Insertion Reaction of a Nucleophilic Carbene. A Molecular Orbital Theoretical Study

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Abstract: The potential surface for the addition of hydrogen to cyclopropenylidene as a model for the insertion and addition reactions of nucleophilic carbenes was computed using a modified CNDO method. The crucial points of the surface were in addition subjected to ab initio SCF and correlation calculations within the coupled electron pair approximation (CEPA). The calculations predict a high activation energy of 41 kcal/mol. This is in contrast to the very small activation energy which was calculated for the addition of hydrogen to methylene. Thus, the carbenes CH_2 and C_3H_2 behave very differently though the often used criteria for chemical reactivity like orbital symmetry, orbital topology, and steric requirements of the reaction apply equally to both systems. Despite the reduced electrophilicity of cyclopropenylidene the symmetry forbidden path is avoided in the same manner as in the $CH_2 + H_2$ system and the electrophilic phase of the reaction is the rate-determining step.

I. Introduction

A thermal reaction for which the maximum symmetry path is "forbidden"[1] may proceed in a concerted way if the system can follow a low symmetry path which avoids the crossing of virtual and occupied orbitals completely. In the case of intramolecular rearrangements such an effective evasion of a symmetry-conserving path is usually not feasible because of steric requirements and one can classify isomers into lumomers and homomers.[2] The same is true for some bimolecular reactions. Thus, any "allowed" [2s + 2a] path for the dimerization of ethylene is very unfavorable sterically.[1]

Theoretically studied examples for reactions which proceed with a low energy barrier along a low symmetry path are the dimerization of methylene,[3,4] the insertion of methylene into hydrogen[5-7] and into methane,[8,9] the addition of methylene to ethylene,[10] and the addition of hydrogen to the vinyl cation[11] (which can be considered as a CH_2^+ substituted methylene). In the theoretical studies of these reactions very different MO methods were used, e.g., EHT,[3,8,10] modified CNDO,[4,5,11] MINDO/2,[9] ab initio SCF,[6] and CI.[7] They all predict the same low-energy, low-symmetry path for these reactions characterized by the approach of a bond of the substrate to the empty p orbital of the singlet methylene from above the methylene plane. The reactions represent an illustration for the frontier orbital model.[12]

As has been shown in detail[5] for the prototype of these reactions, namely the addition of hydrogen to singlet methylene, two well-defined phases can be distinguished along the path of the overall concerted reaction (Figure 1): (i) The H_2 molecule approaches the methylene from above and a three-center bond is formed from the occupied hydrogen MO and the empty p orbital of the carbene in the electrophilic phase of the reaction. (ii) In the second phase of the reaction the H_2 molecule rotates to the final tetrahedral arrangement. This process is coupled with the simultaneous increase of the H–H bond length. It is the nucleophilic phase of the reaction during which the antibonding virtual MO of the hydrogen molecules is populated from the lone pair of the carbene.

It has been the purpose of the present study to determine how the situation is changed if the electrophilicity of the carbene is reduced. As a model reaction we have studied the addition of hydrogen to cyclopropenylidene **1**. In both systems,

1

$CH_2 + H_2$ and $C_3H_2 + H_2$, the steric requirements of the reaction, the symmetry properties, and the topology of the orbitals involved are the same. These are widely used concepts for reactivity in organic chemistry and our results will be a demonstration for their validity and their limitations. In **1** the carbenic center is stabilized by conjugation in the aromatic three-membered ring and the "empty" p orbital of the carbene is partially populated. The main questions are: How does this change affect the activation energy and the reaction path? Does the reaction still start with an electrophilic phase and can the symmetry forbidden path still be avoided so effectively that the reaction is concerted?

