.e., bonds (or lone pairs) that have at least one atom in common. [e] d.b. = distant bonds, i.e., bonds (or lone pairs) that have no atom in common.

broken; only a double bond changes to a single bond, which implies a much smaller change in the C_1C_2 distance. Correlation effects should hence be still smaller than in the $CH_2 + H_2$ case. We expect, of course, that, as in the $CH_2 + H_2$ case, inclusion of correlation lowers the Woodward–Hoffmann-forbidden symmetrical reaction path more than it lowers the reaction path that we have optimized at the SCF level. Again it is extremely unlikely that with correlation the Woodward–Hoffmann-forbidden reaction path becomes competitive. The "avoided crossing", for which we have performed some tentative calculations, lies at the SCF level as much as 20 kcal/mol above the energy of $C_2H_4 + CH_2$.

V. Conclusions

The reaction path for the addition of singlet methylene ($^1A_1$) to ethylene is qualitatively similar to that obtained by Hoffmann[8] in the semiempirical EHT approximation, namely, only C_s symmetry is preserved. However, in contrast to Hoffmann's result[8] there is no barrier; the energy decreases monotonically along the whole reaction path. Although the reaction is smooth and concerted, two mechanistically different phases can be distinguished: an "electrophilic phase" in which charge is transferred from the bonding π MO of ethylene to the empty π MO of methylene and a "nucleophilic phase" in which a charge transfer from the lone pair of methylene to the antibonding MO of ethylene takes place. To be effective the two phases require different geometric arrangements of the partners. Moreover, the internal coordinates not directly involved in the reaction vary considerably along the minimum energy path. These variations are easily explained in terms of the types of interaction and the electronic structures of the components in the various steps.

A qualitatively correct potential curve is obtained with a double ζ type (7,3/3) basis at the SCF level. In order to get the correct reaction energy, polarization functions (d AOs) on carbon, as well as the inclusion of electron correlation, are necessary. The contribution of polarization functions to the reaction energy is ~10 kcal/mol, that of electron correlation ~15 kcal/mol. The change in correlation energy between ethylene + methylene and cyclopropane is mainly due to the larger number of interorbital contributions between neighboring bonds.

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