It is known from experiment that increasing the stabilization of a carbene through conjugation reduces its activity and increases its selectivity in insertion reactions into CH bonds.[13] A carbene like dichlorocarbene hardly inserts at all into CH bonds. As the only derivative of **1**, the existence of diphenylcyclopropenylidene as an intermediate was proved.[14] It is presumed to be somewhat less stabilized through aromatic conjugation than the parent compound **1**. The addition to the reactive double bond in dimethyl fumarate is its only known reaction so far. Better known is cycloheptatrienylidene, the next aromatic homologue of **1**.[15] It undergoes addition reactions with various activated double bonds.[16] From the stereoselectivity of one of those reactions a concerted mechanism was deduced.[17]

II. Methods

The calculation of the reaction surface was performed using a modified[18] CNDO[19] method which has been shown to yield reasonable heats of atomization and equilibrium geometries for hydrocarbons. The previous calculations of the potential surface of the addition of hydrogen to methylene[5] were done with the same method. The results proved to be in good agreement with minimal basis ab initio SCF studies[6,7] which appeared later. The CNDO method was combined with a gradient search procedure for the optimization of the internal coordinates.

Our CNDO still uses the original formula for the electron repulsion integrals, which yield too large values for the one-center repulsion integrals. As a consequence, the absolute stability of compounds such as carbonium ions[20] and carbenes which contain empty p orbitals is overestimated. The magnitude of this error for carbenes has been evaluated by comparison with ab initio calculations and will be discussed in the following section.

In order to verify the semiempirical results certain points of the hypersurface were also computed with ab initio SCF

Table I. Heat of the Reaction Carbene + H$_2$ for Singlet Methylene, Cyclopropylidene, and Cyclopropenylidene (in kcal/mol)

Carbene	Mod. CNDO	Ab initio SCF				With correlation (CEPA)			
		MB	DZ	DZ + d + p	EB[a]	MB	DZ	DZ + p + d	EB[a]
$^1CH_2$	87	167	123	121	118	168	126	132	129
$^1C_3H_4$	63	152	106	101					
$^1C_3H_2$	30	107	53	47		118	61	62	
Differences									
C_3H_2/CH_2	57	60	70	74		50	65	70	
C_3H_2/C_3H_4	33	45	53	54					

[a] Extended basis: 9.5/5 basis of Huzinaga[21] contracted to 5 s and 3 p functions [5, 1, 1, 1, 1.3, 1, 1] for the C atom and 3 s functions at the H atoms augmented by two sets of d functions (exponents 0.3 and 1.0) and one set of f functions (exponent 0.8) for the C and two sets of p functions (exponents 0.4 and 1.0) for the H atoms. The exponents and the energy of methane were taken from ref 32.
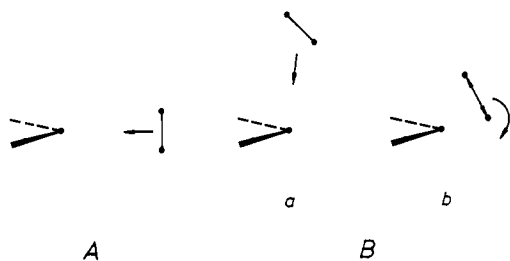
Figure 1. The addition of hydrogen to methylene: (A) the symmetry forbidden "least motion" path; (B) the minimum energy path with (a) the electrophilic and (b) the nucleophilic phase of the reaction.

methods using the following types of basis sets: (i) minimal basis (MB) contracted from a 5.2/2 Gaussian basis set; (ii) double-zeta basis (DZ) contracted from the 7.3/3 basis of Huzinaga[21]; and (iii) DZ augmented by one set of d functions at the carbon atoms (η = 1.0) (DZ + d) and one set of p functions at the hydrogens (η = 0.65) of the approaching hydrogen (DZ + d + p). The integrals over the Gaussian functions were computed with a program developed by Ahlrichs.[22]

As it turned out, the transition state of the reaction is located in a very repulsive region of the potential surface. It is therefore imperative to study the influence of electron correlation as well. The correlation energies were calculated at key points using the CEPA (Coupled Electron Pair Approximation) method.[23]

III. The Electronic Properties of Cyclopropenylidene

The electrophilicity of 1 is very much reduced in comparison to methylene because of the conjugation in the aromatic π system of the three-membered ring.[24] Thus, the "empty" p_π orbital of the carbene center is partially populated. According to CNDO the population of this p_π orbital is 0.47, while the Mulliken populations obtained with ab initio SCF calculations are somewhat smaller (0.35 in MB and 0.37 in DZ basis). The conjugation is also reflected in the orbital energies. Within DZ the lowest virtual orbital of 1 is at +0.14 as compared with +0.08 au in cyclopropylidene, while the energies of the highest occupied orbitals, which correspond to the lone pairs, are very similar in both carbenes, namely −0.37 and −0.36 au, respectively. (The respective CNDO values for the four orbital energies are: +0.25, +0.20, −0.34, and −0.32 au.) The large splitting between the HOMO and the LUMO in 1 causes the triplet to be much higher in energy than the singlet.[24-26]

The energy gain resulting from the aromatic conjugation was calculated directly by computing the increase in total energy which is connected with the omission of p_z-type basis functions (with the carbene in the xy plane) at the carbenic C atom. Within MB we find 47 and within DZ 43 kcal/mol as the resonance energy of the π system in 1. As an alternative method for the evaluation of the stabilization of the carbenic

center in 1, one may as well consider the stability of 1 relative to other carbenes as obtained from the comparison of the exothermicity of addition and of dimerization reactions.

The heat of the reaction of singlet carbene with H$_2$ was calculated for methylene, cyclopropylidene, and 1 using different methods. The results are listed in Table I. Since CNDO overestimates the stability of carbenes, the CNDO values for these reactions are considerably too small (by 30-40 kcal/mol). Our ab initio MB-SCF calculations, on the other hand, give too large values for the heats of reaction (by 40-50 kcal/mol).[27] The calculations with larger basis sets show that inclusion of polarization functions is not essential in this case.

As expected, inclusion of correlation increases the exothermicity of the reactions, since there are more vicinal bonds in the products than there are in the reactants.[28] The correlation effects amount to 11 kcal/mol in the case of methylene and to 15 kcal/mol in the case of 1. The different methods agree much better in the prediction of the relative stabilities. For the stabilization of 1 relative to methylene we obtain 70 kcal/mol (DZ + d + p + correlation). The SCF value of 74 kcal/mol agrees with the value given by Pople et al.[29] for a different but corresponding basis set. The reduction of this value by 4 kcal/mol with the inclusion of correlation is another consequence of the reduced availibility of the lowest virtual orbital in 1 as compared to methylene. Both CNDO and ab inito MB underestimate the stabilization of 1, but the values 57 and 60 kcal/mol, respectively, are still in reasonable agreement with our "best" value of 70 kcal/mol. About ⅔ of the stabilization of 1 with respect to methylene is due to aromatic conjugation. In addition, ring strain and inductive effects contribute to the stability of the cyclic carbene. Those factors are also present in cyclopropylidene. Thus, the relative stability of 1 with respect to its saturated counterpart is a better measure for the aromatic stabilization. The corresponding values are also given in Table I. It should be mentioned that hyperconjugation contributes only 7 kcal/mol to the total energy of cyclopropylidene.

An alternative way for the determination of relative stabilities of carbenes is the comparison of their heats of dimerization. Those were calculated for methylene and for 1 and are listed in Table II. Again, modified CNDO gives much too small and MB ab initio SCF much too large values for the dimerization energies. The relative stabilities agree very well with those obtained from the hydrogen addition reaction. The central double bond in the dimer of 1 is remarkably weak. Assuming the same correlation energy contribution as in the case of the dimerization of methylene we estimate the dissociation energy of the central double bond to be in the order of 70 kcal/mol, which is less than the corresponding value for a standard C-C single bond as in ethane (88 kcal/mol[30]).

The aromatic conjugation is also reflected in the structure of 1. The CNDO optimum structure has single bonds of 1.409 Å and a double bond of 1.388 Å. Compared with the optimum
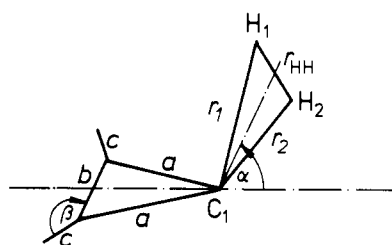
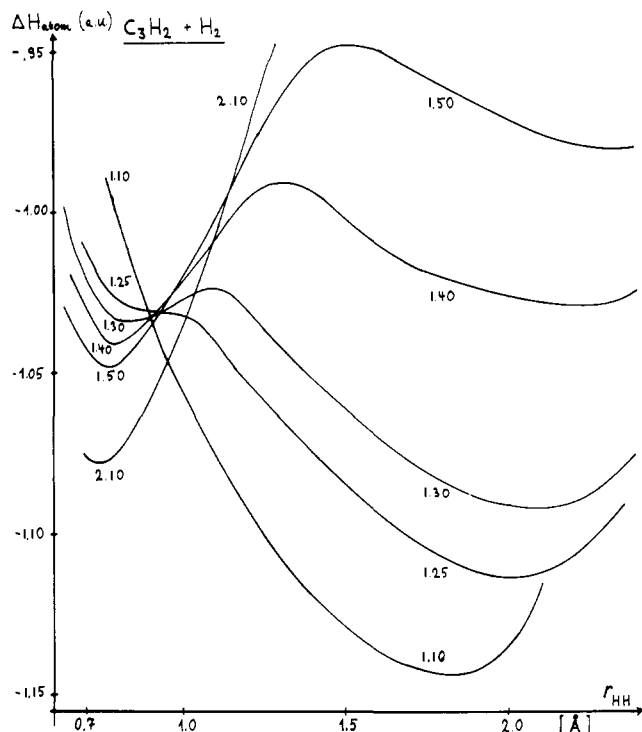Figure 2. The geometrical parameters for the addition of hydrogen to 1.

Figure 4. The optimum value of α vs. the H–H distance for a mean CH distance of 1.40 Å.

Figure 3. The heat of atomization as a function of the H–H distance for different mean CH distances.
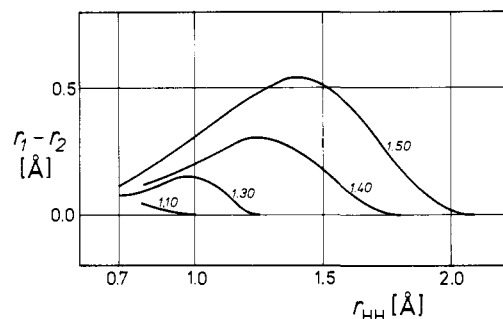
Figure 5. The optimum value for $r_1 - r_2$ vs. the H–H distance for different mean CH distances.

Table II. Heat of the Dimerization of Methylene and of Cyclopropenylidene (kcal/mol)

	Mod. CNDO	Ab initio SCF			+ CEPA		
		MB	DZ	DZ + d	MB	DZ	DZ + d
$^1CH_2$	131	255	181	180	278	201	206
$^1C_3H_2$	14	142	42				
$\Delta E/2$	58	57	70				

values in cyclopropene of 1.512 and 1.320 Å, respectively, the single bonds are shortened by 0.103 Å, while the double bond is stretched by 0.068 Å. Pople et al.[29] report an MB (STO-3G) optimum structure in which the CC bond lengths are 1.442 and 1.314 Å. The corresponding values for cyclopropene were 1.493 and 1.277 Å, which means a shortening of the single bonds by 0.051 Å and a lengthening of the double bond by 0.037 Å. Thus, CNDO seems to overestimate the effect of conjugation on the structure. We did not attempt to optimize the structure within our ab initio calculations but rather used Pople's structure.

IV. CNDO Calculations of the Potential Surface for the Addition of Hydrogen to 1

As previous calculations of the insertion reactions of methylene[5] and the vinyl cation[11] and of other "forbidden" processes[31] have shown, one cannot select a single geometrical
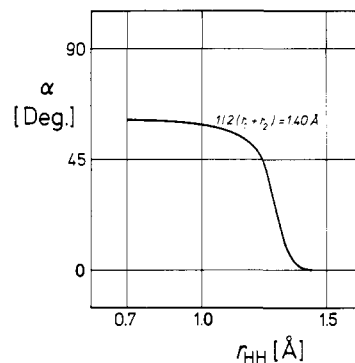
parameter as the reaction coordinate in cases where symmetry forbidden paths have to be avoided. Instead, it is necessary to perform a multidimensional search for the optimum reaction coordinate. In our case we proceeded as follows: For different given values for the arithmetic mean $\bar{r}$ of the two CH bonds formed during the reaction ($0.5(r_1 + r_2)$, see Figure 2) the HH distance (r_{HH}) of the approaching hydrogen molecule was varied over a wide range (0.7 Å $\leq r_{HH} \leq 3$ Å). For each point six other geometrical parameters, which are defined as follows (Figure 2), were optimized (C_s symmetry was assumed throughout): (i) The difference in bond lengths of the two CH bonds formed ($r_1 - r_2$). They tend to be different in certain regions of the potential surface. (ii) The angle α between the methylene plane and the line connecting C_1 with the midpoint of the approaching hydrogen. Thus, α describes the direction from which H_2 approaches the carbene. (iii) The internal coordinates of the three-membered ring a, b, c, and β.

By this approach the energy of the system was obtained as a function of the HH distance for different mean CH distances as shown in Figure 3. We find two energy minima for given mean CH distances larger than 1.30 Å, one with a short and one with a long HH distance. As far as the other geometrical parameters are concerned, the structures belonging to the two minima differ essentially in the values for the angle α and for $r_1 - r_2$. For long HH distances we get C_{2v} symmetry, since α and $r_1 - r_2$ come out to be zero, while for short HH distances large values for α and positive values for $r_1 - r_2$ are obtained, corresponding to the approach of the hydrogen molecule from above the ring plane. Figure 4 shows the optimum angle α as a function of the HH distance with the mean CH distance fixed at 1.4 Å. There is a sudden drop of α at a HH distance of 1.3 Å, close to the maximum of the corresponding energy curve (Figure 3). With further calculation we made sure that there is not an additional double minimum behavior for α.

For the short HH distances the two CH bonds tend to be different with r_1 larger than r_2. Figure 5 shows $r_1 - r_2$ as a function of the HH distance for different mean CH distances.

The inequality of the CH bonds during the approach of the hydrogen molecule leads to a charge separation between the two hydrogen atoms with H_2 more positive than H_1. At the transition state the difference in charge is larger than 0.1 electron (with a total charge of the two hydrogens of 0.2).

Figure 6 shows the two-dimensional contour map of the potential surface. It was constructed from the points of Figure 3. At the beginning of the reaction (small HH and large CH distances) the reaction coordinate is identical with the mean CH distance. The transition state is reached after that distance has decreased to about 1.2 Å. With an HH distance of not more than 0.9 Å, the transition state contains a fairly intact hydrogen molecule. The calculated activation energy is 41 kcal/mol. The reaction coordinate is turning around at the transition state and becomes the HH distance thereafter, which increases to its final value of 1.8 Å, while the energy declines 77 kcal/mol.

V. Ab Initio Calculations

In order to verify the main results of our semiempirical calculations ab initio calculations of selected points of the surface were performed. They were all done within the DZ basis. The geometrical parameters of the three-membered ring (a, b, c, β) were taken from the carbene itself, while the angle α and $r_1 - r_2$ were roughly optimized for selected values of the mean CH and the HH distances. No attempt was made to locate the transition state itself, because it would require too many calculations. Only the repulsive region of the surface (relatively large CH and small HH distances) was investigated, since this part of the surface which describes the electrophilic phase of the reaction is responsable for the large activation energy.

At a mean CH distance of 1.8 Å and a HH distance of 0.77 Å we find the optimum values for α at about 65° and for $r_1 - r_2$ at about 0.4 Å. The energy is 25 kcal/mol above $C_3H_2 + H_2$. One has to expect in such a case of a repulsive interaction that SCF calculations tend to overestimate the repulsion. However, inclusion of correlation with CEPA lowered this value only by 1 to 24 kcal/mol. This clearly indicates that the considered point on the surface is still located far from the forbidden path (cf. the large value of α). At the same mean distance of 1.8 Å, CNDO gives a repulsion of 19 kcal/mol (α = 60° and $r_1 - r_2$ = 0.6 Å).

At a CH distance of 1.6 Å and r_{HH} = 0.8 Å we find α = 85° and $r_1 - r_2 \approx 0.6$ Å and an energy which is 40 kcal/mol above the energy of the components. After inclusion of correlation this value is reduced to 36 kcal/mol. The energy still rises (even with inclusion of correlation) when the HH distance is increased. Thus, the nucleophilic phase cannot yet proceed, and this configuration is still located on the carbene + H_2 side of the transition state. At the same CH distance (1.6 Å), the repulsion calculated with CNDO is 28 kcal/mol (α = 60° and $r_1 - r_2$ = 0.3 Å).

With the restriction $r_1 = r_2$ we would lose 4 kcal/mol at a CH distance of 1.8 Å and 7 kcal/mol at a CH length of 1.6 Å within ab initio SCF. As in CNDO H_2 has more positive charge than H_1 according to a Mulliken population analysis.

Thus, the essential characteristics of the electrophilic phase of the reaction as deduced from the CNDO potential surface were confirmed by ab initio calculations.

VI. Discussion

The reaction coordinate of the addition of hydrogen to either singlet methylene or cyclopropylidene has the same shape in both cases: (i) The hydrogen approaches the carbene from above forming a three-center bond with the "empty" p orbital of the carbene (electrophilic phase). (ii) At fairly small CH
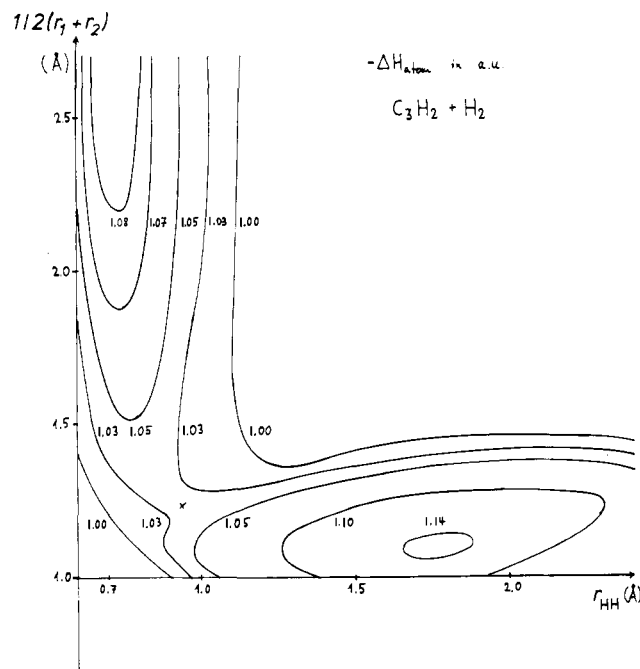

Figure 6. A two-dimensional energy contour map. The heat of atomization as a function of the mean CH distance and the H–H distance.

distances the hydrogen bond is broken and the HCH plane rotates to its final tetrahedral arrangement. The lone pair of the carbene has populated the σ^* orbital of the H_2 (nucleophilic phase).

It is a consequence of the nodal properties of the orbitals involved that in both cases the symmetry-forbidden path is evaded in the same way. The substantial difference between the carbenes is that in the case of **1**, the electrophilic phase of the reaction is hindered very effectively by the partial population of the formally empty p_π orbital at the carbenic center through conjugation. The approach of the hydrogen is now very repulsive and the energy rises during the whole electrophilic phase of the reaction. The transition state is the turning point of the reaction coordinate on the dividing line between the two phases of the reaction. During the nucleophilic phase of the reaction, the total energy declines steadily. That is very different in the case of methylene where the turning point of the reaction coordinate is located far behind the transition state through which the reaction coordinate passes at the beginning of the electrophilic phase (at a CH distance of about 2.5 Å).

It is remarkable that the internal coordinates (CH and HH bond lengths) in the region where the reaction coordinate changes from the electrophilic to the nucleophilic phase are very similar for the addition reactions of the two carbenes. Thus, the highly unfavorable electrophilic phase in **1** did not shift the nucleophilic phase to an earlier stage of the reaction. The stereoelectivity of the addition of cycloheptatrienylidene to 1.3 pentadiene[17] indicates that our system can be regarded as a model even for such addition reactions. If the carbene would react as a nucleophile in that case (i.e., if the nucleophilic phase of the reaction could take part at an early stage of the reaction) the reaction would not be concerted and thus the stereospecity would be low. The situation may be quite different in the case of highly activated ethylene derivatives such as methyl fumarate as substrates in the addition reactions.[16]

The incapability to form a favorable three-center bond between the hydrogen molecule and the partially filled p_π orbital at the carbenic center of **1** can be demonstrated with an energy partitioning analysis.[33] Within semiempirical schemes bond strengths can be described by their resonance energies[33,34]

which we defined in the following way:

$$E_{AB}^{R} = 2 \sum_{\mu \in A} \sum_{\nu \in B} P_{\mu\nu} H_{\mu\nu}$$

(μ, ν denote the atomic orbitals located at the atoms A and B, respectively, $P_{\mu\nu}$ are bond order matrix elements, are $H_{\nu\mu}$ are the resonance integrals used). We can compare the resonance energies of the CH bonds formed during the approach of the hydrogen molecule in the case of **1** with those of methylene. For a CH distance of 1.4 Å and an HH distance of 0.75 Å, the averaged CH resonance energies are 0.19 au in the case of methylene and only 0.14 au in the case of **1**. When the HH distance is stretched to 1.2 Å, the values are 0.31 and 0.22 au, respectively. In the final products, the resonance energies of the CH bonds are almost identical in the two compounds, namely 0.38 au in methane and 0.39 au in cyclopropene.

Since the calculated activation energy of 41 kcal/mol is so high, we have to consider the possibility of nonconcerted processes with cyclopropenyl radical as an intermediate. From the estimated heat of the reaction $C_3H_2 + H_2$ of 60 kcal/mol (Table I) and an assumed dissociation energy of the CH bond in cyclopropene on the order of 100 kcal/mol we estimate C_3H_3 + H to be about 40 kcal/mol above $C_3H_2 + H_2$. Thus, we cannot exclude that a nonconcerted path with a radical intermediate may compete with the calculated concerted process.

With our methods we cannot give a reliable estimate for the activation energy of the symmetry forbidden path (cf. ref 7). The variation of angle α in our ab initio calculations, however, proved that the symmetry forbidden path is certainly less favorable than the low-symmetry path.

The comparison of the carbenic reactions, $CH_2 + H_2$ and $C_3H_2 + H_2$, is an illustration for the limitations of the concepts like orbital symmetry and orbital topology as criteria for chemical reactivity. The reaction $CH_2 + H_2$, which is thermally forbidden along the maximum symmetry path according to the Woodward–Hoffmann rules, proceeds without any activation energy[7] along a low-symmetry path. In the case of **1** + H_2, on the other hand, the reaction is thermally forbidden along any path. However, the optimum reaction path still avoids maximum symmetry and is determined by the topology of the orbitals involved. Whether insertion and addition reactions of carbenes like **1** proceed via concerted or nonconcerted mechanisms will depend on the electronic structure of the substrate (here H_2).

References and Notes

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